



Tunable RF-Responsive Core-Shell Organofullerenyl-Magnetic Hybrid Nanostructures as Multiferroic Nanomaterials

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14. ABSTRACT A sequential synthetic method to fabricate multilayered hybrid nanostructures on either γ -FeO _x @AuNP nanoparticles or sandwiched graphene sheets with measurements of reversible and photoswitchable dielectric property amplification characteristics was performed at 1.0–4.0 GHz. Six variable organic electron donors and two conducting conjugated polymers were also applied to serve as the supply of photoinduced transferrable electrons at the outer shell layer. The design largely increased the number of polarizable charges, leading to a maximum of 387% amplification of the relative dielectric constant (ϵ_r') value. Good recyclability of ϵ_r' back to their original values during each photoactivation cycle of light-on and light-off manipulations may allow the potential uses as dielectrics in photoswitchable modulation of RF reflection signals. In the case of graphene samples, large further increase of reversible dielectric permittivity ϵ_r' amplification of 308% by photoexcitation at the plasmonic gold shell layer using a white LED light was achieved.					
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1.0 SUMMARY

The project is aimed to design, synthesis, structural characterization, and study of photophysical properties of one class of organic–metallic hybrid core-shell (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n nanoparticles and having them underwent an approach of photoactivation using external light source, aiming to induce interfacial plasmonic resonance energy transfer (PRET) among core-shell layers at a near-field in a nanoscale. We discovered unexpected, unusual photoswitching phenomena at microwave frequency range leading to possibility of controlling and tuning dielectric permittivity (ϵ) of nanomaterials upon turning *on* or *off* the LED white light. The generated effect can be applied for the modulation of the material's refractive index at RF frequencies. Accordingly, we studied its uses in creating false images resembling camouflage covering effects of the real target upon upcoming RF frequency detection for enhancing security protection and countering surveillance or reconnaissance detection.

We unexpectedly observed a large amplification of dielectric properties associated with the photoswitching effect and the new unusual phenomenon of delayed photoinduced capacitor-like (*i.e.* electric polarization) behavior at the interface on samples of three-layered core-shell (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n nanoparticles (NPs) in frequencies of 0.5–4.0 GHz. The detected relative dielectric constant amplification was initiated upon switching off the light followed by the relaxation to give an excellent recyclability. These NPs having e⁻-polarizable fullerosomic structures located at the outer layer were fabricated from highly magnetic core-shell γ -FeO_x@AuNPs. It was found to be capable of photoinducing surface plasmonic resonance (SPR) effect by white LED light. The accumulated SPR energy was subsequently transferred to the partially bilayered C₆₀(>DPAF-C₉) fullerosomic membrane layer in a near-field (~1.5 nm) without producing the radiation heat. Since the monostatic SAR signal is dielectric property-dependent, we used these measurements to provide evidence of derived reflectivity changes at 0.5–4.0 GHz upon illumination of a LED white light with a high >99% efficiency of response amplification in image amplitude can be achieved

Accordingly, we further demonstrated the design and synthesis of novel [60]fullerenyl 3D-configured stereoisomers *cis-cup*-tris[C₆₀(>(DPAF-C₉))] and *trans-chair*-tris[C₆₀(>(DPAF-C₉))] in good yields. The former with three C₆₀> cages per molecule facing at the same side of the geometrical molecular cup-shape was proposed to provide excellent binding interaction forces at the gold surface of core-shell γ -FeO_x@AuNP nanoparticles (NPs) to direct the subsequent formation of a fullerene cage array (defined as *fullerosome*). Upon photoactivation of the Au-layer and *cis-cup*-tris[C₆₀(>(DPAF-C₉))] itself, the level of photoinduced intramolecular e⁻-transfer from DPAF to C₆₀> moiety was found to be largely enhanced by the accumulated plasmonic resonance energy at the near-field surface. Distribution of resulting negative charges along the outer (C₆₀>)-derived fullerosome shell layer of trilayered (γ -FeO_x@AuNP)@[*cis-cup*-tris[C₆₀(>(DPAF-C₉))]]_n NPs was correlated to the detected photoswitchable dielectric amplification phenomena, showing a large increase of *reversible* relative dielectric constant (ϵ_r') of 200–280%, using white LED light excitation (12.8 J/cm²) at 1.0 GHz, workable up to 18 GHz of our current instrument capability. This class of new materials exhibit potential in photoswitching microwave applications covering WiFi-bands over 2.4/3.6/5.0 GHz.

Step-by-step fabrication methods of new microwave-responsive organic–inorganic hybrid core-shell nanoparticles were demonstrated to observe large reversible and photoswitchable dielectric property amplification characteristics in a polymer matrix at 1.0–4.0 GHz. The nanomaterial design was made by the construction of a tetralayered core-shell configuration, containing a magnetic core of nanospherical γ -FeO_x particle (NP) encapsulated by one plasmonic gold subshell, one middle layer of electron-polarizable C₆₀(>DPAF-C_n)_x-derived fullerosome membrane, and an outer shell of HMTSF-analogous organic electron-donors. This class of multilayered core-shell nanospherical materials were excellent microwave absorbers. Six variable organic electron donors and two conducting conjugated polymers were applied to serve as the supply of photoinduced transferrable electrons at the outer shell layer. The design largely increased the number of polarizable charges, leading to a maximum of 387% amplification of the relative dielectric constant (ϵ_r') value or a 159%-additional increase from that of the parent trilayered precursor

NPs without organic donors. Good recyclability of ϵ_r' and its derivative ϵ_r'' back to their original values during each photoactivation cycle of light-on and light-off manipulations may allow the potential uses of hybrid nanomaterials as dielectrics in photoswitchable modulation of microwave reflection signals.

A sequential synthetic method to fabricate a multilayered organic–inorganic hybrid sandwiched nanostructure on graphene sheets was developed with measurements of reversible and photoswitchable dielectric property amplification characteristics performed at 1.0–4.0 GHz. The design was made by, firstly, replacing surface stabilizing surfactants by a monolayer array of $C_{60}>DPAF-C_9$ on both top and bottom faces of the graphene–SDS sheet followed by the deposition of core-shell $\gamma\text{-FeO}_x@AuNP$ nanoparticles and a top layer of $C_{60}>DPAF-C_9$ sequentially. We anticipated that the close contact of monolayered $C_{60}>$ cages at the graphene surface should be able to distribute $(C_{60}>)^{-n}$ charges onto graphene sheets that should stabilize the photoinduced polarized, charge-separated state as the approach of ferroelectric simulation for enhancing ϵ_r' amplification. As a result, we detected large further increase of reversible dielectric permittivity ϵ_r' amplification of 308% by photoexcitation at the plasmonic gold shell layer using a white LED light.

2.0 INTRODUCTION

Molecular organic–inorganic hybrid nanomaterials capable of exhibiting interactive response in physical (*i.e.* electric and magnetic) properties to electromagnetic waves in the microwave and radio frequency range (RF) remains relatively unexplored to date. Indeed, design of nanoorganic systems to create extraordinary and synergistic material characteristics in RF range is highly challenging. Artificial structural designs or constructions based on the metamaterial concept were to show unique electromagnetic properties and a tunable refractive index of the material medium.¹ Basic principles of this phenomenon rest on the ability of patterned architectures to interact with the magnetic and electric fields of incident light waves that resulted in physical responses leading simultaneously to unusual electric permittivity (ϵ) and magnetic permeability (μ) not found in nature.^{2–4} However, these artificial designs cannot be extended to the use of organic nanomaterials since they are functionally appropriate only at optical wavelengths.

One of tunable multiferroic materials requires the use of ferromagnetic materials along with ferroelectrics that are capable of undergoing cross-tuning or switching on the induction of magnetization by means of the electric field or polarization by the magnetic field (magnetodielectric effect).^{5,6} Our related recent study demonstrated the possibility of interactive couplings between dielectric charge electrons (e^-) of $C_{60}>DPAF-C_9$ **1** and magnetic *d*-spins,⁷ that is, normally, rare in nature materials. Organic chromophoric systems exhibiting ferroelectric characteristics are limited in availability and remain to be explored.⁸ Early promising organic ferroelectric materials were reported to be two-component co-crystals consisting of phenazine and chloranilic acid.^{9–11} The other example was given by the one-dimensional organic quantum magnet, tetrathiafulvalene–*p*-bromanil charge-transfer complex, via polarization.¹² Majority of known multiferroic materials, which show simultaneous ferroelectric and ferromagnetic ordering, is the class of binary metal oxides, such as BiFeO_3 ¹³ and BiMnO_3 ferrites. In general, organic multiferroic material exhibiting both ferromagnetism and ferroelectricity is not readily accessible.

Refractive index value is a function of the product of ϵ and μ , both being relevant material parameters for electromagnetic waves. Interestingly, negative permittivity ($\epsilon < 0$) can be observed on ferroelectric materials.^{14,15} Ferroelectric characteristics arise from the spontaneous polarization and ordering of electric dipoles in response to the external electrical field. Increasingly common practice to integrate ferroelectric property and ferromagnetism is to fabricate multiferroic magnetoelectric composite systems, such as ferromagnetic–ferroelectric heterostructures, for the flexibility of creating magnetoelectric effects in the magnetic-field control of electric polarization and also the electric-field control of magnetization.¹⁶ Aside from the magnetic- and electric-field modulation, the use of photoenergy to tune electric polarization and magnetization remains uncommon. One example was demonstrated by the study of photoinduced ferroelectric polarization enhancement on the multilayered thin film structure of a ferroelectric insulator

(Ba_{0.1}Sr_{0.9}TiO₃) and a ferromagnetic metal (La_{0.7}CaSr_{0.3}MnO₃).¹⁷ Photoinduced charge trapping at different sides of the layer interface was reasoned for the long-lived screening charges and high polarization. By using these inorganic material systems as guiding models, we designed highly e⁻-polarizable fullerosome membrane with a partial bilayer array of a C₆₀ cage sheet located in the center of the membrane to collect negatively polarized charges.

In the case of microwave applications, tunability of dielectric and magnetic properties with high saturation magnetization and low electrical conductivity based on ferrite–ferroelectric composites would be highly promising materials for the use in tunable microwave devices, such as tunable phase shifters and tunable filters^{18,19} or device.²⁰ Variation of the composition of ferrite–ferroelectric composites may also be possible to increase the microwave absorptivity.²¹ Tunable dielectric property was also proposed to be feasible in polymer composites consisting of short ferromagnetic microwires embedded into a dielectric matrix under dc magnetic field.²² In the organic system, organic ferroelectric phenomena were observed mainly on crystalline charge-transfer complexes.^{9–11} Therefore, we undertook an alternative approach to base on the physical property simulation of ferroelectricity using C₆₀– and C₇₀–light harvesting chromophore antenna conjugates^{23,24} to demonstrate their photoinduced intramolecular electron-transfer from the donor antenna to the fullerene e⁻-accepting cage in an ultrafast kinetic rate in femtoseconds,²⁵ fast enough to simulate “spontaneous polarization” in organic systems. The phenomena produce the intramolecular electron and charge separation of these conjugated C₆₀– and C₇₀–(antenna)_x nanostructures that increases the dielectric characteristics as the real part of complex dielectric constant (ϵ_r').

Our study principles of this type of materials investigation are based on the refractive index manipulation at the surface of the real target. As shown in Fig. 1, in the case of normal incidence of a RF wave, the wave can be either reflected, absorbed, or transmitted through the nanomaterial layer coated on the target object. The ratio of reflectivity, absorptivity, and transmissivity is the corresponding function of the refractive index (n) of the coated material layer which is, in term, the square root of the product of relative permittivity (ϵ_r) and permeability (μ_r). Therefore, by tuning the value of relative permittivity, we should be able to modulate the refractive index to change the reflectivity at the surface. In the measurement, the transverse magnetic reflection coefficient R^{TM} can be collected as a function of scattering parameter (S_{11} in the monostatic measurement or S_{12} in the angle-dependent bistatic measurement that is proportional to the reflected/incident signal intensity ratio) in dB (decibel) reflection. From the value of S_{11} , the real part of relative permittivity (ϵ_r') and the imaginary part of relative permittivity (ϵ_r'') can be determined. The correlation allows us to trace back the reflected wave power by controlling the dielectric constant ϵ_r value of nanomaterials.

Further considering the angle incident waves in our study, RF-reflectivity of an object is defined as the reduction in the reflected power (the return loss in decibels) in a log-ratio to the incident power. The

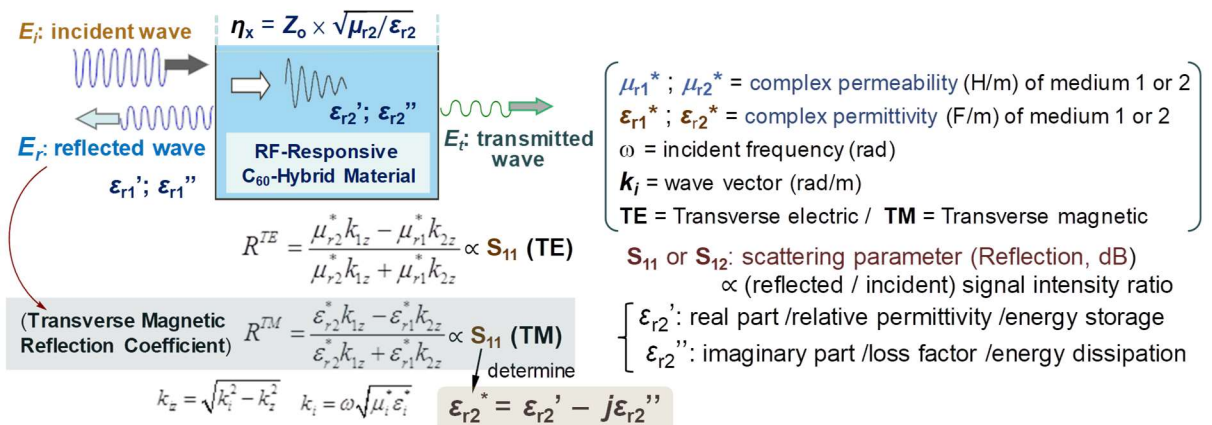


Figure 1. The theoretical base of correlation between reflected wave power and relative permittivity (ϵ_r') of the coated nanomaterial layer on the target object.

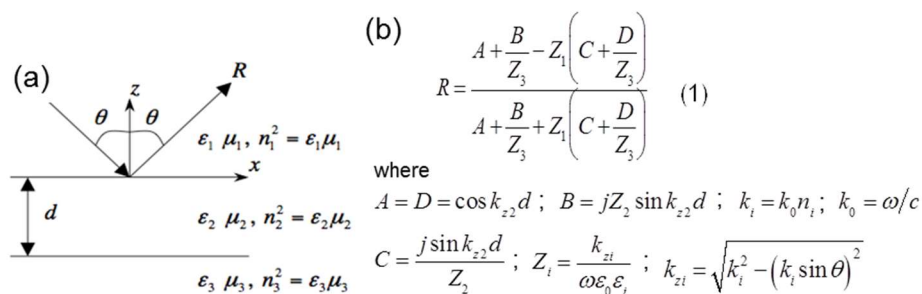


Figure 2. (a) A three-medium/two-layer model for the electromagnetic (EM) wave propagation and (b) the formula of the reflection coefficient R .

mode of electromagnetic (EM) wave propagation in a three-medium, two-layered material with a thickness of d follows those studied^{26–28} that can be briefly depicted, as shown in Fig. 2a. Incidence of a parallelly (p -) polarized transverse magnetic (TM) wave is reflected by the same incident angle (θ) at the surface of the material layer having the refractive index n_2 . Reflection coefficient R can be determined by the eq. (1) of Fig. 2b, where k_i is the wave number, n_i is the refractive index, k_0 is the free space wavenumber, Z_i is the impedance of p -polarized TM wave, ω is the angular frequency, ϵ_0 is the electric permittivity of free space ($= 8.854 \times 10^{-12}$ F/m), ϵ_i the relative complex permittivity (or dielectric constant) of the medium i . Therefore, RF-reflectivity can be modulated by the variation of relative complex dielectric constant (ϵ_r') of the material studied. This is consistent with the fact that the refractive index of a given medium is in a square-root relationship to the product of permittivity (ϵ) and permeability (μ). Both are relevant material parameters responsible for the tunability of EM waves passing through a medium. The former parameter is dependent on material's dielectric properties which can be correlated to the degree of electron (e^-) polarization at the frequency of measurements. Thus, our recent discovery of photoswitching tunability of ϵ_r using photoinduced interfacial plasmonic resonance energy transfer (PRET) among core-shell layers at a near-field of constructed multiple-layered core-shell nanoparticles (NPs) made the above stated hypothesis possible to tune reflected RF signals of the real object.^{29,30} The observed unusual RF-response phenomena upon turning *on* or *off* the light let us to control and modulate dielectric permittivity (ϵ) of nanomaterials in a photoswitching fashion. The effect can be regarded as being generated by modulation of the material's refractive index at microwave frequencies.

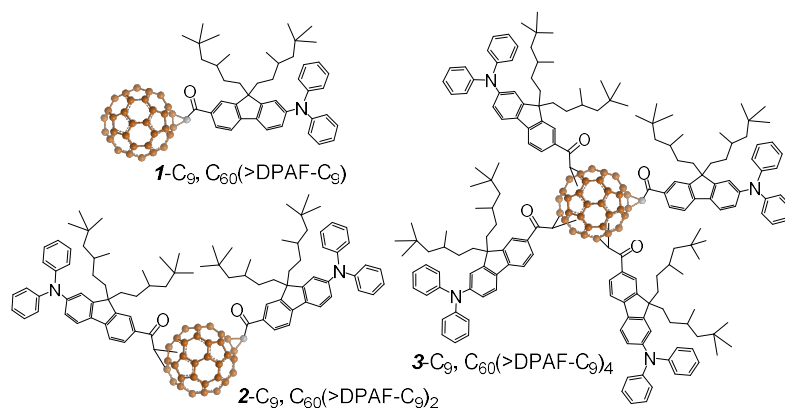


Figure 3. The compound structure of C₆₀-(light-harvesting antenna)_{1,2,or4} conjugates as the monadduct **1-C₉**, the bisadduct **2-C₉**, and the starburst tetraadduct **3-C₉**.

In general, plasmonic metallic nanoparticles^{31,32} capable of producing photoinduced surface plasmon resonance (SPR) energy can lead to the formation of polarizations at the surface region. Polarizability of this particular type of NPs, as a function of the size, refractive index, shape, density, and surrounding medium, is the factor to influence the state of scattering and absorption of light, e.g. absorption cross-section enhancement, as demonstrated in several theoretical studies.^{33,34} The phenomena of light-trapping effect in a thin-film structure can be achieved by implanting or embedding SPR-producing metallic NPs

in a medium of dielectric materials.³⁴ It involves a process that is possible to concentrate or fold the incident photon energy in terms of plasmon oscillations. In such a material configuration, the phenomena lead to potential permittivity or dielectric property increases within a thin semiconducting layer and gives much effect on the medium's dielectric states³⁵ that modulates the outcome of light scattering from and absorption in the particle. Concentrated energy confinement in localized plasmonic oscillations can be converted and transferred to the surrounding semiconducting medium to induce charge separation with the change of dielectric properties. It is a result of conductive electron excitations at the interface between the metal particle surface and dielectric compounds. Therefore, SPR coupled with sufficiently large scattering cross-sections of metallic NPs may scatter the incident light efficiently, enhance effective absorption cross sections, and locally amplify the electromagnetic field at the surface.³⁶ Therefore, these phenomena were applied in solar material composites and devices.^{37–40} When SPR is coupled with C₆₀-(light-harvesting antenna)_{1,2,or4} nano-conjugates (Fig. 3) in a near-field of <5.0 nm, it will be absorbed to induced the intramolecular electron-transfer from the e⁻-donor antenna chromophore moiety to the electron accepting C₆₀> cage moiety forming the corresponding (C₆₀>)⁻·-(light-harvesting antenna DPAF-C₉)_{1,2,or4}⁺ charge complex,⁴¹ as shown in Fig. 4. These transient excited state charges increase the dielectric constant (ϵ_i) or permittivity of the nanomaterial layer. Upon relaxation of photoexcited states back to the ground state, the electron reverses from (C₆₀>)⁻· back to (DPAF-C₉)⁺·. This reversibility of intramolecular electron-transfer between fullerene cages and donor chromophores becomes the foundation of our observed photoswitching phenomena in permittivity enhancement applications in the microwave frequency range.⁴²

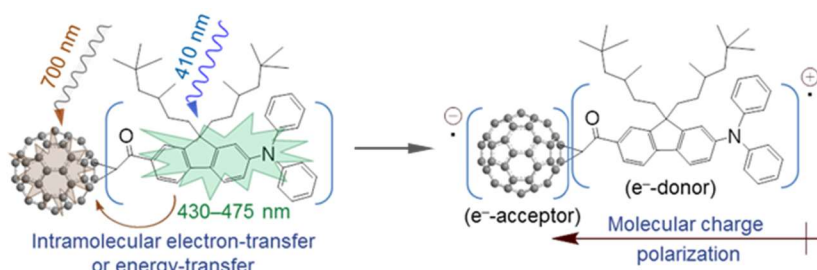


Figure 4. Conjugation structure of C₆₀(>DPAF-C₉), **1-C₉**, at the keto conjunction, where the keto–enol isomerization resonance¹⁶ is omitted, showing optical absorption wavelength ranges of the donor and acceptor moieties and the photoinduced intramolecular e⁻-transfer in a close distance of only few Å leading to the formation of a molecularly polarized charge-separated state.

3.0. METHODS, ASSUMPTIONS, AND PROCEDURES

3.1. Materials

Reagents of sodium *t*-butoxide, α -bromoacetyl bromide, aluminum chloride (AlCl₃), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *rac*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), and tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃(0)] were purchased from Aldrich Chemicals, Natick, Massachusetts, USA and used without further purification. Fullerene materials with a purity of 99% was purchased from Suzhou Dade Carbon Nanotechnology Co., Ltd. Suzhou, Jiangsu, China. Anhydrous grade solvent of THF was used and further dried via refluxing over sodium and benzophenone overnight and distilled under reduced pressure (10⁻¹ mmHg). The precursor compounds including 1,3,5-tris(*N*-phenylamino)benzene (TPAB) and 2-bromo-9,9-di(methoxyethyl)fluorene (BrF-C_{2M}) were synthesized according to our previous procedures.⁴³

3.2. Synthetic Procedures

*Synthesis of 7-(1,2-dihydro-1,2-methanofullerene[60]-61-{1,1-dicyanoethylene})-9,9-di(3,5,5-trimethylhexyl)-2-diphenylamino*fluorene C₆₀(>CPAF-C₉) (**1-C₉**).

The compound 7-bromoacetyl-9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene (BrDPAF-C₉) (3 g, 4.28 mmol) was added to the solution of C₆₀ (3.7 g, 5.13 mmol) in toluene (2600 mL) under an atmospheric pressure of nitrogen. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.62 mL, 4.28 mmol) was then added to the mixture dropwise at room temperature with stirring for a period of 5.0 h. The resulting suspending solids of the reaction mixture were filtered off and the filtrate was concentrated to a 10% volume. Methanol (350 mL) was then added to cause precipitation of the crude product, which was isolated by centrifugation. The purification of C₆₀[>DPAF-C₉] were made by column chromatography on silica gel using a solvent mixture of hexane–toluene/3:2 as eluent (*R*_f = 0.45), yielding brown solids (2.97 g, 70% based on recovered C₆₀). Spectroscopic data: FAB⁺–MS calcd for ¹²C₁₀₅¹H₅₅¹⁴N₁¹⁶O₁ *m/z* 1345.4; found, *m/z* 1345 and 1346; MALDI–MS (TOF) found, *m/z* 1349, 1348, 1347, 1346 (MH⁺), 894, 877, 862, 855, 845, 840, 802, 704, 687, 683, 672, 665, 650, 631, 629, 612, and 585; Anal. Calcd for C₁₀₅H₅₅NO: C, 93.68; H, 4.08; N, 1.04; found: C, 93.52; H, 3.88; N, 0.95; UV-vis (CHCl₃, 2.0 × 10^{−5} M) λ_{max} (ε) 263 (1.7 × 10⁵ L mol^{−1} cm^{−1}), 326 (5.7 × 10⁴ L mol^{−1} cm^{−1}) and 410 nm (4.4 × 10⁴ L mol^{−1} cm^{−1}); FT-IR (KBr) ν_{max} 3435 (br), 2947 (s), 2922, 2861 (m), 1678, 1593 (vs), 1491 (s), 1464, 1426, 1402, 1347 (w), 1274 (s), 1199 (s), 1185, 1155 (w), 1028 (w), 816 (w), 752 (s), 695 (s), 576, and 526 (vs) cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 8.47 (d, 1H), 8.33 (s, 1H), 7.82 (d, 1H), 7.65 (d, 1H), 7.26 (m, 6H), 7.13 (m, 4H), 7.05 (m, 2H), 5.67 (t, 1H), 2.1–1.9 (m, 4H), 1.3–1.1 (m, 4H), and 0.9–0.6 (m, 30H); ¹³C NMR (500 MHz, CDCl₃, ppm) δ 189.3, 153.7, 151.4, 149.1, 148.2, 148.20, 147.6, 147.6, 146.9, 145.6, 145.4, 145.3, 145.1, 145.0, 144.9, 144.7, 144.6, 144.6, 144.5, 143.9, 143.7, 143.3, 143.1, 143.1, 143.0, 142.9, 142.9, 142.8, 142.5, 142.2, 142.1, 141.2, 140.9, 139.6, 136.6, 134.0, 133.5, 129.4, 128.9, 124.5, 123.2, 122.8, 121.8, 119.3, 118.0, 72.6, 55.2, 50.9, 44.6, 38.2, 33.2, 30.9, 30.0, 29.5, and 22.6.

Synthesis of Bisadduct C₆₀[methanocarbonyl-7-(9,9-di(3,5,5-trimethylhexyl)-2-diphenylaminofluorene)]₂, C₆₀(>DPAF-C₉)₂ (2-C₉).

A modified procedure as that reported recently was used.²⁴ Spectroscopic data of 2-C₉: FAB⁺–MS calcd for ¹²C₁₅₀¹H₁₁₀¹⁴N₂¹⁶O₂ *m/z* 1970.8; found, *m/z* 1971; MALDI–MS (TOF) found, *m/z* 1974, 1973, 1972, 1971 (M⁺), 1347, 1346, 870, 861, 710, 705, 672, 666, 630, 629, 612, and 583; UV-vis (CHCl₃, 2.0 × 10^{−5} M) λ_{max} (ε) 255 (1.9 × 10⁵), 310 (1.1 × 10⁵), and 406 nm (8.5 × 10⁴ L/mol-cm); FT-IR (KBr) ν_{max} 3429 (br), 3163, 2951 (s), 2922, 2863, 1680, 1595 (vs), 1492 (vs), 1465, 1420, 1400, 1316(w), 1277, 1200, 1156 (w), 1093, 1030 (w), 816 (w), 753, 670 (s), and 527 (s) cm^{−1}; ¹H NMR (500 MHz, CDCl₃, ppm) δ 8.5–8.1 (m, 4H), 7.9–7.4 (m, 4H), 7.24 (m, 12H), 7.12 (m, 8H), 7.05 (m, 4H), 5.8–5.3 (m, 2H), 2.1–1.8 (m, 8H), 1.35–1.15 (m, 8H), and 1.1–0.5 (m, 60H). ¹³C NMR (500 MHz, CDCl₃, ppm) δ 189.8, 154.1, 151.8, 151.7, 149.4, 148.1, 148.0, 147.7, 147.5, 146.9, 146.8, 146.6, 146.2, 146.0, 145.9, 145.7, 145.5, 145.0, 145.0, 144.9, 144.8, 144.7, 144.5, 144.3, 144.0, 143.9, 143.7, 143.6, 143.3, 143.3, 143.3, 143.1, 143.0, 143.0, 142.9, 142.6, 142.5, 142.3, 142.3, 142.2, 142.1, 140.9, 140.5, 140.0, 139.8, 139.7, 139.5, 134.5, 134.0, 129.8, 129.5, 129.3, 128.65, 124.9, 123.6, 122.3, 119.6, 118.5, 73.4, 73.2, 55.6, 51.3, 51.2, 44.4, 44.4, 42.9, 38.2, 38.2, 38.1, 33.6, 33.5, 33.5, 31.4, 30.4, 29.9, 27.7, 23.1, and 22.9.

Synthesis of N¹,N³,N⁵-Tris(9,9-di(3',5',5'-trimethyl-1'-hexyl)fluoren-2-yl)-1'',3'',5''-tris(phenyl-amino)benzene, tris(DPAF-C₉) as 4-C₉.

Synthetic procedure of tris(DPAF-C₉) (4-C₉) was followed by and slightly modified from the recently reported methods.⁴⁴ A typical procedure was given as follows. A mixture of BrF-C₉ (10.0 g, 20.3 mmol, excess), TPAB (1.16 g, 3.30 mmol), Pd₂(dba)₃(0) (0.023 g, 0.25 mol%), BINAP (0.046 g, 0.75 mol%), and sodium *t*-butoxide (1.94 g, 20.3 mmol) taken in anhydrous toluene (75 mL) was heated to refluxing temperature under nitrogen for a period of 72 h. After being cooled to room temperature, the reaction mixture was washed with water for three times and dried over sodium sulfate. A crude brown colored paste was obtained after evaporating the solvent. It was subjected to column chromatography purification using silica gel as the stationary phase and hexane–ethylacetate (9:1) as the eluent. The product of tris(DPAF-C₉) was collected at *R*_f = 0.8 as light yellow solids in 83% yield (4.35 g).

Since the HPLC indicated a mixture of tris(DPAF-C₉) stereoisomers, further separation and isolation were carried out by thin-layer chromatography (TLC), using silica gel as the stationary phase and hexane–ethylacetate (9.5:0.5, v/v) as the eluent. A mid-broad band at R_f 0.55–0.7 was identified as the tris(DPAF-C₉) products that can be cutted evenly into two parts at R_f 0.55–0.63 (as the bottom cut) and R_f 0.63–0.7 (as the top cut). Based on their corresponding ¹H NMR spectra, the top cut was confirmed to be the pure *cis-cup*-tris(DPAF-C₉) stereoisomer and the bottom cut was consisting of a mixture of *trans-chair*-tris(DPAF-C₉) and *cis-cup*-tris(DPAF-C₉) stereoisomers in the ratio of roughly 2:3. This fraction was subjected to further TLC separation and elution two more times using hexane–ethylacetate (9.7:0.3, v/v) as the eluent for the first run and the similar mixture (9.8:0.2, v/v) for the second run to obtain *cis-cup*-tris(DPAF-C₉) in improved purity and the pure form of *trans-chair*-tris(DPAF-C₉) fraction.

Spectroscopic data of *cis-cup*-tris(DPAF-C₉) (*cis-cup-4-C₉*): FT-IR (KBr) $\nu_{\max}$ 3064 (w, aromatic C–H stretching), 3038 (w), 3011 (w), 2956 (vs, aliphatic C–H stretching), 2908 (m), 2865 (s), 1596 (m), 1584 (s, C=C), 1495 (s, anti-symmetric deformations of CH₃ groups and scissor vibrations of CH₂ groups), 1468 (m), 1450 (s), 1363 (m, symmetric deformations of CH₃ groups), 1296 (m, asymmetric stretching vibrations of C–N–C), 1246 (m, asymmetric stretching vibrations of C–N–C), 1215 (w), 1176 (w), 1157 (w), 1030 (w), 933 (w), 826 (w), 754 (m), 736 (s, C–H out-of-plan deformation), 710 (m, C–H out-of-plan deformation), 694 (m), and 508 (w) cm⁻¹; UV-vis (EtOAc, 1.0×10^{-5} M) $\lambda_{\max}$ (ϵ) 323 (5.62×10^4 L mol⁻¹ cm⁻¹) and 353 nm (5.65×10^4 L mol⁻¹ cm⁻¹); ¹H NMR (500 MHz, CDCl₃) δ 7.58 (s, 3H, br), 7.52 (d, 3H), 7.32–7.21 (m, 9H), 7.09–7.01 (m, 18H), 6.82 (t, 3H), 6.55 (s, 3H), 1.92–1.67 (m, 12H), 1.10 (m, 6H), and 0.97–0.39 (m, 96H); ¹³C NMR (500 MHz, CDCl₃) δ 151.7, 150.0, 149.2, 147.7, 146.5, 141.2, 136.8, 129.2, 126.6, 126.6, 124.0, 122.9, 121.7, 120.0, 119.3, 115.6, 54.5, 51.0, 50.6, 50.6, 38.3, 38.1, 37.4, 37.6, 33.1, 32.7, 31.1, 30.2, 29.6, 29.4, 27.2, 22.9, and 22.4; MALDI-TOF MS calcd for C₁₁₇H₁₅₃N₃, m/z 1600.21; found, m/z 1601.26 (MH⁺), 1602.30, 1603.29, 1260.95, 1092.81, 752.23 and 508.79 (PhN⁺H + fluorene-C₉).

Spectroscopic data of *trans-chair*-tris(DPAF-C₉) (*trans-chair-4-C₉*): FT-IR (KBr) $\nu_{\max}$ 3062 (w, aromatic C–H stretching), 3037 (w), 3012 (w), 2955 (vs, aliphatic C–H stretching), 2925 (vs, aliphatic C–H stretching), 2855 (s), 1630 (vs), 1588 (s, C=C), 1495 (s, anti-symmetric deformations of CH₃ groups and scissor vibrations of CH₂ groups), 1450 (s), 1362 (m, symmetric deformations of CH₃ groups), 1294 (m, asymmetric stretching vibrations of C–N–C), 1250 (m, asymmetric stretching vibrations of C–N–C), 1218 (w), 1158 (w), 1035 (w), 803 (w), 763 (m), 736 (m, C–H out-of-plan deformation), 709 (w, C–H out-of-plan deformation), 691 (m), and 510 (w) cm⁻¹; UV-vis (EtOAc, 1.0×10^{-5} M) $\lambda_{\max}$ (ϵ) 322 (5.50×10^4) and 353 nm (5.68×10^4 L mol⁻¹ cm⁻¹); ¹H NMR (500 MHz, CDCl₃) δ 7.58 (s, 3H, br), 7.51 (d, 3H), 7.34–7.20 (m, 9H), 7.09–7.01 (m, 18H), 6.84 (m, 3H), 6.55 (m, 2H), 6.48 (m, 1H), 2.02–1.67 (m, 12H), 1.11 (m, 6H), and 0.97–0.39 (m, 96H); ¹³C NMR [similar to those of *cis-cup*-tris(DPAF-C₉)]; MALDI-TOF MS calcd for C₁₁₇H₁₅₃N₃, m/z 1600.21; found, m/z 1601.37 (MH⁺), 1602.36, 1603.35, 1604.40, 1260.00, 1093.86, and 508.73 (PhN⁺H + fluorene-C₉).

Synthesis of N¹,N³,N⁵-Tris(7- α -bromoacetyl-9,9-di(3',5',5'-trimethyl-1'-hexyl)fluoren-2-yl)-1'',3'',5''-tris(phenylamino)benzene, cis-cup-Tris(BrDPAF-C₉).

To a suspension of AlCl₃ (1.0 g, 7.5 mmol) in 1,2-dichloroethane (40 ml) at 0 °C was added *cis-cup*-tris(DPAF-C₉) (*cis-cup-4-C₉*, 0.7 g, 0.44 mmol) with vigorously stirring. The compound of α -bromoacetyl bromide (1.0 g, 5.0 mmol) was then slowly added over 10 min while maintaining the temperature between 0–10 °C. The mixture was warmed to ambient temperature and stirred overnight. The reaction was quenched by slow addition of water (50 ml) while maintaining the temperature below 45 °C. The organic layer was washed sequentially with dil. HCl (1.0 N, 50 mL) and water (50 mL $\times$ 2), and dried over sodium sulfate and then concentrated in vacuo to give the crude product as viscous yellow semi-solids. It was purified by column chromatography (silica gel) using hexane–EtOAc (9:1, v/v) as eluent to afford *cis-cup*-tris(Br-DPAF-C₉) in 53% yield (0.46 g). Spectroscopic data: FT-IR (KBr) $\nu_{\max}$ 3066 (w), 3035 (w), 2954 (s), 2907 (m), 2864 (m), 1733 (w), 1675 (s), 1594 (s), 1584 (s), 1492 (m), 1464 (m), 1429 (m), 1393 (w), 1364 (w), 1343 (w), 1288 (s), 1262 (m), 1205 (w), 1180 (m), 1107 (w), 1022 (w), 819 (m), 748 (m),

713 (m), and 696 (m) cm^{-1} ; UV-vis (EtOAc, 1.0×10^{-5} M) λ_{max} (ϵ) 304 (8.88×10^4 L mol^{-1} cm^{-1}) and 395 nm (1.10×10^5 L mol^{-1} cm^{-1}); ^1H NMR (500 MHz, CDCl_3) δ 7.94 (m, 3H), 7.88 (m, 3H), 7.63 (m, 3H), 7.56 (m, 3H), 7.22–6.92 (m, 21H), 6.56 (m, 3H), 4.46 (m, 6H), 2.11–1.67 (m, 12H), 1.10 (m, 6H), 0.99–0.26 (m, 96H).

Synthesis of N^1, N^3, N^5 -Tris(7-(1,2-dihydro-1,2-methanofullerene[60]-61-carbonyl)-9,9-di(3',5',5'-trimethyl-1'-hexyl)fluoren-2-yl)-1'',3'',5''-tris(phenylamino)benzene, cis-cup-Tris[$\text{C}_{60}>(\text{DPAF-C}_9)$] as cis-cup-5-C₉.

A homogeneous solution of C_{60} (0.70 g, 0.97 mmol) in anhydrous toluene (700 mL) was prepared by ultrasonication for a period of 1.0 h that was then stirred overnight under nitrogen. To this was added by *cis-cup*-tris(BrDPAF- C_9) (0.40 g, 0.20 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.21 g, 1.38 mmol) sequentially and stirred at room temperature for a period of 8.0 h. At the end of stirring, the reaction mixture was concentrated to a 10%-volume. Methanol (100 mL) was added to effect precipitation of the crude product, which was isolated by centrifugation. Further purification by column chromatography (silica gel) using a solvent mixture of hexane–toluene (3:2) as the eluent afforded *cis-cup*-tris[$\text{C}_{60}>(\text{DPAF-C}_9)$] (*cis-cup-5-C₉*) as brown solids in 68% yield (0.52 g). Spectroscopic data: FT-IR (KBr) ν_{max} 2951 (m), 2923 (m), 2861 (w), 1681 (m), 1627 (s), 1594 (s), 1585 (s), 1490 (m), 1462 (m), 1429 (w), 1361 (w), 1317 (m), 1292 (m), 1247 (m), 1213 (m), 1184 (m), 1093 (w), 1035 (w), 908 (m), 819 (m), 732 (s), 698 (m), 575 (w), and 529 (s) cm^{-1} ; UV-vis (toluene, 1.0×10^{-5} M) λ_{max} (ϵ) 335 nm (1.76×10^5 L mol^{-1} cm^{-1}) and 402 nm (shoulder band, 4.19×10^4 L mol^{-1} cm^{-1}); ^1H NMR (500 MHz, CDCl_3) δ 8.46 (m, 3H), 8.30 (m, 3H), 7.81 (m, 3H), 7.63 (m, 3H), 7.31–6.70 (m, 21H), 6.60 (m, 3H), 5.67 (m, 3H), 1.92–1.67 (m, 12H), 1.14 (m, 6H), 0.70 (m, 96H); ^{13}C NMR (500 MHz, CDCl_3) δ 148.67, 148.56, 148.46, 147.89, 147.70, 147.18, 145.96, 145.82, 145.72, 145.68, 145.58, 145.47, 145.24, 145.13, 145.05, 144.73, 144.60, 144.48, 144.35, 144.28, 144.18, 144.14, 144.03, 143.94, 143.87, 143.72, 143.50, 143.41, 143.20, 142.92, 142.65, 142.50, 141.64, 141.35, 139.92, 137.07, 134.75, 134.03, 133.86, 129.61, 129.47, 124.34, 124.13, 123.53, 119.78, 116.61, 84.81, 72.88, 55.60, 51.55, 51.32, 51.02, 50.89, 45.07, 38.33, 38.02, 37.85, 37.67, 33.33, 31.31, 30.37, 29.93, 27.66, and 22.99.

Shear Exfoliation of Graphene Nanosheets.

A number of preparation methods developed for the shear exfoliation of graphene sheets have been extensively studied.⁴⁵ There are two general approaches with one most common technique to apply various surfactant agents as the aid in aqueous solutions to stabilize graphene sheets in water during exfoliation. By the use of ionic surfactants, surfactants being coated on nano-sheets due to hydrophobic-hydrophobic binding interactions resulted in ionic charges located on the surface that provided electrostatic repelling effects from each other to minimize aggregations with enhanced stabilization. The other approach was the use of a combination of suitable organic solvents with the surface energy close to that of graphene itself to maximize the compatibility with low mixing energy that can also stabilize the exfoliated nano-sheets against re-aggregation.

Accordingly, we utilized both approaches together by a mixture of *N*-methyl-2-pyrrolidone (NMP), which was proven to be a good choice of organic solvent,⁴⁶ and sodium dodecyl sulfate (SDS) to obtain a high yield of exfoliation while the resulting exfoliated graphene nanosheets were stabilized in NMP–water mixture. In a typical procedure, the graphite (5.0 g) was weighed in a mixing vessel with the solvent and surfactant added in a proportion of NMP (20 mL)–SDS (1.0 g)–D.I. water (180 mL). A mechanical stirring head was applied in the vessel for vigorous blending with the shearing force corresponding to the gradually increased speed to a maximum of 2500 rpm for a period of 3.0 d as the blending time. Unexfoliated graphite particles were removed by centrifuge at 2000 rpm for 30 min. After removal of the most of water by rotary evaporation at 50 °C, the graphene sheets were stocked in NMP as a master solution. The concentration of graphene sheets was estimated to be 80 mg/mL by taking a small portion of sample (1.0 mL) to dry, collect, and weigh the solid remained.

Synthesis of γ -FeO_x ($1.0 < x < 1.5$) Nanoparticles.

Method A1. In a typical reaction, a mixture of FeCl₃·6H₂O (2.70 g, 0.010 mol), FeCl₂·4H₂O (1.98 g, 0.010 mol), sodium acetate (4.92 g, 0.060 mol, as a hydrolyzing agent), H₂O (4.0 mL), and *n*-octylamine (7.3 mL, as a capping agent) in 1,2-propanediol (66 mL) were prepared and stirred under reflux at 150 °C for a period of 5.0 h. It was followed by precipitation upon the addition of 2-propanol to afford the product in a nearly quantitative yield. Spectroscopic data: FT-IR (KBr) ν_{max} 2970 (w), 2924 (s), 2852 (m), 1743 (w), 1630 (s), 1458 (m), 1383 (m), 1134 (m), 1041 (m), 922 (w), 879 (w), 839 (w), 627 (vs), and 584 (vs) cm⁻¹.

Method A2. Iron oleate was firstly prepared by heating iron chloride, FeCl₃·6H₂O (5.4 g, 20 mmol) and FeCl₂·4H₂O (2.0 g, 10 mmol), and sodium oleate (36.5 g, 120 mmol) at 70 °C in a mixture solvent, composed of ethanol (80 mL), distilled water (60 mL), and hexane (140 mL), for a period of 4.0 h. At the end of reaction, the upper organic layer containing the iron oleate complex was washed three times with distilled water (30 mL each), dried over sodium sulfate, and solvent evaporated off to yield iron oleate complex in a waxy solid form. To this resulting organometallic complex, 1-oleic acid (4.3 g, 15 mmol) and 1-octadecene (200 g, act as the solvent) were added at room temperature and refluxed at 320 °C for 1.5 h. Upon the temperature reaching 320 °C, a severe exothermic reaction occurred with the initial transparent solution turning to turbid and brownish black. The product mixture was cooled to room temperature, followed by precipitation with ethanol (500 mL). Resulting nanoparticles were collected using a permanent magnet, washed twice with both 2-propanol (100 mL) and ethanol (100 mL). They were re-dispersed in nonpolar solvent, such as hexane and toluene, via ultrasonication. In general, dark solid particles of γ -FeO_x (Fe₃O₄) obtained by this method were found to be highly magnetic in response to the external magnet and soluble in many nonpolar organic solvents. Distribution of the particle size is fairly homogenous and was measured via TEM as ~20 nm in diameter on average. Spectroscopic data: FT-IR (KBr) ν_{max} 2960 (w), 2921 (s), 2852 (m), 1618 (s), 1459 (w), 1407 (m), and 578 (vs) cm⁻¹.

Synthesis of Au-Nanoparticles Coated γ -FeO_x Nanoparticles, γ -FeO_x@AuNP.

Method B1. Our first trial was involving the direct reduction and deposition of gold acetate, Au(ac)₃, on the surface of iron oxide NPs (10–20 nm, prepared by either methods A1 or A2) in the presence of 1,2-hexadecanediol and 1-oleylamine. Briefly, to the suspension of γ -FeO_x NPs (0.1 g) in phenyl ether (20 mL) was added Au(ac)₃ (0.45 g, 1.2 mmol), 1,2-hexadecanediol (3.0 g, 25 mmol), and oleylamine (4 mL) under N₂ atmosphere. The mixture was heated to 180–190 °C with vigorously stirred for 2.0 h while maintain the temperature constant. After cooling to room temperature, the NPs were collected by a permanent magnet, washed twice with both 2-propanol (100 mL) and ethanol (100 mL). Subsequently, the NPs were collected with a permanent magnet to yield a dark brown solid powder.

Method B2. To the γ -FeO_x nanoparticles (prepared by the method A1 stated above, 100 mg) was added D.I. water (100 mL) and tetramethylammonium hydroxide (1.0 M, 10 mL, 10 mmol). The mixture was ultrasonicated for 1.0 h to dissolve particles and yield a transparent brown solution. The solution was filtered through 0.4- μ m PTFE syringe filter to remove insoluble large particles. The solution was then diluted to 2.0 L by D.I water, added by sodium citrate (0.5 M, 100 mL, 50 mmol), and stirred for 30 min at ambient temperature. While kept stirring, the solution of hydroxylamine hydrochloride (1.0 M, 2.0 mL, 2.0 mmol) and hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 0.025 M, 2.0 mL, 0.05 mmol) were added portionwise in 1/10 quantity each by an interval period of 15 min. After finishing addition, a magnet was used to separate and remove the particles containing γ -FeO_x from the solution. They were washed with D.I water (×2) and ethanol (×2) and, finally, washed with methanol and decanted the supernatant. The suspension solution was then added acetone (10 mL), methanol (10 mL), and 1-octanethiol (1.0 mL) and ultrasonicated for 1.0 h to replace hydrophilic stabilizer (tertiary amine or sodium citrate) on the surface by hydrophobic thiol hydrocarbons. The resulting solids were filtered and washed by water and ethanol to remove remaining residual hydrophilic stabilizers and excessive 1-octanethiol to yield core-shell Au-NPs coated γ -FeO_x nanoparticles. Spectroscopic data: FT-IR (KBr) ν_{max} 2958 (m),

2928 (s), 2852 (m), 1724 (w), 1626 (s), 1496 (m), 1463 (s), 1380 (m), 1330 (w), 1263 (w), 1168 (m), 1130 (s), 1078 (s), 877 (w), 804 (m), 730 (s), 696 (m), 609 (m), 584 (s), and 557 (m) cm^{-1} .

*Preparation of C_{60} (>DPAF- C_9)-Encapsulated $\gamma\text{-FeO}_x\text{@Au}$ Trilayered Core-Shell Nanoparticles, $(\gamma\text{-FeO}_x\text{@AuNP})\text{@}[\text{C}_{60}(\text{>DPAF-}\text{C}_9)]_n$ (**6-NP**).*

We carried out an encapsulation procedure by dissolving $\gamma\text{-FeO}_x\text{@AuNP}$ nanoparticles (100 mg) in toluene with the aid of a small quantity of 1-octanethiol, followed by the addition of $\text{C}_{60}(\text{>DPAF-}\text{C}_9)$ (100 mg) and subsequent sonication for a period of 30 min. After filtration of the solution through celite, an excessive amount of $\text{C}_{60}(\text{>DPAF-}\text{C}_9)$ (est. in <5 mg) remaining in the solution was removed. All encapsulated magnetic nanoparticles filtered off at the top celite surface as brown solids were recovered by toluene extraction and physically removed from the solution by an internal permanent magnet. Solids were washed repeatedly by ethanol and ether, followed by drying in vacuo.

Alternatively, a modified method was used to prevent the possible material loss during celite filtration. In this procedure, both $\gamma\text{-FeO}_x\text{@AuNP}$ nanoparticles (100 mg) and $\text{C}_{60}(\text{>DPAF-}\text{C}_9)$ (**1-C₉**) or $\text{C}_{60}(\text{>DPAF-}\text{C}_9)_2$ (**2-C₉**) in a predefined weight ratio amount were dissolved in toluene (30 mL) with stirring for 30 min and then ultrasonicated for an additional more than 30 min until a clear solution being obtained to homogenize nanoparticles dispersion and increase their interactions with **1-C₉** or **2-C₉**. The solution was concentrated via rotary evaporation to less than 3.0 mL in volume to increase the molecular contact of **1-C₉** or **2-C₉** to $\gamma\text{-FeO}_x\text{@AuNPs}$. It was then diluted by toluene again to a volume of 30 mL with stirring and subsequent sonication for 10 min to dissolve excessive **1-C₉** or **2-C₉**. All encapsulated magnetic nanoparticles were physically removed from the container solution with the assistance of an internal permanent magnet. The nanoparticles were washed repeatedly by ethanol and ether, followed by drying in vacuo to afford dark brown solids of $(\gamma\text{-FeO}_x\text{@AuNP})\text{@}[\text{C}_{60}(\text{>DPAF-}\text{C}_9)]_x$ [$x = 1$ (**6-NP**) or 2 (**7-NP**)]. Spectroscopic data of **6-NP** prepared based on the nanoparticle methods A1 and B2: FT-IR (KBr) ν_{max} 2952 (m), 2920 (s), 2848 (m), 1741 (m), 1675 (m), 1637 (m), 1618 (m), 1591 (s), 1490 (m), 1458 (s), 1429 (m), 1382 (m), 1271 (m), 1203 (s), 1168 (m), 1110 (m), 1076 (m), 1029 (m), 875 (w), 811 (w), 748 (m), 694 (m), 617 (m), 582 (s), and 526 (s) cm^{-1} .

*Preparation of *cis-cup*-Tris[C_{60} (>DPAF- C_9)]-Encapsulated $\gamma\text{-FeO}_x\text{@AuNP}$ Yielding Trilayered Core-Shell Nanoparticles, $(\gamma\text{-FeO}_x\text{@AuNP})\text{@}\{\textit{cis-cup-tris}[\text{C}_{60}(\text{>DPAF-}\text{C}_9)]\}_n$ (**8-NP**).*

Nanoparticles of $\gamma\text{-FeO}_x$ and the corresponding plasmonic metallic gold-coated $\gamma\text{-FeO}_x\text{@AuNP}$ nanoparticles were synthesized according to a slightly modified procedure prepared above. A large scale preparation was carried out for the subsequent fabrication procedure using the same batch of materials to give consistency of $\gamma\text{-FeO}_x\text{@AuNP}$ characteristics in terms of the particle size and the Au-layer thickness. Spectroscopy data: FT-IR (KBr) ν_{max} 3027 (w), 2956 (w), 2923 (m), 2856 (m), 1631 (s), 1492 (m), 1461 (s), 1378 (m), 1328 (w), 1263 (w), 1166 (w), 1128 (w), 1076 (w), 1037 (w), 804 (m), 728 (m), and 588 (s) cm^{-1} .

Encapsulation of *cis-cup*-tris[C_{60} (>DPAF- C_9)] (*cis-cup-5-C₉*) on nanoparticles of $\gamma\text{-FeO}_x\text{@AuNP}$ was carried out by the method as follows. A mixture of $\gamma\text{-FeO}_x\text{@AuNPs}$ (100 mg) and *cis-cup-5-C₉* in a predefined weight ratio amount were dissolved in toluene (30 mL) with stirring for 30 min and then ultrasonicated for an additional >30 min until a clear solution being obtained showing a homogenized nanoparticles dispersion. The solution was concentrated via rotary evaporation to less than 3.0 mL in volume to increase the molecular contact of *cis-cup-5-C₉* to $\gamma\text{-FeO}_x\text{@AuNP}$. It was then diluted by toluene to a volume of 30 mL with stirring and subsequent sonication for 10 min to dissolve *cis-cup-5-C₉* fully. All encapsulated magnetic nanoparticles were physically removed from the container solution by the assistance of an external permanent magnet. The separated nanoparticles were washed repeatedly by ethanol and ether, followed by drying in vacuo to afford dark brown solids of **8-NP**. Spectroscopy data: FT-IR (KBr) ν_{max} 3089 (w), 3064 (w), 3031 (w), 2952 (m, aromatic C–H stretching), 2927 (s, aliphatic C–H stretching), 2860 (m), 1679 (m, –C=O), 1636 (m), 1587 (s, –C=C–), 1492 (m), 1463 (m), 1430 (m), 1363 (w), 1291 (m, asymmetric stretching vibrations of C–N–C), 1247 (w), 1214 (m), 1187 (m), 1126

(w), 1091 (w), 1035 (m), 904 (m), 815 (w), 730 (m, C–H out-of-plan deformation), 695 (m), 576 (m), and 526 (s, C₆₀>) cm⁻¹.

Synthesis of Multi-layered Nanoparticle Configuration of GN@{(γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n}_m [GN@(FeAuF_n)] (9-NP).

A layer-by-layer coating approach was applied for the preparation of multilayered GN@(FeAuF_n) nanomaterials, containing graphene nanosheets, C₆₀(>DPAF-C₉), and γ-FeO_x@AuNP samples. The final quantity of C₆₀(>DPAF-C₉) as comparing to that of graphene sheets was counted by a weight ratio of 1:8, 1:4, 1:2, 1:1, and 2:1 for comparison. In the first step of nanostructure fabrication procedure, C₆₀(>DPAF-C₉) (1.0 g) was dissolved in toluene (25 mL) and added to the suspension solution of graphene nanosheets in NMP (1.0 g of GN per 12.5 mL, stabilized by SDS). The mixture was subjected to vigorously stirring and sonication repeatedly to force the ligand exchange between C₆₀(>DPAF-C₉) and the SDS surfactant molecules. The exchange reaction was observed by the evidence of improved solubility of graphene nanosheets in a toluene–NMP mixture with precipitation of some SDS in a small quantity as white solids. After removing toluene and NMP solvents, via rotary evaporation, and washed away the precipitated SDS with water and ethanol, the partially C₆₀(>DPAF-C₉)-encapsulated graphene nanosheets, GN@[C₆₀(>DPAF-C₉)]_n, were obtained as dark brown-black loose dry flake-pastes.

In the second step, γ-FeO_x@AuNP nanoparticles (1.5 g, to keep the same total weight as that of 1-C₉) in toluene (10 mL) were added to coat and cap on the top of C₆₀(>DPAF-C₉) layer by mixing with the C₆₀(>DPAF-C₉)-coated graphene sheets in toluene (10 mL), prepared in the first step. The mixture was sonicated for 30 min and concentrated, via rotary evaporation, to a concentrated solution (2.0–3.0 mL remaining). An external permanent magnet was used to remove, with the solvent decanted, and collect the γ-FeO_x@AuNP-containing solid nanoparticles. They were washed by ethanol and ether to afford wet flake-like pastes of the products, GN@[(γ-FeO_x@AuNP)–C₆₀(>DPAF-C₉)]_n.

In the third step, the second batch of C₆₀(>DPAF-C₉) (0.5 g, a half amount as that for the first-step layer coating) in toluene (25 mL) was added for further coating as the outer shell layer materials on the surface of core-shell γ-FeO_x@AuNP nanoparticles, prepared in the second step procedure with GN@[C₆₀(>DPAF-C₉)]_n stated above. The mixture was stirred and sonicated for a period of 30 min and concentrated, via rotary evaporation, to a remaining solution volume of 2.0–3.0 mL. An external permanent magnet was then used to remove, with the solvent decanted, and collect the magnetic solid nanoparticles. They were washed by ethanol and ether to afford the final multilayered GN@{(γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n}_m [GN@(FeAuF_n)] (9-NP), as very dark brown flake-like solids, in a final weight ratio of 1-C₉:GN:γ-FeO_x@AuNP as 1.5:1.0:1.5. Spectroscopic data: Spectroscopic data: UV-vis (CHCl₃, 1.0 × 10⁻⁵ M based on the quantity of C₆₀(>DPAF-C₉)) λ_{max} (ε) 269 (2.62 × 10⁴ L mol⁻¹ cm⁻¹), 328 (3.33 × 10⁴ L mol⁻¹ cm⁻¹), 394 nm (1.98 × 10⁴ L mol⁻¹ cm⁻¹), and 536 (1.72 × 10⁴ L mol⁻¹ cm⁻¹); FT-IR (KBr) ν_{max} 2956 (m, C–H stretching), 2925 (s, aliphatic C–H stretching), 2850 (s), 1731 (m), 1660 (m, stretching vibrations of C=O), 1591 (m), 1492 (m), 1456 (m), 1434 (m), 1415 (m), 1376 (m), 1259 (s), 1191 (w), 1091 (s, stretching vibrations of C–N/C–N–C), 1018 (s), 865 (w), 796 (s), 754 (m, C–H out-of-plan deformation), 721 (m), 696 (s), 665 (m), 574 (s, C₆₀>), and 526 (vs, C₆₀>).

3.3. Spectroscopic Measurements

Infrared spectra were recorded as KBr pellets on a Thermo Nicolet AVATAR 370 FTIR spectrometer. UV-vis spectra were recorded on a PerkinElmer Lambda 750 UV spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on Bruker & Spectrospin Avance 500. The high performance liquid chromatography (HPLC) was performed using the μPorasilTM 125 Å Column (10 μm, 35×300 mm) with a mixture of hexane–EtOAc as the mobile phase and the flow rate of 1.0 mL/min. The eluted compounds were detected by their UV absorption at λ 350 nm.

Cyclic voltammetry (CV) was record on EG&G Princeton Applied Research 263A Potentiostat/galvanostat. Cyclic voltammograms of several electron-donors were collected at different

voltages vs Ag/Ag⁺ using Pt as the working and counter electrodes and Ag/AgCl as the reference electrode at a scan rate of 10 mV/s. A solution in a concentration of 1.0×10^{-3} M in CH₃CN–CH₂Cl₂ containing the electrolyte (*n*-butyl)₄N⁺-PF₆⁻ (0.2 M) was used for all CV measurements. A collimated white LED light with an output power of 2.0 W (Prizmatix, USA) was used for the collection of irradiated CV data. Transmission electron microscopy (TEM) measurements were carried out on Philips EM400T Transmission Electron Microscope. In the sample preparation for collection of TEM micrographs, a carbon–copper film grid in a 200-mesh size were used as the supporting plate for directly coating of a nanoparticle sample in a solution of 1.0×10^{-6} M on the grid. All solvent was removed and dried by the freeze-dry technique to prevent the solvent-removal induced particle aggregation. Energy-dispersive X-ray spectroscopy (EDS) was recorded on the JEOL JSM 7401F Field-emission Scanning Electron Microscope equipped with EDAX Genesis XM2 Imaging System consists of a 10 mm² Si(Li) detector with SUTW window for the detection of all elements down to Be atom. The system is also equipped with the digital electronics and software for the image acquisition and X-ray signal mapping, with qualitative and quantitative analysis capabilities.

3.4. Dielectric Constant (ϵ_r') and RF Reflectivity Measurements

Dielectric property measurements were carried out by an Agilent Network Analyzer (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with an open-ended Agilent 85070E dielectric probe kit in a detection range of 200 MHz to 50 GHz. We conducted the system base-line calibration by using open-ended, close-ended, and attenuated calibrators prior to each measurement to ensure removal of instability, induced by the cable connection, and system drift errors. In the experiment, a complex scattering parameter, defined as S₁₁, was measured and converted to relative complex electric dielectric constant values using Agilent 85071E Materials Measurement Software. This complex form consists of both a real and an imaginary part. The former term represents the value of dielectric constant and the latter is defined as the loss factor. The light source used in the measurement included a collimated white LED light with an output power of 2.0 W (Prizmatix, USA). All permittivity measurements were performed in a custom-built chamber that was conducted under a circumferentially uniform illumination environment. The uniformness was achieved by the installation of a reflective half-circular aluminum plate at the back-wall side surrounding the testing tube which was located at the center of the chamber. A LED light beam was allowed to pass through a small window opening at the front side of the chamber for the sample irradiation. Some reflected light beams were designed to refocus from the back-side aluminum mirror plate back to the sample-containing tube. We installed four small fans with two at the top and one at each side-wall of the chamber to control and prevent the temperature increase inside the chamber during the experiment. The illumination period was fixed at 60-min to provide a total light fluence of roughly estimated 12.8 J/cm². Poly(dimethylsiloxane) (PDMS, 1.0 g) semi-solid was applied as a polymer matrix host which is capable of forming a paste-like material sample in mixing with a predefined quantity of nanoparticles. In a typical preparation, a mixture of PDMS and one of several RF-responsive core-shell nanoparticle materials (100 mg) were blended by dissolving both components in ethyl acetate (20 mL) in a testing tube under sonication. It was followed by solvent evaporation to yield paste-like semi-solid materials filling in the tube.

3.5. RF Transmittance and Distance Bistatic Angle (θ)-Dependent Reflective Signal Measurements

A partially coated rectangular glass plate (25.4 × 30.5 cm) with 20.3 × 25.4 cm coating area (in the center of the plate) was used for both RF transmittance and bistatic angle (θ)-dependent reflectivity measurements under illumination of a small LED white light (2.0 W). The sample coating preparation was performed as follows. To a mixture of multilayered core-shell nanoparticle-grafted GN@(FeAuF_n) nanosheet samples (2.0 g) and PDMS (20 g) were added Sylgard 184 (2.0 g, Dow Corning, dielectric constant of 2.6–2.7). The matrix polymer contained a base of dimethylvinyl terminated dimethyl siloxane, dimethylvinyl and trimethylated silica, and tetra(trimethoxysiloxy)silane with a crosslinking cure agent of methylhydrogenated dimethylsiloxane copolymer and a palatinate catalyst. The mixture was molded via coating on the glass plate which was placed horizontally after polymer curing and dried in a vacuum oven.

Since the blending and mixing procedure of a viscous mixture can produce many air bubbles, a pre-treatment procedure in a vacuum oven connected with a pump for at least 1.0 h at room temperature was necessary to remove the trapped air bubbles prior to the chemical crosslinking initiation reaction of Sylgard 184. After curing, the coated thin film sample on the plate were fully fixed and non-sticky.

In RF transmittance measurements, the glass plate was illuminated by a small LED white light, which was placed 50 cm in the back-side of glass plate next to the receiving horn to ensure that the entire coated area was covered. The RF emitting horn was placed in front of glass plate with the major emitting wave perpendicular to the plate. The receiving horn was placed behind the glass plate facing the RF emitting horn without any position shifting. The distance between each horn to the plate was 20 cm, making two horns having distance of 40 cm in total to each other. Measurements were carried out under three conditions: (1) without light irradiation for comparison, (2) with light irradiation for a period of 60 min, and (3) post-irradiation investigation at the light-off stage. All the wall, floor, and accessory surface areas were covered by non-reflective micro-absorbing foam materials.

In bistatic RF reflection coefficient (R , dB) measurements, two doubly-rigged horn antennas (operating from 0.8 to 18 GHz with a gain from 2.8 dBi to 43.8 dBi, VSWR under 4:1) were used as signal transmitter and receiver. The $\text{GN}@\text{(FeAuF}_n\text{)}$ nanosheet-coated sample glass plate was mounted and controlled by an automated biaxial positioner to achieve accurate spatial registration of coordinates to the horn antenna. In rendering all signal images, a standard strip signal imaging mode with algorithm was applied. A small white LED light source was placed at a position of 50-cm behind the glass plate with the incident light beam perpendicular to the face of the plate to ensure full light exposure coverage of the entire coating area. Two doubly-rigged horn antennas were positioned and coupled at the incidence of 10° with the reflection coefficient for measuring the S21 scattering parameter of the object. The RF emitting horn was placed in front of the glass plate with the emitter facing the central position of the plate. The main emitting wave had an angle of 45° with respect to the plate plane. The receiving horn was placed on the same side of the emitting horn at a mirror image position. The distance of both horns to the central position of the plate was 20 cm. In the angle (θ)-dependent reflection coefficient measurement, the glass plate object was placed on a wooden rotary stage panel controlled by a digital controller with an electric rotary motor underneath to achieve a precise angular increment resolution of 0.1° . The rotating angle was controlled by controller that can rotate the panel at 15° per step for the full range of 360° . The initial position of the glass plate was considered as 0° . The θ -angle was then defined by the degree of center rotation of the glass plate from 0° . Angle rotation for the data collection was carried out from 0° to 180° . All RF-signal data collections were conducted at the frequency range of 0.8–18 GHz inside an anechoic chamber equipped with non-reflective wall-padding foams to eliminate the effect of electromagnetic background noise. Reflectivity of the object was measured by fixing the antenna pair configuration and rotating the rotary stage at either 0° , 15° , 30° , 45° , 60° , 75° , or 90° to develop a quantitative assessment of the angle (θ)-dependent S21 scattering parameter responses of the plate object with or without the continuous light irradiation for comparison.

4.0 RESULTS AND DISCUSSION

4.1. Synthesis and Material Characterization by Spectroscopic Methods

Synthetic sequence of the core-shell nanoparticle preparation is depicted in Fig. 5. Fabrication of bilayered core-shell NPs ($\gamma\text{-FeO}_x@\text{AuNP}$) with highly magnetic $\gamma\text{-FeO}_x$ ($1.0 < x < 1.5$) NPs, as the nearly monodisperse nanocrystalline core material. To make a consistent evaluation of plasmonic properties of the Au layer, the same weight ratio of the precursor reagent $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ to the quantity of iron oxide NPs was applied. Surface of the resulting gold layer was stabilized by 1-octanethiol as a capping agent in sufficient binding to render moderate solubility of NPs in toluene that facilitated the subsequent encapsulation by $\text{C}_{60}(>\text{DPAF-C}_9)_x$. Purification of core-shell NPs was carried out by the use of an external magnet to retrieve and isolate only the magnetic NP solids and to separate out any possible nonmagnetic Au-NP byproduct formed during the preparation. Encapsulation of $\gamma\text{-FeO}_x@\text{AuNP}$ by either **1-C**₉, **2-C**₉,

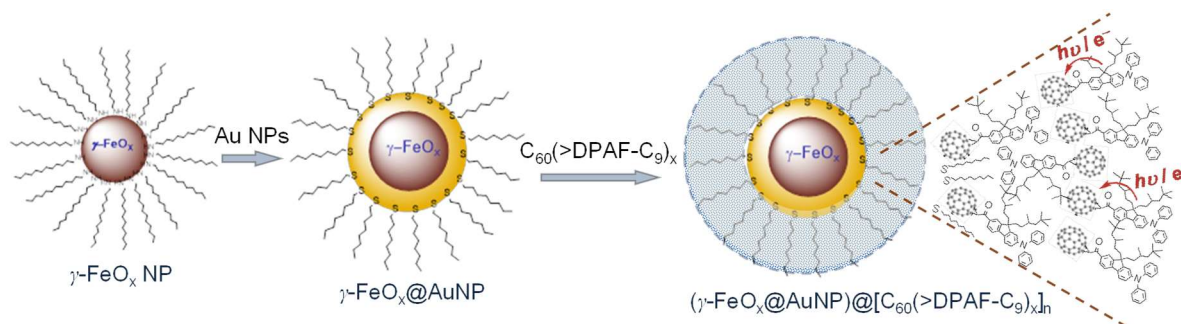


Figure 5. Schematic description of core-shell nanoparticle preparation sequence.

or **3-C₉** was performed under ultrasonication in toluene to replace surface-bound 1-octanethiol by C₆₀-adducts that resulted in the formation of trilayered core-shell (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)_x]_n ($x = 1, 2$, or 4) NPs (Fig. 5). Ligand exchange was effective in a concentrated solution via sonication to increase the molecular contact of **1-C₉** or **2-C₉** to **6-NP** or **7-NP**, respectively. With assistance of an external permanent magnet, the procedure made the removal of residual capping agents and an excessive amount of C₆₀(>DPAF-C₉)_x on surface easy by repeated rinsing with ethanol and ether. The ability of **1-C₉** or **2-C₉** to replace 1-octanethiol on gold surface relies on strong C₆₀ bonding interactions to metal or gold surface in a form of a monolayer.^{47–49} In the presence of both sulfur-ligands and C₆₀ cages, their surface binding forces to Au can be competitive to each other for attaching to chemisorption sites with the surface binding energy of C₆₀–Au calculated to be higher than the Au–S bond strength.⁵⁰ This makes the alkylthiol–C₆₀ exchange equilibrium shifted more favorably toward the effective attachment of C₆₀ cages to Au. In addition, multilayered self-assembly formation of fullerene derivatives may also be possible owing to strong fullerene–fullerene and fullerene–gold interactions.⁵¹

Under our experimental conditions, application of the ultrasonication energy was able to dissociate the S–Au interactive binding that allowed C₆₀(>DPAF-C₉)_x ($x = 1$ or 2) to penetrate the 1-octanethiol layer and intercept chemisorption sites. It was then followed by the strong hydrophobic–hydrophobic interaction forces of (C₆₀>)-(C₆₀>) cages that may favor monolayer molecular self-assemblies of C₆₀> at the gold surface. This should push weaker Au-interactive DPAF-C₉ ring moieties outward with 3,5,5-trimethylhexyl chain moieties phasing the solvent. Subsequent packing of fullerene dyads, by keeping the same preference of (C₆₀>)-(C₆₀>) and aliphatic–aliphatic interactive forces, would lead to a partial bilayer or bilayer packing configuration of **1-C₉** or **2-C₉** at the outer surface. This structure resembles that reported on nanovesicles of amphiphilic C₆₀(>DPAF-EG_x) conjugates showing bilayered fullerosome (ordered C₆₀> assemblies) membrane spheres,⁵² as detected by tunneling electron microscopic (TEM) micrographs.

In the other material's design, we also replaced **1-C₉** by *cis-cup*-tris[C₆₀(>DPAF-C₉)] (*cis-cup-5-C₉*, Fig. 6) as the outer shell donor-acceptor nanoconjugates on the construction of core-shell nanoparticles. It was derived from a C₃-symmetrical 1,3,5-triaminobenzene ring as the central core for connecting three fused 2-diphenylaminofluorene moieties, forming a new class of 3D-stereomeric tris(fluorenylphenylamino)-benzene as tris(DPAF-C₉) **4-C₉**. These 3D-stereomers faces high torsional stress at the central benzene core region that forces all fluorene chromophore groups located at the outer-edge area to be oriented in a non-coplanar 3D-configuration.⁴³ Two stereoisomeric forms are possible, namely, *cis-cup-4-C₉* and *trans-chair-4-C₉* (Fig. 6). They can be separated by thin-layer chromatographic technique with the former as the major product. Based on the density functional theory (DFT) calculation with the geometries optimized at the B97-D3/SVP level of theory,⁴⁴ the *cis-cup*-form having three bis(3',5',5'-trimethylhexyl)fluorene moieties on 1,3,5-tris(phenylamino)benzene was found to be essentially C₃ symmetric with a higher formation tendency than the corresponding *trans-chair*-form. It is owing to the influence by strong dispersion interactions within the alkyl chains that are enhanced in the

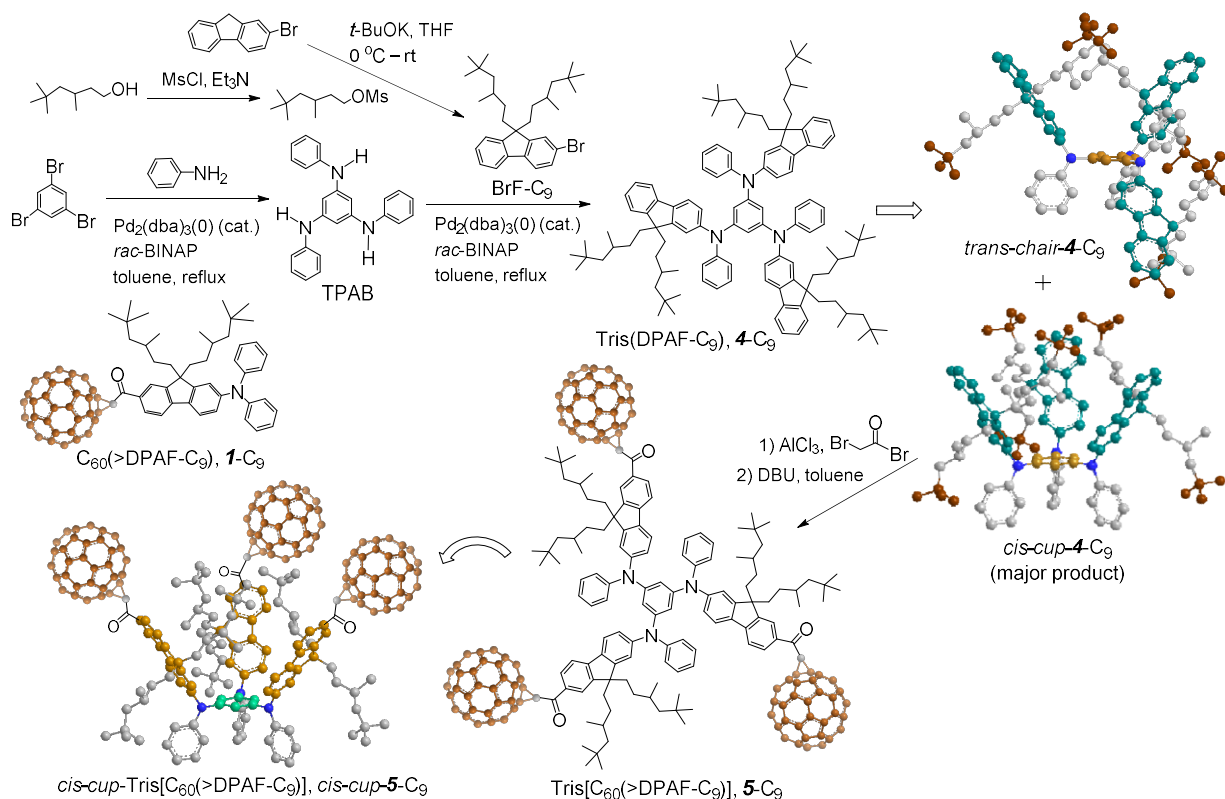


Figure 6. Synthetic route to the preparation of *cis-cup*-tris[C_{60} (>DPAF- C_9)] (*cis-cup*-5- C_9) from the isolated precursor *cis-cup*-tris(DPAF- C_9) (*cis-cup*-4- C_9) with reaction reagents provided.

presence of more polar media. Upon a 180° -rotation of one of three amino groups, the structure changes to produce a conformational isomer in a *trans-chair*-form which is less cup-like than the *cis-cup*-form. In principle, subsequent attachment of three C_{60} > cages on *cis-cup*-4- C_9 should lead to *cis-cup*-5- C_9 having all C_{60} > moieties facing outward from the central benzene core at the same side with each other. This will facilitate the cup-attachment on the gold layer of core-shell nanoparticles induced by the strong C_{60} -Au binding force^{47,49} and, thus, enhance the distribution of polarized negative charges at gold surface bound monolayered fullerosome region, as the positive contribution to the photoswitchable relative dielectric properties.

Attachment of three C_{60} > cage to tris(DPAF- C_9) was carried out by Fiedel-Crafts reaction first followed by fullerenylation in toluene with DBU as the reagent (Fig. 6). To understand the trend in preferential formation of 3D conformers of the electron donor molecule tris(DPAF- C_9) during the stepwise synthetic reaction mechanism, involving a sequential linkage of three bis(3',5',5'-trimethylhexyl)fluorene moieties on 1,3,5-tris(phenylamino)benzene, we carried out density functional theory (DFT) calculations of 4- C_9 as the model. The result will lead to a view of the favorable or preferred geometry and orientation of each fluorenyl moiety when it is bonded on a rather rigid diphenylamino functional group. Our computations relied on semiempirically optimized geometries whereas the geometries are optimized at the B97-D3/SVP level of DFT. The corresponding structural configurations are labelled *chair* and *cup* for appropriately characterizing the nature of the geometries. The tris-cup form (or cup-*cis* form) is essentially C_3 symmetric and is influenced strongly by dispersion interactions within the alkyl chains. These dispersion interactions involving the alkyl chains would be enhanced in more polar media. In addition to the tris-cup form, one of the amino groups may be rotated $\sim 180^\circ$ to create a conformation resembling a tris-*chair* (or chair-*trans* form). In this tris-cup conformation, one of two 3',5',5'-trimethylhexyl arms attached on the DPAF unit is positioned above the central benzene ring and serves to fill that cavity which is likely driven by dispersion. The tris-chair form is less cage-like and symmetric than the tris-*cup* form.

Synthetic procedure for the preparation of tris(DPAF- C_{60}) with the detailed spectroscopic characterization was reported previously.⁴⁴ Geometrically conformational isomer *cis-cup-4-C₉* was clearly isolated from the *trans-chair*-stereoisomer and confirmed by the use of high performance liquid chromatography (HPLC, μ PorasilTM 125 Å, 10 μ m, 35×300 mm, mobile phase: hexane–EtOAc (9.0:1.0, v/v), flow rate: 1.0 mL/min, detector: UV at λ 350 nm) in an analytical scale. For the scale-up separation, column chromatography (CC) using the same solvent system did not provide satisfactory results. However, the application of thin-layer chromatography (TLC) technique using the solvent eluent in slightly lower polarity (hexane–ethylacetate/9.5:0.5, v/v) than those of HPLC or the CC formed an overlap band of the stereoisomers *cis-cup-4-C₉* and *trans-chair-4-C₉*. By cutting the corresponding fluorescent TLC band of tris(DPAF- C_{60}) into two portions and performing several repeated TLC procedures, we were able to significantly increase the degree of product purity sufficiently enough to allow our confirmation of their entity by ¹H NMR spectrum.⁴⁴ It indicated a higher *R_f* value for *cis-cup-6-C₉* than that of *trans-chair-4-C₉*. With a *C₃* symmetry in structure, the former displayed a differentiable singlet peak for three central benzene protons (*cis-H_b*) at δ 6.55 (Fig. 7Aa), while the latter with a less symmetry resulted in two proton peaks (*trans-H_b*) at δ 6.48 (1H) and 6.55 (2H).

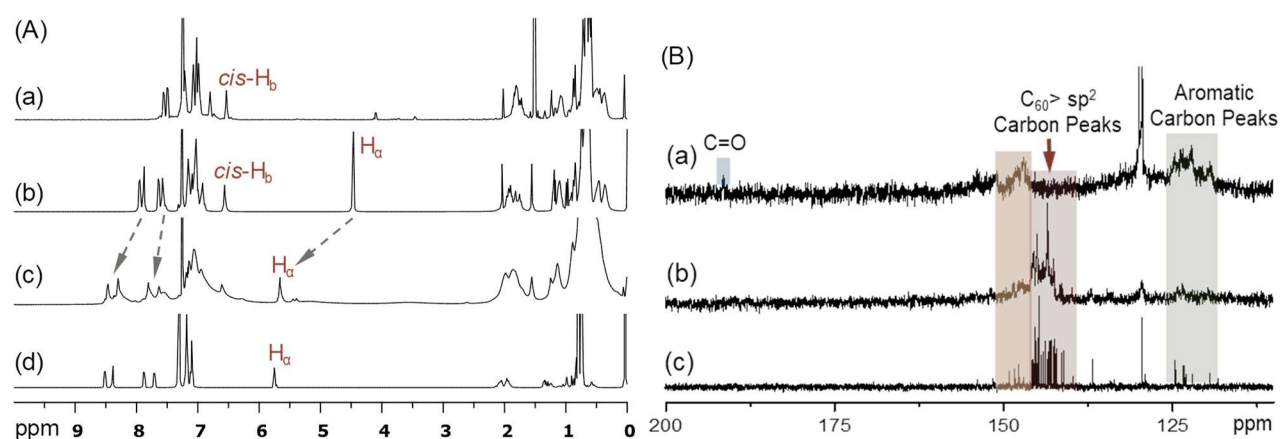


Figure 7. (A) ¹H NMR spectra (CDCl₃) of (a) *cis-cup-tris*(DPAF- C_{60}) (*cis-cup-4-C₉*), (b) *cis-cup-tris*(BrDPAF- C_{60}), (c) *cis-cup-tris*[C_{60} (>DPAF- C_{60})] (*cis-cup-5-C₉*), and (d) C_{60} (>DPAF- C_{60}) (1- C_{60}) as a reference for comparison. (B) ¹³C NMR spectra of (a) *cis-cup-tris*(BrDPAF- C_{60}), (b) *cis-cup-tris*[C_{60} (>DPAF- C_{60})], and (c) C_{60} (>DPAF- C_{60}) (1- C_{60}), showing in (b) the main group of fullereryl sp² carbon peaks at δ 140–147 that indicated the attachment of C_{60} > cages on 2- C_{60} , as compared with those of (Bc).

Prior to the attachment of three C_{60} > cages on *cis-cup-4-C₉*, it was functionalized by the Friedel–Crafts acylation at C7 position of diphenylaminofluorene moiety with α -bromoacetyl bromide in the presence of aluminum chloride (6.0 eq.) in 1,2-dichloroethane at 0 °C to ambient temperature overnight to afford the corresponding α -bromoacetylfluorene derivative, as the intermediate step of reactions. It resulted in yellow semi-solids in 53% yield of *cis-N¹,N³,N⁵-tris(7- α -bromoacetyl-9,9-di(3',5',5'-trimethyl-1'-hexyl)fluoren-2-yl)-1'',3'',5''-tris(phenylamino)benzene* as *cis-cup-tris*(BrDPAF- C_{60}). It was purified by either column or TLC chromatography (silica gel, hexane–toluene, 3:2, *R_f* = 0.3 on TLC). The functional structure of *cis-cup-tris*(BrDPAF- C_{60}) was verified by both infrared (FT-IR) and ¹H NMR spectra with the former showing a strong carbonyl (–C=O) stretching absorption band centered at 1675 cm^{–1} indicating this functional group being linked on a phenyl moiety since a clear band absorption shift from 1725 cm^{–1}, normally detectable for an alkyl carbonyl group, was evident. In the case of ¹H NMR spectrum, tris(Br-DPAF- C_{60}) displayed characteristic new peak signals of two methylene protons (*H_a*) next to the carbonyl group of the α -bromoacetyl moiety at δ 4.46 (Fig. 7Ab). Subsequence attachment of a C_{60} > cage to each of three DPAF moieties was made via a cyclopropylacetyl bridge by the treatment of three α -bromoacetylfluorene moieties of *cis-cup-tris*(BrDPAF- C_{60}) with C_{60} in toluene in the presence of DBU at ambient temperature for 8.0 h. An excessive amount of C_{60} (4.5 eq.) was applied to avoid the formation of C_{60} -bisadducts or trisadducts during the cyclopropanation reaction. The product of *cis-cup-tris*[C_{60} (>DPAF- C_{60})] stereoisomer as *cis-cup-5-C₉* was confirmed by the evidence of changing solubility

characteristics matching those of C_{60} and a slight shift of cyclopropyl keto group absorption in IR spectrum to $\nu_{\max}$ 1627 cm^{-1} , which was assigned to the carbonyl stretching band. It was also accompanied by two typical fullereryl cage signals at $\nu_{\max}$ 575 (w) and 529 (s) cm^{-1} . These two bands are characteristic absorptions used to provide evidence of $(C_{60}>)$ -related monoadduct with relative intensity ratio differentiable from those of starting C_{60} itself. They will disappear from the spectrum once becoming a $(C_{60}>)$ -bisadduct. Therefore, this IR technique was applied often in the [60]fullereryl product structure verification. In addition, disappearance of α -proton peaks of the α -bromoacetyl group at δ 4.46 (Fig. 7Ab) with the appearance of new peaks centered at δ 5.67 (Fig. 7Ac) can be indicative of successful formation of the cyclopropanyl keto-bridge between a $C_{60}>$ cage and the fluorene moiety, using previously reported $C_{60}>\text{DPAF-C}_9$ characterization (Fig. 7Ad) as the reference.²⁴ The latter peak δ 5.67 was assigned to the chemical shift of α -proton (H_α) of **5-C**₉. Its large down-fielded shift from the normal chemical shift value of a alkyl acetyl proton at $\sim\delta$ 2.1–2.6 is due to the influence of strong [60]fullereryl current in the close vicinity. Accordingly, the detection of δ 5.67 peak can also be served as the verification of short covalent-bonding between $C_{60}>$ and DPAF moieties. The half-height width of H_α peak in Fig. 7Ac is slightly wider than that of Figure 7Ab that revealed less symmetrical environment among three H_α protons of *cis-cup-5-C*₉. Similarly, by using ¹³C NMR spectrum of $C_{60}>\text{DPAF-C}_9$ (Fig. 7Bc) as the reference for comparison, we were able to detect calculated 29 fullereryl sp^2 carbon peaks corresponding to the $C_{60}>$ moiety (C_2 symmetry) of *cis-cup*-tris[$C_{60}>\text{DPAF-C}_9$] as a matching multi-peak band in the range of δ 140–147 (Fig. 7Bb). The reduced spectrum resolution is due to the increasing molecular complexity along with the reduced solubility of *cis-cup-5-C*₉.

Synthetic procedures for the preparation of core-shell $\gamma\text{-FeO}_x\text{@AuNP}$ nanoparticles in an average particle diameter of ~ 20 nm were described above. A slightly modified method was applied in this study to afford similar results based on the verification by transmission electron microscopy (TEM) micrographs and microanalyses of energy dispersive x-ray spectra (EDS). Subsequent encapsulation of $\gamma\text{-FeO}_x\text{@AuNPs}$ by *cis-cup*-tris[$C_{60}>\text{DPAF-C}_9$] leading to the formation of trilayered core-shell **8-NP** was performed by mixing these two components in a predefined ratio in solvent under ultrasonication. The initial binding force of *cis-cup-5-C*₉ to $\gamma\text{-FeO}_x\text{@AuNP}$ was governed by strong binding interaction forces of $C_{60}>$ cages to the gold surface that should result in the partial replacement of 1-octanethiol capping molecules on the gold surface via alkylthiol ligand- $C_{60}>$ exchange induced by sonochemical energy to invert *cis-cup-5-C*₉ molecules under ultrasonication. The exchange should form a monolayer of *cis-cup*-tris[$C_{60}>\text{DPAF-C}_9$] with the orientation of all three $C_{60}>$ cages per nanomolecule in a cup-capping manner facing on the surface of Au layer with interlinked three DPAF-C₉ moieties facing outward. Attachment of additional *cis-cup-5-C*₉ nanomolecules will follow the strong hydrophobic–hydrophobic interactions among $(C_{60}>)$ – $(C_{60}>)$ cages to form a partial trilayered fullerosome membrane resembling that of reported fullereryl nanovesicle.⁵² Since all encapsulated magnetic nanoparticles were physically removed from the container solution by the assistance of an external permanent magnet and washed

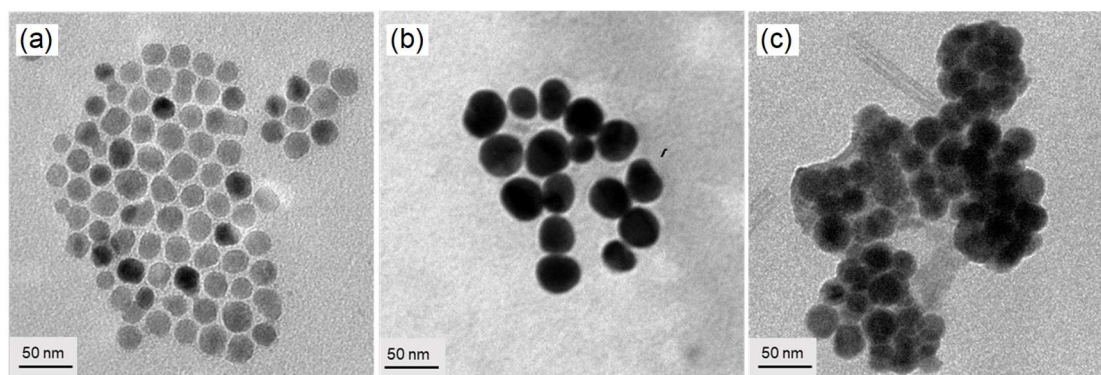


Figure 8. TEM micrograph images of (a) $\gamma\text{-FeO}_x$ NPs, (b) $\gamma\text{-FeO}_x\text{@AuNP}$, and (c) $(\gamma\text{-FeO}_x\text{@AuNP})\text{@}\{cis\text{-cup-tris}[C_{60}>\text{DPAF-C}_9]\}_n$ (**8-NP**), showing evolution of particle morphology changes and the soft organic material encapsulation on dark nanoparticles on the latter micrograph.

repeatedly by ethanol and diethyl ether, we were able to ensure the products being free from residual non-binding *cis-cup-5-C₉* molecules at the NP surface. We assigned the resulting trilayered core-shell nanostructures of $(\gamma\text{-FeO}_x\text{@AuNP})\text{@}\{cis\text{-cup-tris}[C_{60}(>\text{DPAF-C}_9)]\}_n$ as **8-NP**.

TEM micrographs of Fig. 8 showed the morphology and topography of NPs that indicated a roughly homogeneous narrow size distribution of the parent $\gamma\text{-FeO}_x$ NPs (Fig. 8a) in a diameter of ~ 20 nm on average. Subsequent deposition of solid gold nanocrystals on the surface of $\gamma\text{-FeO}_x$ NPs to a structure of core-shell $\gamma\text{-FeO}_x\text{@AuNP}$ was controlled to a shell layer thickness of 6.0–8.0 nm by the calculated quantity of HAuCl₄ applied. This thickness was measured by the comparison of average particle size between Fig. 8a and 8b, where the latter displayed much higher contrast of the Au layer shell. With the encapsulation of $\gamma\text{-FeO}_x\text{@AuNP}$ by *cis-cup-5-C₉*-derived fullerosome (array of C₆₀> cages) as the outer shell layer, the morphology of soft organic materials in lighter contrast covering all hard nanoparticles can be observed that allowed us to measure an average thickness of roughly 10 nm (Fig. 8c), matching well with the weight ratio of $\gamma\text{-FeO}_x\text{@AuNP}$ and *cis-cup-5-C₉* applied in the core-shell nanoparticle fabrication.

Photophysical properties of *cis-cup-tris*[C₆₀(>DPAF-C₉)] are dominated by two components, namely, C₆₀> cages as the electron (e[−])-acceptors and light-harvesting DPAF antenna units as electron (e[−])-donors. Both components are photoresponsive at a different wavelength range. For example, optical absorption of C₆₀> cages occurs mainly the band centered at 335 nm (1.76×10^5 L mol^{−1} cm^{−1}), whereas the band centered at 402 nm (4.19×10^4 L mol^{−1} cm^{−1}) is attributed to the absorption of DPAF moieties, as shown in the UV-vis spectra of Fig. 9c. Characteristics of the latter band were compared with that of *cis-cup-2-C₉* (Fig. 9a), *cis-cup-tris*(BrDPAF-C₉) (Fig. 9b), and C₆₀(>DPAF-C₉) (**1-C₉**, Fig. 9d) showing a clear bathochromic shift of the 353-nm band of the former to 395 nm (1.10×10^5 L mol^{−1} cm^{−1}), which is matching roughly with the 404-nm band of **1-C₉** and the 402-nm band of *cis-cup-5-C₉* for the peak assignment. This assignment was also consistent with the observation of 2.9-folds higher in the absorption extinction coefficient (ϵ) value for *cis-cup-tris*(BrDPAF-C₉), having three DPAF moieties per molecule, as comparing with that of **1-C₉** with one DPAF moiety per molecule. Upon the attachment of three C₆₀> cages, optical absorptions of fullerene moieties of *cis-cup-5-C₉* became dominating in the spectrum with a much higher ϵ value for the 335-nm band (Fig. 9c). It was accompanied by a weak characteristic (forbidden) steady state absorption band of the C₆₀> moiety appearing at 692 nm (the insert of Fig. 9c) that provided further confirmation of a fullerene conjugate structure.

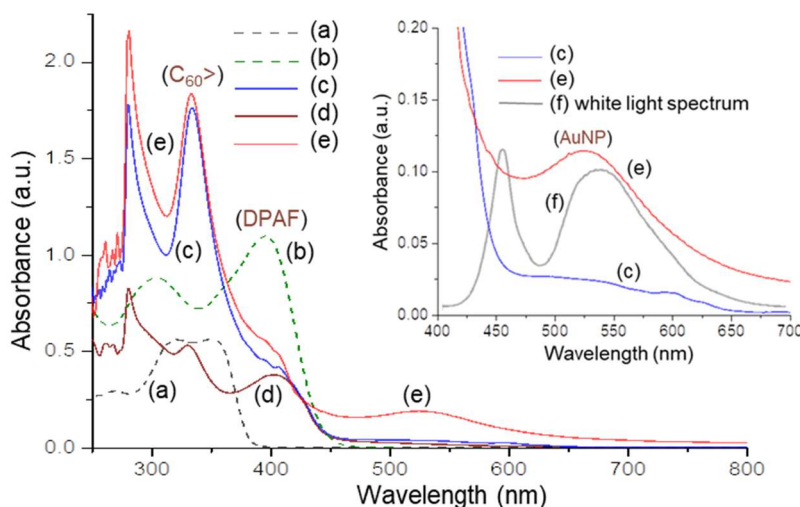


Figure 9. UV-vis spectra of (a) *cis-cup-tris*(DPAF-C₉) (*cis-cup-4-C₉*), (b) *cis-cup-tris*(BrDPAF-C₉), (c) *cis-cup-tris*[C₆₀(>DPAF-C₉)] (*cis-cup-5-C₉*), (d) C₆₀(>DPAF-C₉) (**1-C₉**), (e) $(\gamma\text{-FeO}_x\text{@AuNP})\text{@}(cis\text{-cup-5-C}_9)_n$ (**8-NP**), and (f) white light emission spectrum, where (a) and (b) were taken in EtOAc and (c), (d), and (e) were taken in toluene. The concentration of all samples is 1.0×10^{-5} M.

Interestingly, distinctly 3.3-folds lower in the ϵ value of the 402-nm peak in Fig. 4c than that of **1-C₉**, making it as a shoulder band to the main C₆₀> absorption, was interpreted by a phenomenon likely caused by the specific molecular 3D-conformation of *cis-cup*-tris[C₆₀(>DPAF-C₉)]. Owing to good solubility and compatibility of fullerenes to toluene solvent used, the orientation of three C₆₀> cages was likely to face outward into the solvent phase while DPAF moieties were hidden inside the partially aggregated cluster nanoparticle. The hypothesis was also verified by observation of the distinguishable solubility decrease of *cis-cup*-**5-C₉** in CHCl₃, however, increase in toluene and CS₂ matching well with the solubility characteristics of C₆₀.

Our study of photoswitchable dielectric amplification phenomena is based on photoexcited plasmonic resonance energy transfer to induce the intramolecular charge polarization of *cis-cup*-tris[C₆₀(>DPAF-C₉)] forming the corresponding dielectric ion-radical components (C₆₀>)^{-•} and DPAF^{+•}-C₉. In this event, C₆₀> served as an electron (e⁻)-acceptor, whereas light-harvesting DPAF antenna worked as an electron (e⁻)-donor. Accordingly, we first investigated the characteristics of redox potentials of both C₆₀> and DPAF moieties in the 3D-configured nanostructure. Measurements of the cyclic voltammetry (CV) were carried out on the sample of *cis-cup*-**5-C₉** in a mixture of toluene and (*n*-butyl)₄N⁺-PF₆⁻ electrolyte, using Pt as both working and counter electrodes and Ag/AgCl as the reference electrode. To provide a clear data interpretation, CV characteristics of C₆₀ (>DPAF-C₉) were applied as the reference under variation of cyclic oxidation and reduction voltages vs. Ag/Ag⁺ from -2.0 to 1.5 V. It displayed one reversible oxidation (¹E_{ox} of 0.95 V)–reduction (¹E_{red} of 1.07 V) cycle wave at positive voltages and at least two reversible reduction (¹E_{red} of -0.43 V and ²E_{red} of -0.88 V)–oxidation (¹E_{ox} of -0.62 V and ²E_{ox} of -1.10 V) cycle waves at negative voltages (Fig. 10Ac). These potential values were compared by those of a set of separated molecular components using a C₆₀> monoadduct and *cis-cup*-tris(DPAF-C₉) as models for confirmation, showing reversible ¹E_{red}/¹E_{ox} of -0.40/-0.71 V, ²E_{red}/²E_{ox} of -0.82/-1.14 V, and ³E_{red}/³E_{ox} of -1.33/-1.62 V vs. Ag/Ag⁺ for the C₆₀> monoadduct (Figure 5Aa) and one reversible cyclic wave of ¹E_{ox}/¹E_{red} as 0.93/1.03 V for *cis-cup*-tris(DPAF-C₉) (Figure 5Ab). Once the compound **1-C₉** was molecularly tripled to *cis-cup*-**5-C₉**, the cyclic redox wave corresponding to DPAF moieties at positive voltages fully disappeared, as shown in Fig. 10Ad. However, two clearly reversible ¹E_{red}/¹E_{ox} (-0.23/-

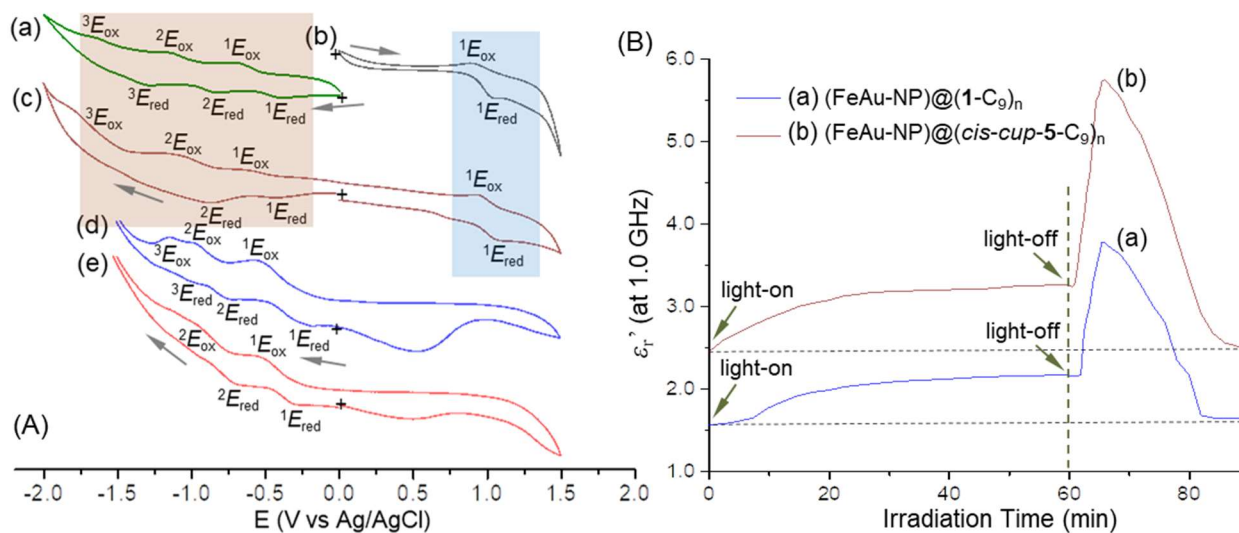


Figure 10. (A) Cyclic voltammograms (CV) of (a) C₆₀>, (b) *cis-cup*-tris(DPAF-C₉), (c) C₆₀ (>DPAF-C₉) (**1-C₉**), (d) *cis-cup*-tris[C₆₀(>DPAF-C₉)] (with no light), and (e) *cis-cup*-tris[C₆₀(>DPAF-C₉)] (after white LED light irradiation for 30 min) at different voltages vs Ag/Ag⁺ in a solution concentration of 1.0 × 10⁻³ M in CH₃CN-CH₂Cl₂, containing (*n*-butyl)₄N⁺-PF₆⁻ electrolyte (0.2 M), using Pt as working and counter electrodes and Ag/AgCl as the reference electrode at a scan rate of 10 mV/s. (B) Irradiation time-dependent relative dielectric constant (ε_r') amplification of trilayered core-shell nanoparticles of (a) (γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n (**6-NP**) and (b) (γ-FeO_x@AuNP)@[*cis-cup*-tris[C₆₀(>DPAF-C₉)]]_n (**8-NP**) at the frequency of 1.0 GHz. White LED light irradiation period was 60 min.

0.55 V) and ${}^2E_{\text{red}}/{}^2E_{\text{ox}}$ (−0.75/−0.99 V) with one less obvious cyclic wave of ${}^3E_{\text{red}}/{}^3E_{\text{ox}}$ (−0.97/−1.15 V) vs. Ag/Ag⁺ corresponding to the redox characteristics of C₆₀> moieties of *cis-cup-5-C*₉ were observed. This revealed the occurrence of a partial one-electron oxidation process of e[−]-donor DPAF-C₉ moiety in the structure of *cis-cup-5-C*₉ in the presence of three C₆₀> cages. This inhibited the further electron-oxidation event in a clear manner. Since C₆₀> is capable of undergoing at least three reversible reduction/oxidation waves (Fig. 10Aa), partial e[−]-transfer from DPAF may not give significant influence on its CV diagram, except the first and second reduction potentials being modified from −0.43 to −0.23 and −0.88 to −0.75 V vs. Ag/Ag⁺, respectively.

Most importantly, we were able to apply the white LED light irradiation (30 min) concurrent with the CV measurement to obtain the insight of redox characteristics of *cis-cup-5-C*₉ under similar photoexcitation conditions used in the dielectric property measurements of the same compound in a form of core-shell nanoparticles, as described below. As a result, Fig. 10Ae displayed a similar cyclic wave profiles as those of Fig. 10Ad showing two clearly reversible waves with ${}^1E_{\text{red}}/{}^1E_{\text{ox}}$ (−0.32/−0.55 V) and ${}^2E_{\text{red}}/{}^2E_{\text{ox}}$ (−0.70/−0.99 V) vs. Ag/Ag⁺ that was attributed to the redox characteristics of C₆₀> moieties. No clear oxidation waves of DPAF moieties were detected that was indicative of an effective intramolecular e[−]-transfer from DPAF-C₉ to C₆₀> upon light irradiation to produce three ion-radical pairs per molecule as *cis-cup*-tris[C₆₀^{•−}(>DPAF-C₉)^{•+}]. At this polarized charge-form, DPAF moieties were not able to undergo further electron-oxidation process, consistent with the observed data. Furthermore, these CV results may be correlated to or indicative of similar charge-polarization phenomena to occur in the solid state of (*cis-cup-5-C*₉)-encapsulated core-shell 8-NP.

Stepwise fabrication of multilayered core-shell nanoparticles of GN@{(γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n}_m [GN@(FeAuF_n)] was also investigated. Based on the proposed dielectric enhancement strategy stated above, a fullerosome membrane monolayer of C₆₀(>DPAF-C₉) has to be built on the surface of graphene nanosheets (GNs) to achieve a gapless topological boundary for effective interfacial interactions. Deposition of 1-C₉ molecules on the surface of GNs in a form of monolayer was achieved by the competitive binding forces of much stronger hydrophobic–hydrophobic interactions between oligo-aromatic C₆₀> and GN and among (C₆₀>)-(C₆₀>) cages to form a monolayer membrane [60]fullerosome vs. weaker binding between aliphatic SDS surfactant ligand and GN. During the preparation of shear exfoliated GN nanosheets, the surface was stabilized by SDS ligands. Upon the applied shearing sonochemical energy of sonication, a portion of these weaker monolayered ligands was detected to be replaced and exchanged by 1-C₉ by the evidence of a small quantity of white ionic SDS solid salts being precipitated from the toluene–NMP solution. The ligand exchange reaction also largely improved the solubility of resulting C₆₀(>DPAF-C₉)-encapsulated graphene nanosheets, GN@[C₆₀(>DPAF-C₉)]_n, in toluene. It is due to two structurally branched 9,9-di(3,5,5-trimethylhexyl) (C₉) sidechains of 1-C₉ giving high compatibility to nonpolar organic solvents. The quantity of 1-C₉ required to make a monolayer coverage was evaluated by TEM micrographs and discussed below. We selected a GN@[C₆₀(>DPAF-C₉)]_n sample with a weight ratio of 1-C₉:GN as 1:1 for the second step nanostructure fabrication process. In this step, the control of γ-FeO_x@AuNP nanoparticles deposition was governed by the strong binding force between C₆₀> cage and thin Au nanocrystal shell layer surface on γ-FeO_x core, as stated above. By the application of ultrasonication, nanoparticles of γ-FeO_x@AuNP should have the preference of making the physical attachment on the C₆₀> moiety of GN@[C₆₀(>DPAF-C₉)]_n nanosheets. It was occurred by the partial replacement of 1-octanethiol capping molecules, via alkylthiol ligand–C₆₀> exchange, induced by sonochemical energy. This exchange was possible by the fact that the calculated surface binding energy of C₆₀–Au was found to be higher than the bond strength of Au–S. We found that the reaction was easily accomplished and verified when these GN nanosheets becoming magnetic in characteristics that allowed us to isolate and remove the products from the toluene medium by an external permanent magnet as dark flake-like materials of GN@[(γ-FeO_x@AuNP)–C₆₀(>DPAF-C₉)]_n. By repeated experiments with TEM micrographic evaluations, we found that the quantity of γ-FeO_x@AuNP nanoparticles was best with a weight ratio of 2:1 with respect to that of 1-C₉ used in the GN@[C₆₀(>DPAF-C₉)]_n sample to achieve an even coverage on GNs.

In the third step, the another same portion of **1-C₉** molecules as that of GN@[C₆₀(>DPAF-C₉)]_n in toluene was applied as the outer shell layer materials on nanoparticle-encapsulated GNs. Similar isolation technique and purification procedure as those of the second step, using an external permanent magnet, were applied to afford the final products of multilayered GN@{(γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n}_m or GN@(FeAuF_n) (**9-NP**) as dark brown flake-like solids.

Characterization and verification of **1-C₉** or nanoparticle-encapsulated GNs was performed using transmission electron microscopy (TEM) micrographs to investigate their morphology and topography. In general, shear-exfoliated graphene nanosheets obtained by the current experimental procedure led to mostly stacking sheets consisting of an assembly of 3–6 single-layers. Upon deposition of various quantities of **1-C₉** in form of a monolayer to a **1-C₉**-encapsulated GN nanostructures of GN@[C₆₀(>DPAF-C₉)]_n, C₆₀> cages (each in a diameter of ~1.0 nm) was observed in TEM micrographs of the corresponding samples having a C₆₀(>DPAF-C₉) vs. graphene weight ratio of 1:4 (Fig. 11Ba), 1:2 (Fig. 11Bb), and 1:1 (Fig. 11Bc). They all showed a combination of single, bis-, tris-, and tetra-caged (~5.0–6.0 nm in diameter) clusters with more single cages in Fig. 11Ba when a much less quantity of **1-C₉** molecules was applied. As the quantity of **1-C₉** being increased from the samples of Fig. 11Ba to those of Fig. 11Bc, C₆₀> cages tends to attract with each other to form various clusters in a diameter of roughly 2.0–6.0 nm while remaining a monolayer configuration. The attraction tendency is owing to strong aromatic hydrophobic–hydrophobic (C₆₀>)-(C₆₀>) interactions. Since Fig. 11Bc displayed approximate confluence of **1-C₉** as a fullerosome monolayer, we used this C₆₀(>DPAF-C₉):GN weight ratio as 1:1 for the fabrication of an additional layer of core-shell γ-FeO_x@AuNP nanoparticles. These magnetic NP cores of γ-FeO_x were prepared in an average diameter of 10–20 nm at 320 °C with the outer gold shell thickness of roughly 3.0–5.0 nm. Incorporated Au shell layer was stabilized by 1-octanethiol as a ligand in toluene. The weaker binding force of Au–S interaction allowed a portion of 1-octanethiol to be replaced by the Au–C₆₀> bonding during the preparation of GN@[(γ-FeO_x@AuNP)–C₆₀(>DPAF-C₉)]_n nanosheets. After the top-layer encapsulation on the remaining particle surface of γ-FeO_x@AuNPs by **1-C₉**, the atomic composition of the final products GN@{(γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n}_m prepared by various weight ratios of

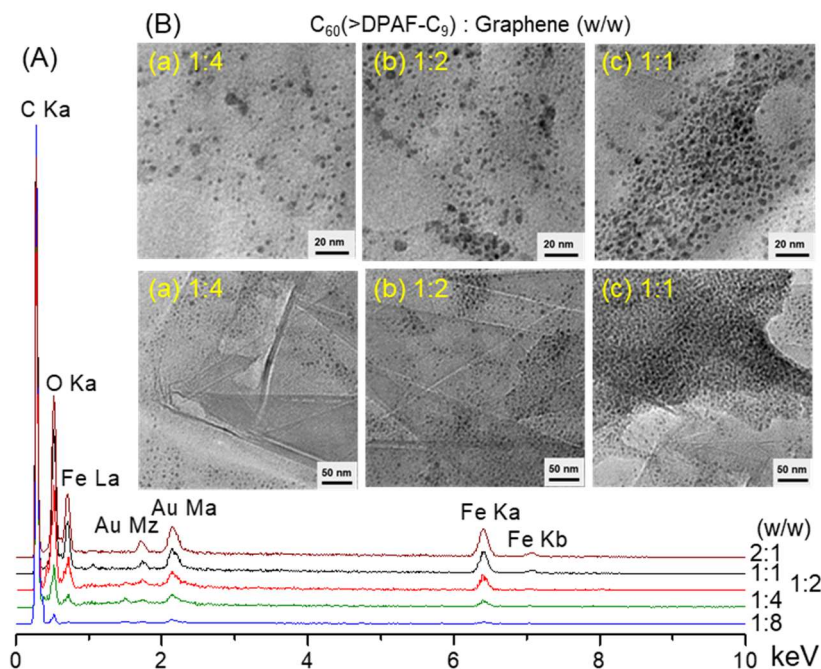


Figure 11. (A) Energy dispersive spectrum (EDS) of GN@{(γ-FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n}_m with a weight ratio of C₆₀(>DPAF-C₉) vs. graphene as 2:1, 1:1, 1:2, 1:4, and 1:8, showing the corresponding atomic compositions where some carbon contents may arise from the background tape used for the sample holding at the surface. Oxygen content peak was from both the sample and the environment. (B) TEM micrograph images of three corresponding GN@[C₆₀(>DPAF-C₉)]_n samples with a weight ratio of (a) 1:4, (b) 1:2, and (c) 1:1.

1-C₉ vs. graphene was characterized by energy dispersive spectroscopy (EDS), as shown in Figure 2A. Based on our recent studies on these types of core-shell nanoparticles,^{19,20} the C₆₀(>DPAF-C₉)-derived fullerosome capping on γ -FeO_x@AuNP increased the average nanoparticle diameter by roughly 20 nm in diameter. This was accounted for the [60]fullerosome layer thickness of ~6.0–8.0 nm, matching well with a bilayered to a partial trilayered molecular width of **1-C₉** with the molecular long-axis length of ~3.2 nm.

The elemental compositions of multilayered GN@(FeAuF_n) nanosheets were measured by EDS microanalyses with the sample deposited on a supporting tape. As a result, with a low weight ratio of C₆₀(>DPAF-C₉) vs. graphene as 1:8 applied, the atomic percentages of carbon, Fe, and Au were measured to be 95.53, 0.95, and 0.14%, respectively, (Fig. 11A) giving an atomic C:Fe:Au ratio of 682:6.8:1.0, revealing insufficient coverage of γ -FeO_x@AuNP (the same material weight as that of **1-C₉** used) on GN nanosheets. Therefore, a large quantity of carbon detected was obviously derived from GNs underneath the nanoparticles. As this weight ratio being increased to 1:2, 1:1, or 2:1, the corresponding atomic percentages of the same carbon, Fe, and Au were measured to be 78.15, 4.28, and 0.67%, 69.50, 6.91, and 0.88%, or 68.05, 7.02, and 0.95%, respectively, that resulted in the atomic C:Fe:Au ratio being changed to 116.6:6.4:1.0, 79.0:7.9:1.0, or 71.6:7.4:1.0, respectively. The atomic ratio between Fe and Au remains relatively constant with an average of 7.4 among all three samples. As each **1-C₉** molecule contains 104 carbon atoms, these EDS results may reveal that the latter two compositions, with a steadily less C:Au ratio, were capable of giving a full coverage on GNs by both **1-C₉** conjugates and γ -FeO_x@AuNPs, in the same weight quantity. Less carbon atoms detected implied the minimum contribution from GN underneath. It corresponds to an average of one **1-C₉** molecule per 1.5 Au atoms (an atomic radius of 0.146 nm) in the product of GN@(FeAuF_n). These atomic ratios led us to estimate roughly a trilayered fullerosome shell thickness on the Au layer of core-shell NPs, consisting with the shell width of ~8.0 nm. Based on the combination of TEM micrographic images and EDS results and analyses, we concluded the best material component ratios of multilayered GN@(FeAuF_n) nanosheets to be applied in the investigation of their photophysical properties should be either 1.5:1.0:1.5 or 2.0:1.0:2.0 by weight for **1-C₉**:GN: γ -FeO_x@AuNP.

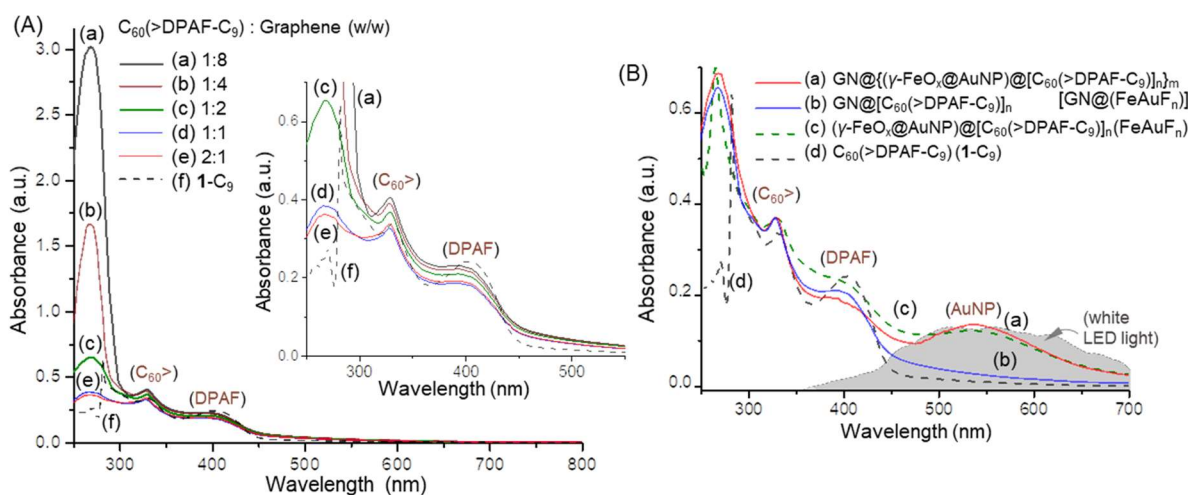


Figure 12. Steady state UV-vis absorption spectra of (A) intermediate GN@[C₆₀(>DPAF-C₉)]_n sheets with an increasing weight ratio of C₆₀(>DPAF-C₉) vs. graphene as indicated from (a) to (e) and (f) **1-C₉**. (B) comparison of optical absorbance of three **1-C₉** with or without γ -FeO_x@AuNP nanoparticles-encapsulated GNs with the nanostructure products indicated. All samples were prepared in CHCl₃ with the concentration of 1.0×10^{-5} M.

Photophysical properties of GN@(FeAuF_n) were compared with those of starting compounds and precursor GN intermediates using UV-vis spectroscopic technique. Upon grafting a monolayer of **1-C₉** on GN to the intermediate GN@[C₆₀(>DPAF-C₉)]_n sheets at different applied weight quantities, steady state optical absorption spectra displayed clearly three main absorption bands with the peak maximum centered

at 268 (s), 328, and 394 nm, as shown in Fig. 12A. The former band was assigned for the absorption of graphene nanosheet moieties. Its extinction coefficient value changes were indicative of a composition variation among several samples studied, as shown in Fig. 12Aa–3Ae. The latter two bands match well with those of **1-C₉** (Fig. 12Af) corresponding to absorptions of photoresponsive C₆₀> and DPAF moieties, respectively. This revealed the success in grafting **1-C₉** conjugates on GNs. With the increase of **1-C₉** conjugates quantity ratio vs. GN applied from 1:8 to 2:1, the peak intensity ratio of GN (at 268 nm):C₆₀> (at 328 nm or DPAF at 394 nm) decreases progressively in extension coefficient (ϵ) value. It implied that the GN nanosheet surface being nearly fully covered by immobile **1-C₉** conjugates leading to GNs underneath less detectable by the scanning light. It is worthwhile to mention that the DPAF moiety is serving as the light-harvesting antenna to enhance the optical absorption capability at UVA to short visible wavelengths covering 350–425 nm that allowed us to utilize either UVA or 405-nm light as the energy source for photoactivation.

After deposition of γ -FeO_x@AuNP nanoparticles on intermediate GN@[C₆₀(>DPAF-C₉)]_n sheets, optical absorptions contributed from AuNP moieties became obvious showing a significant band covering the range of 450–650 nm and beyond (Fig. 12Ba) as compared with those of GN@[C₆₀(>DPAF-C₉)]_n (Fig. 12Bb). The extension coefficient value of this band was found to be nearly identical to that of **1-C₉**-encapsulated γ -FeO_x@AuNP (Fig. 12Bc), providing the evidence of efficient grafting both **1-C₉** conjugates and γ -FeO_x@AuNPs on GN@[C₆₀(>DPAF-C₉)]_n. It was also verified by the Infrared spectra of the same series of nanostructures showing strong fluorenyl carbonyl (–C=O) stretching absorption band centered at $\nu_{\max}$ 1660 cm^{–1} nearly identical to that of **1-C₉**. Most importantly, we were able to detect two typical fullereryl cage bands at $\nu_{\max}$ 574 (s, br) and 526 (vs) cm^{–1}. These two bands are corresponding characteristic absorptions used to provide evidence of (C₆₀>)-related monoadducts with absorption wavenumber and relative intensity ratio differentiable from those of C₆₀ and indistinguishable to **1-C₉** signaling its attachment on GNs.

Photoinduced intramolecular electron (e[–])-transfer capability within the nanostructure of multilayered GN@(FeAuF_n) nanosheets is the most plausible photomechanism to induce the dielectric properties. Therefore, we first investigated the unit character of redox potentials among all structural components using cyclic voltammetric (CV) technique to include samples of the monoadduct C₆₀(>DPAF-C₉), shear exfoliated graphene nanosheet (GN), GN@[C₆₀(>DPAF-C₉)]_n (with a weight ratio of **1-C₉**:GN as 1.0:1.0), and multilayered GN@(FeAuF_n) nanosheets (with a weight ratio of **1-C₉**:GN: γ -FeO_x@AuNP as 1.5:1.0:1.5) for comparison with or without LED light irradiation. By using these combination of samples, we were able to deliver appropriate redox potential analyses and data interpretation with all measurements being carried out in a solution of CH₂Cl₂ containing (*n*-butyl)₄N⁺-PF₆[–], as the electrolyte, and Pt as both working and counter electrodes with Ag/AgCl as the reference electrode. They were performed under the same CV conditions over cyclic oxidation and reduction voltages vs. Ag/Ag⁺ from –2.0 to 2.0 V to cover both the oxidative cycle of the DPAF-C₉ e[–]-donor moiety at positive voltage of 0.0 to 2.0 V and reductive cycles of e[–]-accepting C₆₀> cage and GN moieties at negative voltage of –2.0 to 0.0 V.

As a result, we detected one reversible oxidation (¹*E*_{ox} of 1.47 V)–reduction (¹*E*_{red} of 1.32 V) cyclic wave with the first half-wave oxidation potential (¹*E*_{1/2,ox}) of 1.40 V versus Ag/Ag⁺ for the DPAF-C₉ moiety at positive voltages (Fig. 13Aa and 13Ba), indicating reversible formation of the corresponding (DPAF-C₉)⁺. In the negative voltage region, this CV diagram profile displayed three reversible reductions at –0.31 [¹*E*_{red} for (C₆₀>)•], –0.76 [²*E*_{red} for (C₆₀>)^{2–}], and –1.16 V [³*E*_{red} for (C₆₀>)^{3–}] with the corresponding cyclic oxidation waves at –0.16 (¹*E*_{ox}), –0.50 (²*E*_{ox}), and –0.96 (³*E*_{ox}), respectively. These data corresponded to the first to third half-wave reduction potentials of –0.24 (¹*E*_{1/2,red}), –0.63 (²*E*_{1/2,red}), and –1.06 V (³*E*_{1/2,red}), respectively, versus Ag/Ag⁺. In the case of GN sheets, only a broad one-electron reduction signal was detected at –0.67 V (¹*E*_{red}) vs. Ag/Ag⁺ (Fig. 13Ab and 13Bb) indicating a higher voltage of 0.36 V more negative required to inject the first electron. These values corresponding to either e[–]-donor or e[–]-acceptor moieties of C₆₀(>DPAF-C₉) and GNs were applied for comparison to those of GN@[C₆₀(>DPAF-C₉)]_n and GN@(FeAuF_n) nano-sheets.

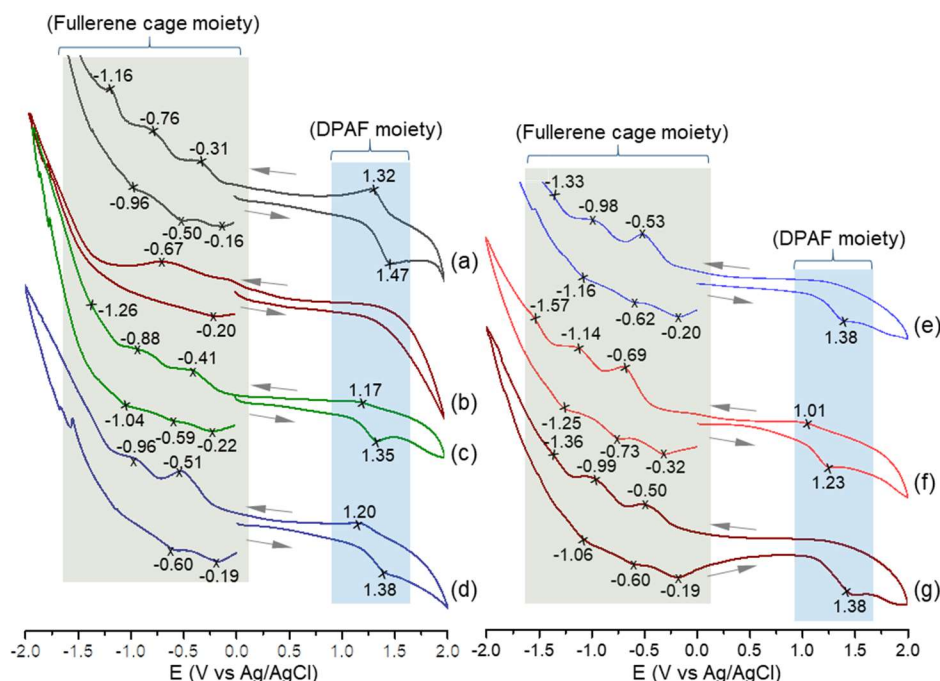


Figure 13. Cyclic voltammograms (CV) of (a) $C_{60}(>DPAF-C_9)$, (b) graphene nanosheet (GN), (c) $GN@[C_{60}(>DPAF-C_9)]_n$ (a weight ratio of $1-C_9:GN$ as 1.0:1.0), and multilayered $GN@(FeAuF_n)$ nanosheets (with a wt. ratio of 1.5:1.0:1.5 for $1-C_9:GN:\gamma-FeO_x@AuNP$) under the condition of (d) without LED light, (e) with LED light (2.0 W, a total fluence of 36.7 J/cm^2), and (f) a period of 2.0 min and (g) 8.0 min after LED light being turned off, where potential voltage values at either the peak maximum or minimum of each redox cycle were displayed. All solutions were in a concentration of $5.0 \times 10^{-3}\text{ M}$ in CH_2Cl_2 using $Ag/AgCl$ as the reference electrode at a scan rate of 20 mV/s.

The monolayer contact of $1-C_9$ conjugates on GNs of $GN@[C_{60}(>DPAF-C_9)]_n$ (Fig. 13Ac and 13Bc) gave the signal broadening effect with a slight shift of reduction/oxidation potentials showing similar three reversible reductions at -0.41 V [$^1E_{red}$ for $(C_{60}>)^{\cdot-}$], -0.88 V [$^2E_{red}$ for $(C_{60}>)^{2-}$], and -1.26 V [$^3E_{red}$ for $(C_{60}>)^{3-}$] with the corresponding first to third half-wave reduction potentials shifted to -0.32 V ($^1E_{1/2,red}$), -0.74 V ($^2E_{1/2,red}$), and -1.15 V ($^3E_{1/2,red}$), respectively, versus Ag/Ag^+ . They revealed a parallel shift of roughly 0.1 V more negative to perform the same three reductive cycles, consistent with the degree of influence by GNs. A similar effect was occurred on the DPAF donor moiety. Upon deposition of $\gamma-FeO_x@AuNP$ nanoparticles and the top-coat of $1-C_9$ to afford the products of multilayered $GN@(FeAuF_n)$ nano-sheets, only two reversible reductive cycles were detectable at -0.51 V [$^1E_{red}$ for $(C_{60}>)^{\cdot-}$] and -0.96 V [$^2E_{red}$ for $(C_{60}>)^{2-}$] (Fig. 13Ad and 13Bd) with nearly identical corresponding cyclic oxidation waves at -0.19 V ($^1E_{ox}$) and -0.60 V ($^2E_{ox}$), respectively, to those of $GN@[C_{60}(>DPAF-C_9)]_n$.

To investigate the photo-effect on the CV behavior in correlation to the observation of photoinduced relative dielectric constant (ϵ_r') amplification, described below, the sample was subjected to exposure of a collimated white LED light, with an output power of 2.0 W, for a period of 60 min (a total fluence of 36.7 J/cm^2) followed by the CV measurement while the LED light remained on. The main light emission wavelength range covered the optical absorption of the Au layer centered at $\lambda_{abs,max}$ 520–560 nm (Fig. 12Ba) while DPAF- C_9 antenna has a minimum absorption in this range. Therefore, the photoexcitation was intended for the plasmonic energy activation. As a result, we observed a nearly identical CV diagrams in Fig. 13Ae and 13Be as those of Fig. 13Ad and 13Bd, except the returning $^1E_{red}$ cycle of DPAF moiety becoming less visible, revealing no change on the electronic structure of $1-C_9$ during this photo-process, consistent with a minimum change of ϵ_r' detected (described below) under the same conditions. Upon turning off the light, we immediately began the CV data collection with a 2.0-min period required to finish one experimental cycle. The second cycle of CV data collection also subsequently followed the first cycle, with the similar repeats for a total of four CV cycles to catch the entire events of interlayer SPR energy-

transfer processes of GN@(FeAuF_n) nano-sheets, discussed above and below. It was consistent with the time length needed for the photo-amplified ϵ_r' to return back to its original value at time zero reversibly, as shown in Fig. 14. Interestingly, a slight shift of reduction potentials to more negative as -0.69 for $^1E_{\text{red}}$, -1.14 for $^2E_{\text{red}}$, and -1.57 V for $^3E_{\text{red}}$ (Fig. 13f) as compared with those of Fig. 13d. The observation revealed the possible SPR energy-induced partial formation of $(\text{C}_{60})^{\cdot-}$ that led the surrounding C_{60} moieties slightly more difficult to be reduced electrochemically. At the time 8.0-min after the light-off, the CV profile (Fig. 13g) showed a nearly identical diagram as that of Fig. 13d indicating the full recovery of photochemical processes back to its initial state with good reversibility and recyclability of **1-C₉** on GNs.

4.2. Photoswitchable Relative ϵ_r' Amplification Effects at GHz Frequency

The reflectivity of a subject is controlled by the refractive index of the subject surface medium that is a function of the product of permittivity (ϵ_r) in a complex form and permeability (μ). Both are relevant material parameters in response to incident electromagnetic waves. The former complex permittivity can be presented by the equation $\epsilon_r^* = \epsilon_r' - i\epsilon_r''$, where ϵ_r' is the real part as the relative dielectric constant and ϵ_r'' is the imaginary part as the loss factor. The former parameter ϵ_r' is dependent on charge-polarization of the material at the wavelength of measurements. In the experimental data collection, the complex relative electric permittivity (and) values were measured in terms of complex reflection coefficient of electromagnetic waves in proportion to a complex scattering parameter, defined as S_{11} . The scattering parameter S_{11} was measured by a high-performance coaxial probe (Agilent 85070E).⁵³ It was then converted to complex relative electric permittivity (ϵ_r^*) values using the Nicolson-Ross algorithm.⁵⁴ From this measurement and calculation, the value of ϵ_r' was derived.

Surface plasmon resonance (SPR) energy phenomena has been demonstrated and applied in many technological areas including the use of it as an alternative means to increase either light absorption or scattering in a thin film to enhance solar cells efficiency.^{39,40} In principle, SPR energy occurs as the result of collective oscillation of surface electrons in gold nanoparticles that is induced by the interaction with the incident light. It leads to polarization with the formation of polaritons leading to the influence of absorption cross-section enhancement and light emitting.³² In our study, we applied core-shell nanoparticles to investigate the possibility of tuning the SPR energy band to match with absorptions of dielectric materials for the induced intramolecular electron polarization that led to the modulation of dielectric constant and related physical property of the material layer on core-shell nanoparticles of **9-NPs**. The approach coincides with our recent results of ultrafast photoinduced intramolecular e^- -transfer phenomena in femtoseconds.^{25,55} Therefore, we found that a near-field effect within few nanometers was crucial to enhance SPR energy accumulation during the energy-transfer event between plasmonic AuNPs and C_{60} -(antenna)_x core-shell layers by direct contacts.

Permittivity and dielectric properties of $(\gamma\text{-FeO}_x\text{@AuNP})\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ (**6-NP**) were investigated in measurements carried out using an open-ended coaxial probe and a network analyzer in the frequency range of 0.5–4.5 GHz. Elucidation and conversion of measured scattering parameter (S_{11}) data provided information of the relative dielectric constant (ϵ_r' , the real part of complex permittivity) and the relative dielectric loss factor (ϵ_r'' , the imaginary part of complex permittivity). For comparison purposes, several samples were first evaluated to establish the reference values. They included $\text{C}_{60}(>\text{DPAF-C}_9)$ alone, $\gamma\text{-FeO}_x$ nanoparticles alone, $\gamma\text{-FeO}_x\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ NPs, and $\gamma\text{-FeO}_x\text{@AuNP}$ in PDMS as a mixture to show either none or insignificant changes of ϵ_r' under both switch-on and switch-off irradiation conditions. We selected a LED white light with the output power of 2.0 W for the study. Under the emission wavelength range and the band intensity of a white light, the emission spectrum matched with optical absorptions of the gold layer over the full range and a part of DPAF-C₉ moiety at 415–450 nm, indicating the main photoexcitation processes occurring at these two components. The absorption peak of C_{60} cage with a maximum (λ_{max}) centered at 326 nm is outside the range. Therefore, it should not be involved directly in initial photoexcitation events. Measurements were conducted inside a custom-built chamber to create a circumferentially uniform illumination environment. Its inner chamber

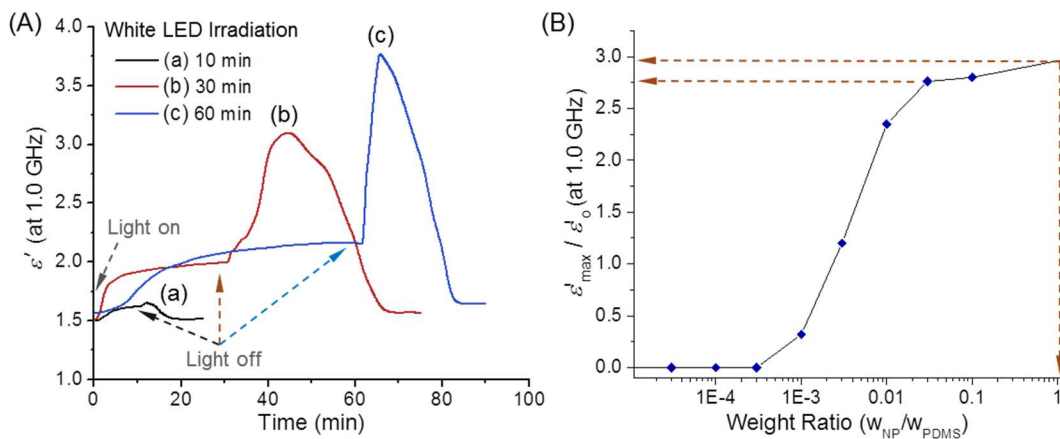


Figure 14. (A) Irradiation fluence-dependent relative dielectric constant (ϵ_r') amplification of core-shell (γ - $\text{FeO}_x\text{@AuNp}$)@[$\text{C}_{60}(>\text{DPAF-C}_9)$] $_n$ (6-NP) without PDMS at the RF frequency of 1.0 GHz. Irradiation period was (a) 10 min, (b) 30 min, and (c) 60 min. (B) Concentration-dependent relative ϵ_r' value of 6-NP in PDMS.

temperature was maintained and controlled using several fans to minimize heat building up, showing only a small increase from 25 to 45–46 °C when the light was turned on for a period of 60 min. The chamber temperature dropped quickly back to 25 °C after light-off. In the study, illumination periods were chosen to be 10, 30, and 60 min giving the corresponding light fluence of 2.13, 6.41, and 12.8 J/cm², respectively. As a result, interestingly, the quantity of relative dielectric constant amplification collected on core-shell nanoparticle materials 6-NP without PDMS at the RF frequency of 1.0 GHz (Fig. 14A) was found to be highly dependent on the quantity of irradiation fluence. At a low fluence accumulated over a period of 10 min (Fig. 14A-a), insignificant changes of ϵ_r' at the light-off stage was detected. When the light fluence was accumulated over a period of 30-min (Fig. 14A-b), a large increase of ϵ_r' with the profile showing as a broad band at the light-off stage was observed. The peak ϵ_r' at maximum ($\epsilon_{\max}'$) value of 3.09 at the light-off stage represented a 206% increase from $\epsilon_r' = 1.5$ at the time zero. Further increase of the accumulated light fluence to 12.8 J/cm² (Fig. 14A-c), a much sharper jump of ϵ_r' quantity was noticed immediately after turning off the light. Its peak maximum $\epsilon_{\max}'$ value of 3.63 corresponds to an amplification of 242%. The data strongly support our hypothesis that the molecular polarization of $\text{C}_{60}(>\text{DPAF-C}_9)$ is SPR energy-induced and the polarized charge quantity in the fullerosome layer is in dependence of the accumulated total SPR energy.

To facilitate or enable the use of 6-NP in the film coating process, we investigated the concentration-dependent relative ϵ_r' value of 6-NP in PDMS polymers with the results shown in Fig. 14B. Soft elastic property of PDMS as a polymer host was able to provide a tight packing in filling up air-gaps among particles after solvent evaporation that is critical for eliminating the air contribution to the ϵ_r' value obtained. Its dielectric constant is comparable in value to that of $\text{C}_{60}(>\text{DPAF-C}_9)$. Variation of the nanoparticle 6-NP concentration in PDMS was estimated in terms of the weight ratio as w_{NP}/w_{PDMS} based on the consistent amount of 1- C_9 per unit weight (mg) of NPs applied in the preparation of core-shell materials. At a low ratio of 2×10^{-4} , nearly no detectable ϵ_r' was found, as shown in Fig. 14B. By increasing the weight ratio above 10^{-3} to 10^{-2} , the measured magnitude of $\epsilon_{\max}'/\epsilon_o'$, where ϵ_o' is ϵ_r' at the time zero and $\epsilon_{\max}'$ is the maximum ϵ_r' after 60-min irradiation, sharply surged from 0.26 to 2.31. The curve ascending slop became smaller above the weight ratio of 0.03 and 0.1 giving the $\epsilon_{\max}'/\epsilon_o'$ values as 2.75 and 2.76, respectively, which is close to the $\epsilon_{\max}'/\epsilon_o'$ magnitude of nearly neat 6-NP as 2.95. Therefore, we select a ratio of w_{NP}/w_{PDMS} as 1:10 to be an optimal mixture composite to maintain a good viscosity and the film strength of the sample mixture for coating applications and to balance a minimum reduction of the ϵ_r' signal as compared with that of the neat 6-NP.

We also carried out frequency-dependent permittivity measurements under similar experimental setup and conditions described above. The reflected signal was evaluated in terms of ϵ_r' and relative loss factors (ϵ_r'') at 0.5–4.5 GHz under illumination with a LED white light. Fig. 15 shows relative dielectric

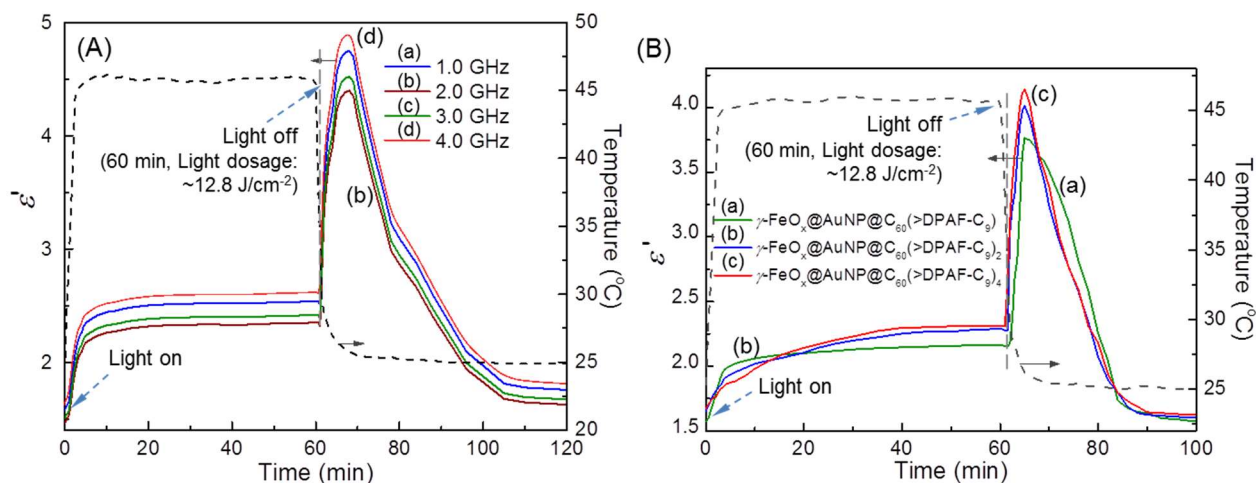


Figure 15. Large sharp relative dielectric constant (or permittivity) amplification of (A) (γ - FeO_x @AuNP)@[C_{60} (>DPAF- C_9)] $_n$ (6-NP) in a mixture with PDMS (1:10 by wt.) detected by the data taken at different frequencies (1.0–4.0 GHz) and (B) 6-NP and 7-NP prepared by a different batch of core-shell formation from those of (A) for comparison at 1.0 GHz. Both (A) and (B) used a collimated LED white light showing rapid switch-on increase of ϵ_r' at the light-off stage after 60-min irradiation.

constant (or permittivity, ϵ_r') curve profiles of 6-NP NPs in PDMS (1:10 by wt.) with the data taken at different frequencies (1.0–4.0 GHz) during and after 60-min illumination using a collimated white LED light. Total accumulated light fluence over a period of 60 min was 12.8 J/cm^2 . The initial increase of ϵ_r' measured from the time zero to the time 5-min matched well with the sharp surging profile of the chamber temperature from 25 to 47 °C, indicating increased ϵ_r' magnitudes from the time zero value to 2.34, 2.40, 2.47, and 2.59 at 2.0 (Fig. 15Ab), 3.0 (Fig. 15Ac), 1.0 (Fig. 15Aa), and 4.0 (Fig. 15Ad) GHz were owing to the chamber-related thermal effect. These magnitudes remained relatively steady over the illumination period of 20 to 60 min. Shortly after the light being turned off, we observed an interesting rapid upsurge of permittivity to a maximum magnitude of 4.34, 4.50, 4.72, and 4.88 at 2.0, 3.0, 1.0 and 4.0 GHz, respectively, reached at roughly 7.0 min after the start of light-off state. These permittivity magnitudes correspond to a ratio of $\epsilon_{\text{max}}'/\epsilon_0'$ ($\epsilon_0' = 1.58$ at the time zero) in a roughly 2.75-, 2.85-, 2.99-, and 3.09-folds at the peak maximum for 2.0, 3.0, 1.0 and 4.0 GHz, respectively. Extent of the photoswitchable dielectric amplification on permittivity was the highest that we have observed to date, especially, on the samples at the frequency of 4.0 GHz. Since no detectable changes of ϵ_r' values were observed during or after the irradiation period (60 min) with the samples of 1- C_9 , γ - FeO_x NPs, and core-shell γ - FeO_x @[C_{60} (>DPAF- C_9)] $_n$ NPs (without Au) measured at 1.0 GHz, observed amplification phenomena of ϵ_r' can be correlated solely to the influence of the gold layer of 6-NP or 7-NP after light illumination. As discussed above, it is owing to the generation of plasmonic energy at the surface which was photoinduced by the light applied.

As the number of e^- -donor chromophore per C_{60} > increases from 1 to 2 in the conjugates 2- C_9 , the corresponding core-shell NPs 7-NP exhibited similar phenomena of dielectric amplification at the permittivity maximum in less than 7.0 min after the light being turned off, as shown in Fig. 15B. It was then followed by a relaxation process of ϵ_r' back to a value of 1.57 nearly identical to the initial ϵ_r' value, indicating a good recyclability of photoswitching characteristics in light-on and light-off cycles. By considering a nearly identical dielectric constant among 6-NP and 7-NP at the time zero, the maximum permittivity magnitude of 3.76, 4.0, and 4.14, respectively, at the time of 67 min indicated a 6.4% increase of ϵ_r' for 7-NP from that of 6-NP. We have previously demonstrated the phenomena of efficient photoinduced intramolecular charge separation of 2- C_9 and 3- C_9 in polar media using nanosecond transient spectroscopic measurements.²³ Photoexcitation processes resulted in the formation of corresponding transient charge-separated (CS) state of these nanomaterials consisting of a positively charged (DPAF- C_9) $^+$ and a negatively charged (C_{60} >) $^-$. With the increase of the number of DPAF- C_9

antenna moieties attached per C_{60} cage to 4, the CS transient state lifetime (τ_{CS}) was found to be prolonged, sufficiently long enough for its contribution to permittivity properties. Therefore, we considered the generation of these CS states within the outer shell layer of 6-NP and 7-NP being the source of electric charges to amplify the observed permittivity in RF frequency range.

Conducting Electron Donors Enhanced Dielectric Amplification on Similar Systems of Core-Shell (γ - $FeO_x@AuNP$)@[$C_{60}(DPAF-C_9)$] $_n$ Fullerosome NPs.

Based on the hypothesis that instantaneous electron polarization (i.e. ferroelectric-like) among donors and acceptors is crucial to achieve high photo-switched permittivity ϵ_r' , we proposed the use of several conductive electron donors and polymers to further enhance *intermolecular* (other than *intramolecular* process in the above studies) electron-transfer process to enlarge the degree of dielectric amplification in RF frequencies. Accordingly, we added an outer layer of such conducting donors on core-shell nanoparticles of (γ - $FeO_x@AuNP$)@[$C_{60}(DPAF-C_9)$] $_n$ in a close contact. These donors are poly(3-hexylthiophene-2,5-diyl) (P3HT), bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), polyaniline (PANI), and camphorsulphonic acid doped polyaniline (PANI-CSA) for comparison. As a result, stronger donors, such as BEDT-TTF and P3HT, gave a higher degree of permittivity amplification of 248 and 230% increase ($\epsilon_r'_{max}/\epsilon_r'_{0 min}$), respectively, or 208 and 198% increase ($\epsilon_r'_{max}/\epsilon_r'_{60 min}$), respectively, as shown in Fig. 16. It indicated the ability of strong conducting electron donors to be ionized easily indirectly via C_{60} and to distribute or delocalize the positive charges along the π -conjugation system, thus, giving prolonged the charge-separated state. This is not the case for the use of neutral PANi, resulted in the decrease of the degree of permittivity amplification due to its lower electron-donating capability. In the case of PANi-CSA, there is no intermolecular electron transfer involved. However, it was already in the electron conducting state itself capable of delocalize positive charges by contact from intramolecularly generated (DPAF- C_9) $^{+}$ moieties that gave a higher $\epsilon_r'_{max}/\epsilon_r'_{60 min}$ ratio of 191% as compared with 156% of using neutral PANi.

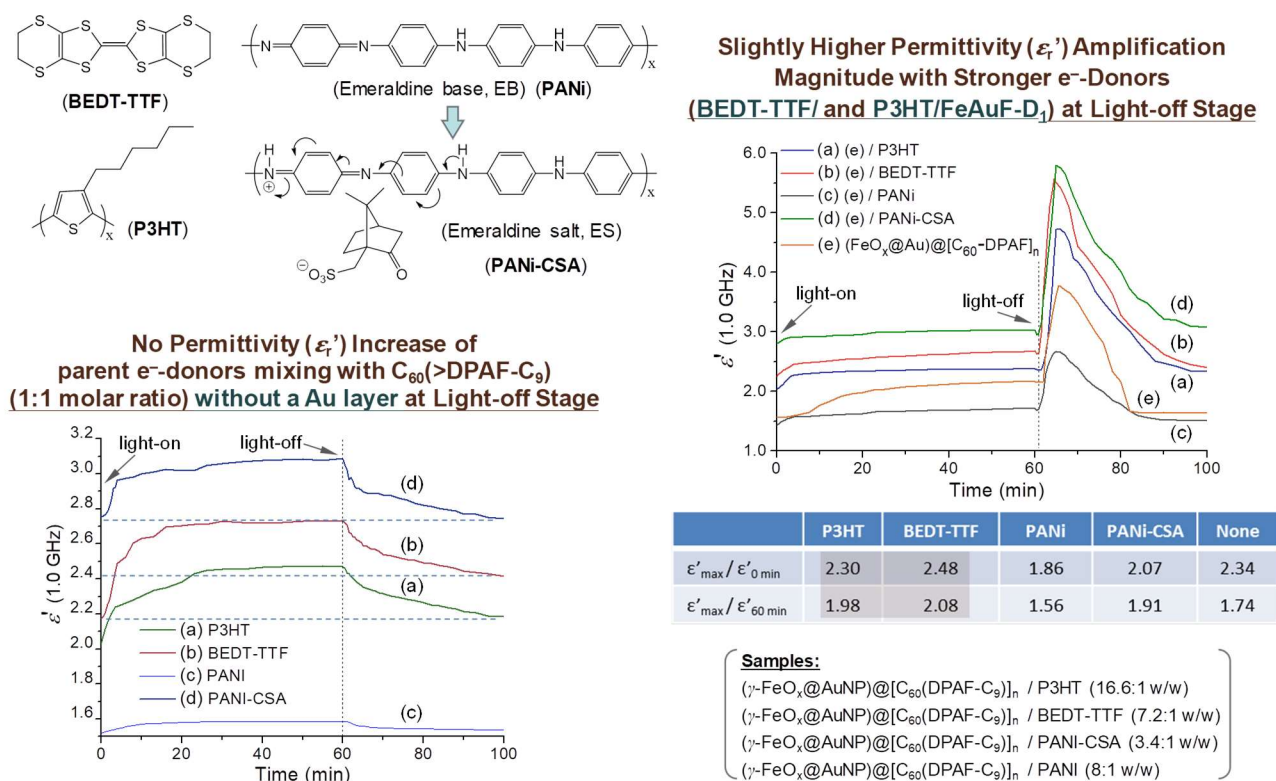


Figure 16. Time-dependent relative dielectric constant (ϵ_r') profiles of e-donors incorporated at the outer layer of core-shell (γ - $FeO_x@AuNP$)@[$C_{60}(DPAF-C_9)$] $_n$ ($FeAuF-D_1$) nanoparticles at the frequency of 1.0 GHz under illumination using a LED white light, showing large photoswitchable amplification of ϵ_r' at the light-off state.

Dielectric Constant of cis-cup-Tris[C₆₀>(DPAF-C₉)]-Encapsulated γ -FeO_x@AuNP Yielding Trilayered Core-Shell Nanoparticles, (γ -FeO_x@AuNP)@{cis-cup-tris[C₆₀>(DPAF-C₉)]_n (8-NP).

We assembled a multiple layered structure of NPs having an inner magnetic γ -FeO_x@AuNP core encapsulated by an outer *cis-cup*-tris[C₆₀>(DPAF-C₉)] shell, as described above. The NP fabrication was coupled by the control of the layer thickness of *cis-cup*-5-C₉ in terms of the quantity weight ratio to that of γ -FeO_x@AuNP (8-NP). We first evaluated the degree difference of dielectric property amplification between 1-C₉ (giving 6-NP) and *cis-cup*-5-C₉ (giving 8-NP) using the same plasmonic core-shell γ -FeO_x@AuNP core. As a result, Fig. 10B showed irradiation time-dependent relative dielectric constant (ϵ_r') curves of 6-NPs and 8-NPs taken at the microwave frequency of 1.0 GHz during and after a 60-min white LED light illumination (corresponding to a total light fluence of 12.8 J/cm²). Apparently, microwave EM wave showed a higher sensitivity to the NP surface materials for us to note the detected initial dielectric constant value at the time zero min being comparable in value to that of organic 1-C₉ ($\epsilon_r'_{0\min} = 1.55$) and *cis-cup*-5-C₉ ($\epsilon_r'_{0\min} = 2.48$) even though the inner shell layer of AuNPs and the core γ -FeO_x NPs having a much higher $\epsilon_r'_{0\min} (= 9.0)$ value. A slightly higher $\epsilon_r'_{0\min}$ for the latter is interesting since higher dielectric constant organics may be advantageous in energy devices. In all experiments, white light illumination led to a slight rise in temperature to 35–45 °C in the first 15 min. Slight increase of chamber temperatures away from 25 °C resulted in a small increase of the ϵ_r' value in a similar degree among these two samples. The ϵ_r' value was then remaining relatively steady during the rest of irradiation period up to 60 min. Upon turning-off the light at the end of 60-min irradiation, we observed a large sharp raise of the ϵ_r' value for both samples while the chamber temperature dropped quickly back to 25 °C. Sharp increase of the permittivity at the light-off stage was found to reach a peak maximum ($\epsilon_r'_{\max}$) value of 5.75 for 8-NP (Fig. 10Bb) and 3.75 for 6-NP (Fig. 10Ba). They can be accounted by a ratio of $\epsilon_r'_{\max}/\epsilon_r'_{0\min}$ in a 2.35- and 2.42-fold increase for 6-NP and 8-NP, respectively. Similar calculations based on the ratio of $\epsilon_r'_{\max}/\epsilon_r'_{60\min}$ (the ϵ_r' value at time 60-min) were found to be 1.76- and 1.74-fold increase in the ϵ_r' value for 8-NP ($\epsilon_r'_{60\min} = 3.26$, Fig. 10Bb) and 6-NP ($\epsilon_r'_{60\min} = 2.16$, Fig. 10Ba), respectively. Apparently, fabricated core-shell structural configurations were capable of inducing permittivity amplification at a RF-frequency of 1.0 GHz.

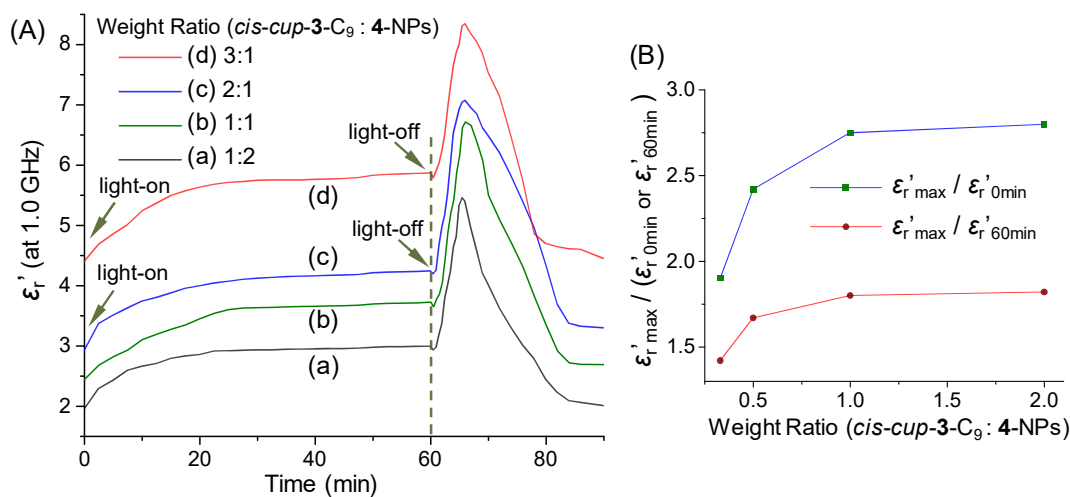


Figure 17. (A) Irradiation time-dependent relative dielectric constant (ϵ_r') amplification of trilayered core-shell nanoparticles of (γ -FeO_x@AuNP)@{*cis-cup*-tris[C₆₀>(DPAF-C₉)]_n (8-NP) with a different weight ratio of *cis-cup*-5-C₉ vs γ -FeO_x@AuNP (4-NPs) at the frequency of 1.0 GHz with a white LED light irradiation period of 60 min. (B) Relative dielectric constant (ϵ_r') ratios of the values at peak maximum vs that at either 0 min or 60 min, showing a progressive increase of the degree of dielectric amplification.

We also investigated the weight ratio (*cis-cup*-5-C₉/ γ -FeO_x@AuNP)-dependent dielectric property of trilayered (γ -FeO_x@AuNP)@{*cis-cup*-tris[C₆₀>(DPAF-C₉)]_n (8-NP) for the comparison at the frequency of 1.0 GHz. Similar sharp increase of the permittivity at the light-off stage was found for all samples to reach a peak maximum ($\epsilon_r'_{\max}$) value of 5.46 (Fig. 17Aa), 6.60 (Fig. 17Ab), 7.03 (Fig. 17Ac), and 8.39

(Fig. 17Ad) for the weight ratio of 1:2, 1:1, 2:1, and 3:1, respectively. They can be accounted by a corresponding ratio of $\epsilon_r'_{\max}/\epsilon_r'_{0\min}$ in a 2.80- ($\epsilon_r'_{0\min} = 1.95$), 2.75- ($\epsilon_r'_{0\min} = 2.40$), 2.42- ($\epsilon_r'_{0\min} = 2.90$), and 1.90-fold ($\epsilon_r'_{0\min} = 4.42$) increase, respectively. Interestingly, a higher quantity of *cis-cup-5-C9* applied led to a progressively increase of the initial dielectric $\epsilon_r'_{0\min}$ value up to 4.42 higher than that of many organic materials and polymers. This higher $\epsilon_r'_{0\min}$ value resulted in a lower degree of amplification $\epsilon_r'_{\max}/\epsilon_r'_{0\min}$. However, a high dielectric $\epsilon_r'_{\max}$ value of 8.39 (Fig. 17Ad) achieved in organic-inorganic hybrid nanomaterials is significant for potential applications. Finally, similar calculations based on the ratio of $\epsilon_r'_{\max}/\epsilon_r'_{60\min}$ were found to be 1.82- ($\epsilon_r'_{60\min} = 3.0$, Fig. 17Aa), 1.80- ($\epsilon_r'_{60\min} = 3.67$, Fig. 17Ab), 1.67- ($\epsilon_r'_{60\min} = 4.21$, Fig. 17Ac), and 1.42-fold ($\epsilon_r'_{60\min} = 5.91$, Fig. 17Ad) increase, respectively. Relative dielectric constant ratios of either $\epsilon_r'_{\max}/\epsilon_r'_{0\min}$ or $\epsilon_r'_{\max}/\epsilon_r'_{60\min}$ as the ϵ_r' value shown at each peak maximum vs that at either 0 min or 60 min, respectively, in Fig. 17B indicated a progressive increase of the degree of dielectric amplification upon the quantity increase of *cis-cup-5-C9* up to a weight ratio of *cis-cup-5-C9*/ γ -FeO_x@AuNP as 2.0/1.0.

Reversible and Photoswitchable Dielectric (ϵ_r') Properties of RF-Responsive Multilayered GN@(FeAuF_n) Nanosheets.

The purpose to incorporate graphene nanosheets in the design of plasmonic core-shell nanoparticles for enhancing dielectric characteristics, using C₆₀(>DPAF-C₉) as the intramolecular photoinduced charge generator, was hypothesized that the distribution and delocalization of negative (C₆₀>)⁻ charge on GNs should provide further stabilization with a longer lifetime of charge-separated transient state to simulate ferroelectric-like (or capacitor-like) behavior. To achieve this goal, fabrication of a homogeneous monolayer C₆₀(>DPAF-C₉) as a fullerosome array layer on GNs became the most crucial step of nanosheet sample preparation. Based on the materials characterization results discussed above, we selected multilayered GN@(FeAuF_n) nanosheet samples with a particular composition close to a component weight ratio of 1-C₉:GN: γ -FeO_x@AuNP as 1.5:1.0:1.5 for the dielectric and RF-response studies. During the measurement, a white LED light (2.0 W) with the main emission output spectrum wavelengths covering 420–750 nm matching well with Au-layer absorptions at 450–650 nm and beyond, as shown in shadow area of Fig. 12B. In this range, both C₆₀> and DPAF components may not be involved directly or only minimum absorptive in initial photoexcitation events. Therefore, photoinduced physical events should initially occur at the surface of Au-shell layer nanocrystals leading to the generation of SPR energy. Subsequent interlayer energy-transfer events have to be correlated to it during the investigation and measurement. Irradiation time-dependent relative dielectric constant (ϵ_r') values were collected on several multilayered GN@(FeAuF_n) nanosheet samples each with a different weight ratio of 1-C₉:GN: γ -FeO_x@AuNP as either 2.0:1.0:2.0, 1.0:1.0:1.0, 1.0:2.0:1.0, 1.0:4.0:1.0, 1.0:8.0:1.0, or 1.0:0.0:1.0 with the last sample as core-shelled (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n without GNs for the purpose of comparison.

In the sample preparation for relative dielectric constant (ϵ_r') measurements, elastic semi-solid of poly(dimethylsiloxane) (PDMS) was used as a supporting polymer host to provide a tight packing and filling on air-gaps among nanosheet samples during slow solvent evaporation process. It is critical to ensure elimination of the possible air contribution to the measured ϵ_r' value. The measurement was carried out using an open-ended coaxial probe and a network analyzer in the range of 0.5–4.5 GHz to study properties including the relative dielectric constant (ϵ_r' , the real part of complex permittivity) and the relative dielectric loss factor (ϵ_r'' , the imaginary part of complex permittivity). The data collection was performed inside a custom-built chamber designed to maintain a circumferentially uniform illumination environment during the measurement by a reflecting half-circular aluminum plate installed at the back surface of the chamber. Illumination periods were chosen to be 60 min in consistent with that used in our previous reports.^{30,56} As a result, the data of Fig. 18 were taken at the microwave frequency of 1.0 GHz during and after a 60-min illumination, corresponding to a total light fluence of roughly estimated 12.6 J/cm² (calculated by the light-to-sample distance and the diameter of light beam at the object with 2.0 W power output). As a result, the detected initial dielectric constant value of a sample mixture at the time zero min ($\epsilon_r'_{0\min}$) was found to increase progressively from that of core-shelled (γ -

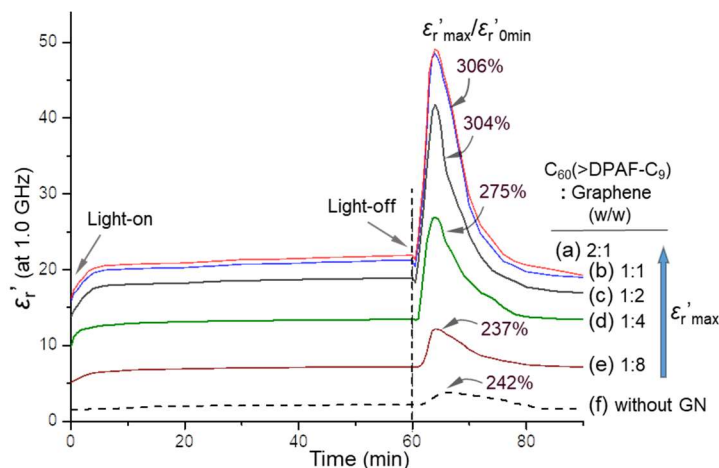


Figure 18. Irradiation time-dependent relative dielectric constant (ϵ_r') amplification effect of multilayered GN@(γ -FeO_x@AuNP)_n nanosheets with a wt. ratio of 1-C₉:GN indicated in (a) to (e) and (f) core-shelled (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n without graphene sheets under LED light (2.0 W) irradiation during 60 min and 25 min after light being turned off at the RF frequency of 1.0 GHz.

FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n at 1.56 (Fig. 18f) to a high $\epsilon_r'_{0\min}$ value of more than 16.05 (Fig. 18a) as the quantity of both γ -FeO_x@AuNP and 1-C₉ conjugates grafted on GNs were proportionally increased from 12% to 200% by wt. vs. GN. We assumed the contribution of AuNPs in the shell layer with a high ϵ_r' value of ~ 9.0 . This is in contrast to that of nanospherical core-shell (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n samples where only very outer layers of 1-C₉ materials dominated the measured dielectric property (Fig. 18f). Slight increase of chamber temperatures from 25 °C to 35–45 °C in the first 6.0-min in all experiments resulted in a small increase of the ϵ_r' value in a similar degree among all samples. The ϵ_r' value was then remaining relatively steady during the rest of irradiation period up to 60 min.

Upon turning-off the light at the end of 60-min irradiation, a large sharp raise of the ϵ_r' value for all samples was detected in Fig. 18 while the chamber temperature dropped quickly back to 25 °C. Sharp increase of the relative dielectric constant at the light-off stage was found to reach a peak maximum ($\epsilon_r'_{\max}$) value of 12.12 (Fig. 18e) and 26.91 (Fig. 18d), 41.80 (Fig. 18c), 48.50 (Fig. 18b), and 49.07 (Fig. 18a) for five multilayered GN@(γ -FeO_x@AuNP)_n nanosheet samples having a 1-C₉:GN: γ -FeO_x@AuNP weight ratio of 1.0:8.0:1.0, 1.0:4.0:1.0, 1.0:2.0:1.0, 1.0:1.0:1.0, and 2.0:1.0:1.0, respectively. They can be accounted by a ratio of $\epsilon_r'_{\max}/\epsilon_r'_{0\min}$ ratio corresponding to a 2.37- ($\epsilon_r'_{0\min} = 5.06$), 2.75- ($\epsilon_r'_{0\min} = 9.77$), 3.04- ($\epsilon_r'_{0\min} = 13.76$), 3.08- ($\epsilon_r'_{0\min} = 15.74$), and 3.06-fold ($\epsilon_r'_{0\min} = 16.05$) increase, respectively. Similar calculations based on the ratio of $\epsilon_r'_{\max}/\epsilon_r'_{60\min}$ (the ϵ_r' value at time 60 min) were found to be 1.70-, 2.0-, 2.21-, 2.28-, and 2.24-fold increase in the ϵ_r' value for Fig. 18e ($\epsilon_r'_{60\min} = 7.12$), 5d ($\epsilon_r'_{60\min} = 13.46$), 18c ($\epsilon_r'_{60\min} = 18.92$), 18b ($\epsilon_r'_{60\min} = 21.22$), and 18a ($\epsilon_r'_{60\min} = 21.85$), respectively. It was then followed by a relaxation process of ϵ_r' back to a value nearly identical to their initial $\epsilon_r'_{0\min}$ indicating a good recyclability of photochemistry involving C₆₀(>DPAF-C₉)-derived fullerosome membrane and Au-shell layer of (γ -FeO_x@AuNP) grafting on GNs.

By the comparison of these data with those of nanospherical core-shell (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n reference samples of Fig. 18f, detected progressively large increasing $\epsilon_r'_{0\min}$ values in response to the quantity increase of γ -FeO_x@AuNP applied are of interesting as high steady-state dielectric constant materials having their own implications and significances in technological applications. Apparently, thin Au-layered nanoparticles coating on graphene nanosheets may induce already the inherent local sheet-conductivity to drive up the dielectric characteristics and the $\epsilon_r'_{0\min}$ values. We proposed that the phenomena of a large ϵ_r' jump on all samples, immediately following the light irradiation being turned off at 60-min, can be correlated to the contribution of photoinduced generation of plasmonic resonance energy at the AuNP layer with the storage of such energy during the stage of irradiation. This accumulation of SPR energy were found to occur via a near-field effect since no

plasmonic energy conversion to the heat release (no significant temperature increase) was detected during the irradiation period of 10–60 min, as discussed in recent reports.^{29,30} Quick SPR energy release after light-off at the interface to the outer [60]fullerene layer resulted in the activation or induction of intramolecular polarization within the $C_{60}(>>DPAF-C_9)$ conjugate, forming the corresponding transient CS state of $1-C_9$ with a molecular configuration consisting of a positively charged $(DPAF-C_9)^+$ and a negatively charged $(C_{60}>)^-$. This intramolecular charge-transfer efficiency of $C_{60}(>>DPAF-C_9)$ was measured by nanosecond transient spectroscopic technique.²⁵ Distribution of negatively $(C_{60}>)^-$ charges in [60]fullerene monolayer stabilized the CS polarization in the solid-state on GNs. We believe that further e^- -transfer from $(C_{60}>)^-$ at the interfacial surface to the GNs may be a factor to observe more than 300% amplification of dielectric ϵ_r (Fig. 18a, 18b, and 18c) with a sufficient quantity of $C_{60}(>>DPAF-C_9)$ conjugates to provide a monolayer coverage.

4.3. RF Signal Modulation by Tunability of Reflection Coefficient Changes

Distant Monostatic Reflective Synthetic Aperture RF-signal (SAR) Measurements.

We applied the above stated photoswitchable dielectric amplification effect toward the tunability and switching capability study of distant monostatic reflective RF-signal image modulations to provide certain insights to our study of RF-signal tunable coating applications. They were performed by a monostatic SAR measurement of a triangular glass plate with or without the partial coating of $(\gamma-FeO_x@AuNP)@[C_{60}(>>DPAF-C_9)]_n$ core-shell NPs in PDMS as a thin film on a glass plate under front LED-white illumination for a defined period of time. In this measurement scheme, only one RF antenna horn is needed, as shown in Fig. 19A. We first examined the sample reflectivity, defined as the reduction in reflected power in decibels (dB) by the relationship of $\log(P_i/P_r)$, where P_i is the incident power and P_r is the reflected power, at the light-on and light-off stages. Figs. 19B-a and 19B-b displayed the frequency-dependent reflectivity curve profiles over 1.0–18 GHz at 1.0 and 5.0 min, respectively, after turning off the light. The total accumulated light fluence was measured to be $\sim 1.3 \text{ J/cm}^2$. Magnitude of reflection changes was not uniform over the full frequency range. We arbitrarily selected three frequencies at 12.0 (Fig. 19C-a), 15.2 (Fig. 19C-b), and 15.5 (Fig. 19C-c) GHz as examples to demonstrate their time-dependent reflection characteristics that covered an illumination period of 30 min and a period of 8.0 min at the light-off stage. During the light-on stage, magnitude of reflection curves derived from these three

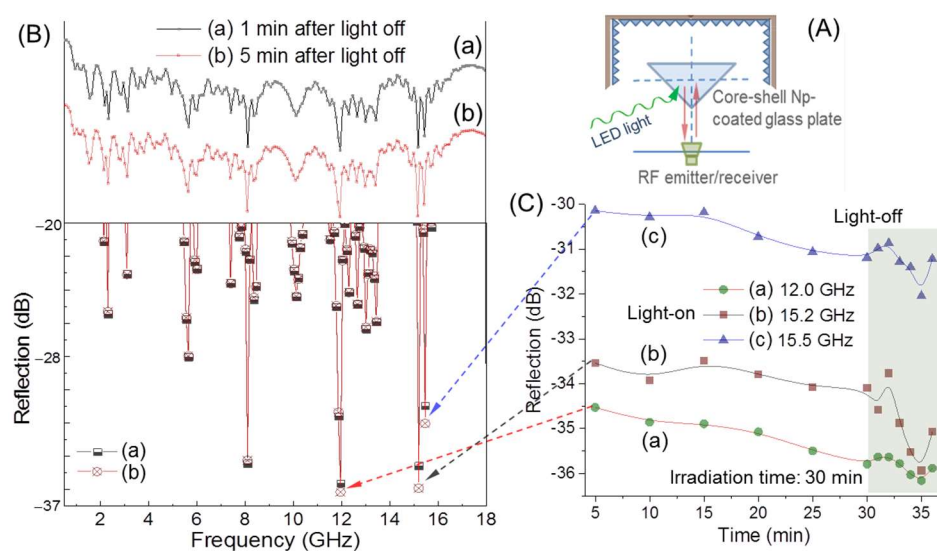


Figure 19. (A) Experimental setup of monostatic RF-reflection measurement. (B) Frequency-dependent reflectivity of $(\gamma-FeO_x@AuNP)@[C_{60}(>>DPAF-C_9)]_n$ core-shell NPs (6-NP) in PDMS coated glass plate at (a) 1.0 min and (b) 5.0 min after 30-min (1.3 J/cm^2) front illumination by a LED white light and (C) time-dependent curve profiles of reflection at three specific frequencies to show changes (marked by green) of reflectivity at light-off state at 30–38 min.

frequencies was relatively smooth with no significant fluctuation. Immediately after the light being switched off, clear reflection fluctuations were detected by an initial increase at the time 30–32 min followed by a decrease to a minimum at the time 35 min in a similar manner for all three curve profiles. Among them, RF reflectivity responses at 15.2 GHz were measured to be larger. This demonstrated that the magnitude of reflectivity change may be frequency-dependent with more at one frequency than the others.

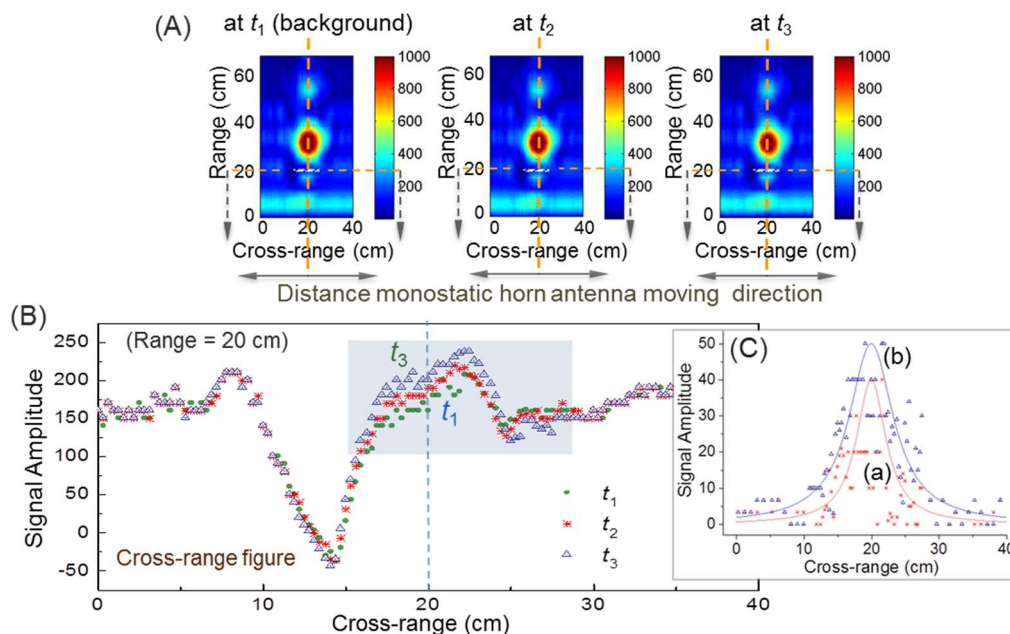


Figure 20. (A) Distant monostatic SAR images (where the central red spot was the image of a back-light unit) and (B) the cross-range RF-signal amplitude of a $(\gamma\text{-FeO}_x\text{@AuNP})\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ core-shell (6-NP)-coated triangular glass plate collected at the range distance of 20 cm with or without LED-white back-light illumination, where t_1 with no light; t_2 with a 15-min and t_3 with a 30-min irradiation at 10 GHz. (C) Calculated signal changes by the difference of (a) $|t_2 - t_1|$ and (b) $|t_3 - t_1|$, showing fluence-dependent change amplitudes.

In the case of distant monostatic SAR measurement, via scattering parameter S_{11} , on a similar triangular glass plate partially coated by $(\gamma\text{-FeO}_x\text{@AuNP})\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ core-shell NPs in PDMS, the SAR sensor bearing a carrier frequency at 10 GHz and a bandwidth of 1.5 GHz with FMCW (frequency modulated continuous wave) signals was used in the experiment. Both electrical and magnetic properties were accounted in the measurement. It is controlled by an automated two-axis positioner to achieve accurate spatial registration of coordinates of the horn antenna. RF-signal scanning is conducted in both vertical and horizontal directions to render the scattering imagery (or RF-signal imagery) of the target. RF-signal images of a triangular glass plate with or without any coating were scanned in either horizontal and or vertical directions for comparison. Information contained in SAR images (e.g., shape, amplitude) can be used for assessing the scattering response of an object, which is dependent on the object's dielectric properties. We determined the geometry of the triangular glass plate first. The same glass plate was subsequently partially coated in an area dimension of 5.0×6.8 cm (as a 7%-area of the plate) with $(\gamma\text{-FeO}_x\text{@AuNP})\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ core-shell nanoparticle-derived thin film using PDMS as a matrix material. The total signal reflectivity measured under the condition without or with a defined back-light irradiation period was counted to indicate the overall response to signal profile changes. Integrated RF-signal scattering response was represented by the spatial distribution (range vs. cross-range) of SAR amplitude indicating the combined effect of dielectric property, surface roughness, size of NPs-coated area, and inspection angle. We used the collected responses at t_1 (Fig. 20A, without irradiation) as the reference baseline. Two reflectivity amplitude peak profiles and photoinduced intensity changes over the range (r , vertical direction) and cross-range (r_x , horizontal direction) distance in measurements were evaluated for the signal comparison via illumination ($h\nu$) by a LED-white light for a period of 15 (t_2) or

30 (t_3) min (Fig. 20A). To better assess the effect of dielectric amplification upon light illumination, cross-range SAR amplitude curves were extracted at the range distance $r = 20$ cm and shown in Fig. 20B. As a result, photoinduced dielectric amplification was observed with the cross-range SAR amplitude curve displaying the relationship of $I(t_3, 30\text{-min } h\nu) > I(t_2, 15\text{-min } h\nu) > I(t_1, 0\text{-min } h\nu)$ at $r_x = 20$ cm, as an example. The main RF-response deviation area was found to be focused at the vicinity of the coated sample zone located at the cross-range distance of 20 cm (marked by a dash line in Fig. 20B). To assist the visualization of the changing magnitude, we calculated signal changes by the difference of amplitude $|t_2 - t_1|$ and $|t_3 - t_1|$ and having the results plotted in Figs. 20C-a and 20C-b, respectively. By using a curve fitting technique over largely scattered data points, trend of the plotted $|t_3 - t_1|$ band became clearly shifting upward from that of Figs. 20C-a to 20C-b. It revealed a positive deviation of RF-signals in amplitude as observed in the cross-range of 12–27 cm with the progressive increase of changes in a light fluence-dependent manner as exhibited by $|t_3 - t_1| > |t_2 - t_1|$, indicating higher values for a 30-min irradiation (4.0 J/cm² fluence) than those with 15-min irradiation (2.0 J/cm² fluence) or no light (zero fluence). In addition, total accumulative reflective signal amplitude increase ratios $(|t_2 - t_1|)/t_1$ and $(|t_3 - t_1|)/t_1$ integrated over the full cross-range of 0–40 cm were found to be 2.01 and 6.92%, respectively. Since the coated area ratio $A_{\text{coated area}}/A_{\text{total area}}$ was ~ 0.07 , the effective SAR amplification ratios $[(|t_2 - t_1|)/t_1]_{\text{effective}}$ and $[(|t_3 - t_1|)/t_1]_{\text{effective}}$ were calculated to be 29.5 and 99.1%, respectively.

Angle-Dependent Bistatic Reflective RF-signal Imaging Measurements.

An angle-dependent bistatic reflective RF-signal measurement was applied on either a triangular plexiglass plate or a semicircular casting iron plate with or without the coating of (γ -FeO_x@AuNP)@[C₆₀(>DPAF-C₉)]_n core-shell NPs in PDMS under illumination of the white LED light from the front side. Two doubly-rigged horn antennas were positioned and coupled at the incidence of 10° with the reflectance for measuring the S₂₁ scattering parameter of the object with or without light illumination. The object was installed on a rotary stage controlled by a digital controller (angular resolution of 0.1°) to achieve a precise angular increment. All RF-signal measurements were conducted at the frequency range of 0.5 to 18 GHz inside an anechoic chamber equipped with non-reflective wall-padding foams to eliminate the effect of electromagnetic background noise. Reflectivity of the object was measured by fixing the antenna pair configuration and rotating the rotary stage at either 0°, 15°, 30°, 45°, 60°, 75°, or 90° to develop a quantitative assessment of the angle-dependent scattering responses of the object with or without the coating of core-shell nanoparticles.

We also carried out bistatic scattering parameter S₂₁ measurements, with the setup scheme depicted in Fig. 21F using one emitter and one receiver horn antenna, positioned at 90° ($\theta = 45^\circ$) to each other, to substantiate the application feasibility. The reflectivity data were collected on a partially-coated triangular plexiglass plate at the frequency range of 1.0–18 GHz and two inspection angles ($\delta = 0^\circ$ and 75°) with or without the front illumination. Selection of these two angles was arbitrary for the demonstration purpose of angle-dependent characteristics. At 0° incidence (Fig. 21A) significantly increased or reduced scattering responses of the target by roughly ± 2.0 –3.5 dB (ΔdB , defined as the difference or change between Figs. 21A-b/21A-c and 21A-a) at the frequency range of 2.5–9.5 and 15–17.5 GHz, considering only $\sim 7\%$ of coated area applied. A slightly lesser extend of 0.5–1.5 dB in changes was detected over the other frequency range of 1.0–2.0 and 10–15 GHz. When the incident angle was increased from 0° to 75°, main signal deviation areas shifted to the frequency range of 9.5–12 and 16.5–17.8 GHz (Fig. 21B) with the spectrum profile of the rest of frequency ranges remaining relatively similar among all three conditions taken. Different spectral profiles obtained might be due to the surface roughness of uncoated metal plate in a rather small size that resulted in drastic increase or reduction of S₂₁ values during the bistatic data collection. This implied that photoinduced effects leading to signal amplitude alternation of the scattering response and reflectivity may not be homogeneous throughout various frequencies. For example, S₂₁ parameter values by the incidence horn angle of 0° decreased (the shielding effect induced by photoexcitation) in frequency ranges of 8.0–9.7 and 16.5 GHz, but increased at 15.7 and 17.4 GHz when compared by the ones with or without light illumination. Therefore, we selected some of these frequency ranges to investigate their angular scattering responses using the same partially coated plate sample.

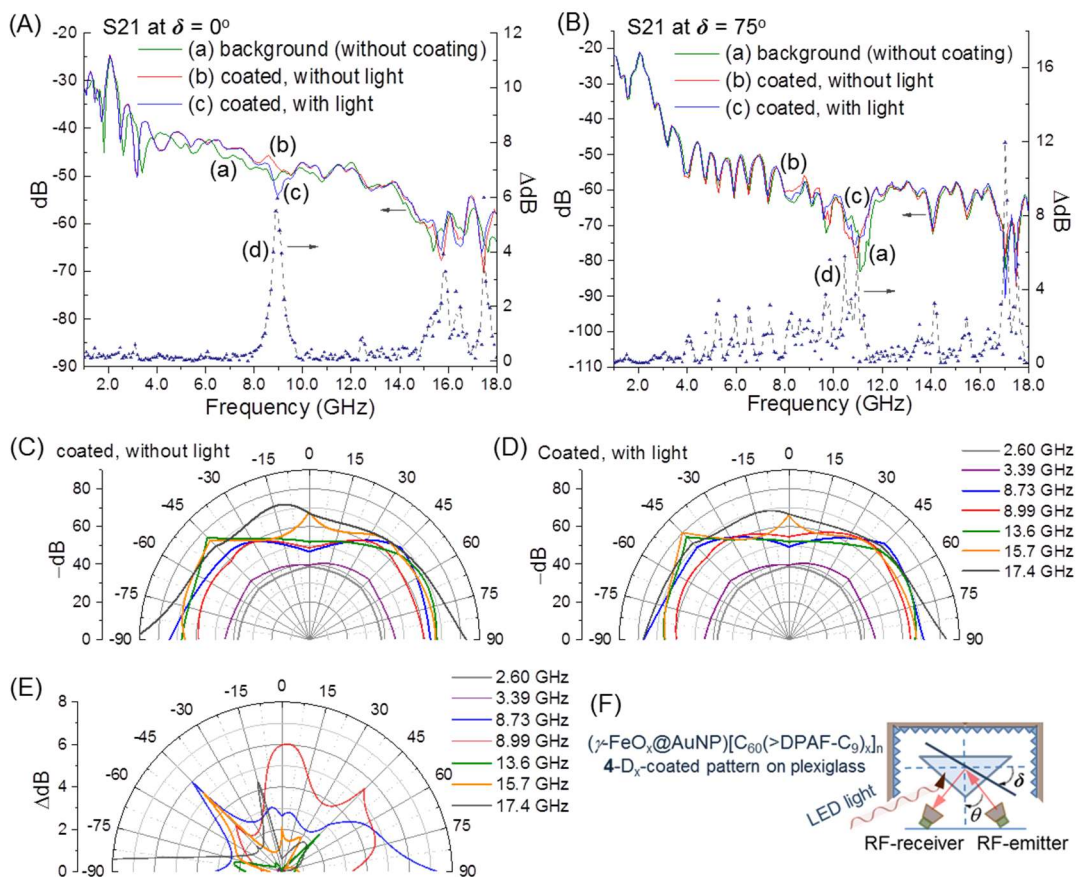


Figure 21. Frequency-dependent S21 scattering parameter based reflectivity (dB) of $(\gamma\text{-FeO}_x\text{@AuNP})\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ core-shell NPs (6-NP) in PDMS coated rectangular pattern on a plexiglass plate at the δ angle of (A) 0° and (B) 75° with or without the front illumination by a LED white light. The light-induced differences or changes (ΔdB) is calculated by $|(D) - (C)|$. Angle (δ)-dependent RF-reflection at seven different frequencies selected from (A) or (B) under conditions of (C) no light and (D) 30-min of front illumination (1.3 J/cm^2). (E) Calculated difference (ΔdB) by $|(D) - (C)|$ and (F) experimental setup of bistatic RF-reflection measurement with two horn antenna.

Results were displayed in Figs. 21C (without light) and 21D (with 30-min illumination and a total fluence of $\sim 1.3 \text{ J/cm}^2$). All frequencies higher than 3.5 GHz gave appreciable signal profile changes over the most of angular range. As these angle-dependent illumination-induced reflective signal changes (ΔdB) by $|(D) - (C)|$ were plotted over 0° – $(\pm 90^\circ)$ with the value shown in Fig. 21E, we noticed that all curve profiles displayed a rather clear image of reflectivity variation over all inspection angles. Among them, reflectivity changes at 8.73, 8.99, 15.7, and 17.4 GHz were the most pronounced in photoresponses. They all responded in their own unique manner at each selected inspection angle. It is interesting to note that a small frequency variation from 8.73 to 8.99 GHz can lead to significantly large differentiable changes in photoresponses at different angles, indicating a high frequency-dependent sensitivity involved. Since this particular frequency range is used for maritime and aeronautical mobile communications, appreciable photoswitching tunability of reflective signals by $(\gamma\text{-FeO}_x\text{@AuNP})\text{@[C}_{60}(>\text{DPAF-C}_9)]_n$ core-shell NPs could have implication in the corresponding applications.

Bistatic Angle (θ)-Dependent Reflectivity and Transmittance Signal Changes by Photoinduced RF-Responsive Multilayered GN@(FeAuF_n) Nanosheets.

In the demonstration of one potential nanomaterials application, multilayered GN@(FeAuF_n) nanosheet materials showing photoswitchable dielectric amplification properties, as stated above, were applied for the investigation of plausible tunability and switching capability of RF-signals. It was performed by bistatic angle (θ)-dependent reflection coefficient (R) data collection for measuring the S21

scattering parameter of the object to provide certain insights to our coating application study toward photoinduced RF-signal morphology modulation. They were performed on a glass plate with the partial coating of GN@(FeAuF_n) nanosheets in PDMS polymers matrix as a thin film with or without under continuous back LED-white illumination during the measurement period. The θ -angle (0° – 180°) was defined by the degree rotation of the sample plate controlled by an automated biaxial positioner to achieve accurate spatial registration of coordinates to the horn antenna with the main emitting wave direction positioned at 45° in respect to the front plate face.

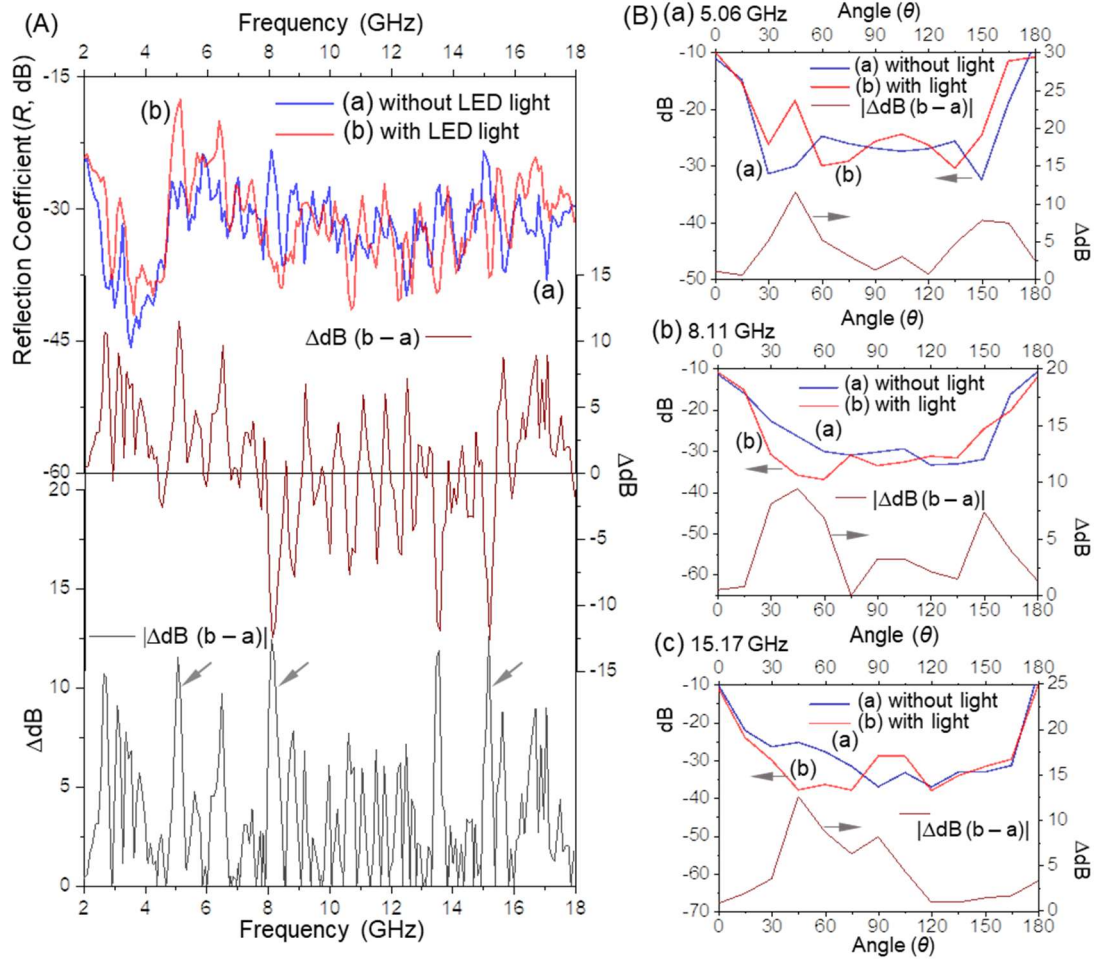


Figure 22. Frequency-dependent reflection coefficient (R , dB) of GN@(FeAuF_n) nanosheets in PDMS polymers as coated in a rectangular pattern on a glass plate by bistatic angle (θ)-dependent measurements with two examples at the θ angle of (A) 45° and (a) without or (b) with the back illumination by a small LED white light. The light-induced differences or changes (ΔdB or $|\Delta dB|$) was calculated by dB of $[(b) - (a)]$ (the middle plot) or dB of $|(b) - (a)|$ (the bottom plot), respectively. (B) Three different frequencies selected from (A), as indicated by arrows, were used in the angle (θ)-dependent RF-reflectivity plots at (a) 5.06, (b) 8.11, and (c) 15.17 GHz.

We investigated the RF reflectivity of all nanosheet-coated sample objects, defined as the reduction in reflected power in decibels (dB) by the relationship of $\log(P_i/P_r)$, where P_i is the incident power and P_r is the reflected power, under either the continuous light-on condition or without light illumination over the frequency range of 0.5–18 GHz. Photoinduced reflectivity differences or changes, defined as ΔdB or $|\Delta dB|$, was calculated by subtracting the reflection coefficient values collected under continuous light-on conditions by those taken without the application of light illumination at the same frequency. As a result, we found that the magnitude of reflection coefficient changes (ΔdB) was not uniform over the full frequency range in all measurements. We arbitrarily selected the reflectivity data profile using one particular angle of 45° as an example to demonstrate its frequency-dependent reflectivity characteristics over 2.0–18 GHz, as shown in Fig. 22A. Significant reduction of the object reflectivity was observed over

the frequency range of 2.0–5.5 GHz reaching over -44 dB with the rest of frequency ranges remaining roughly in the width of -30 to -40 dB. Since we focused on the study of irradiation effects on materials reflection coefficient values, photoinduced changes of dB values were plotted as a Δ dB-data profile in the middle of Fig. 22A with the corresponding absolute Δ dB values displayed in the bottom of the same Figure. Apparently, majority of Δ dB changes went above an intensity of 5.0–10 dB over the most of frequencies that provided a more-or-less uniform impact. We considered this strength of RF reflection signal modulation being significant enough to result in the modification of morphological RF signal images over this frequency range. We then selected three frequencies of 5.06 (Fig. 22Ba), 8.11 (Fig. 22Bb), and 15.17 GHz (Fig. 22Bc) from Fig. 22A, as marked by arrows, to demonstrate their angle (θ)-dependent reflectivity over 0° to 180° . For the former two frequencies, similar θ -dependent trends on Δ dB changes higher than 5.0–10 dB at lower angles of 30° – 60° or higher angles of 135° – 165° were displayed, whereas the latter frequency gave higher influence of Δ dB > 5.0 dB over 40° – 100° .

Examination of reflection coefficient (R) changes during the light-off stage was carried out by selecting one specific angle of 45° for the purpose of demonstration. In this particular measurement, the GN@(FeAuF_n) nanosheets in PDMS polymers coated glass plate was illuminated for a period of 60 min (with accumulated total fluence of 10.6 J/cm^2) with the frequency-dependent R value collection every 5.0 min during the 60-min period and every 1.0 min for a total of 10 min at the light-off stage. The frequency-dependent R value collection was performed at zero ($R_{0\text{min}}$), 1.0 ($R_{1\text{min}}$), and 2.0 min ($R_{2\text{min}}$) immediately following the light being switched off with the former and the latter shown in Fig. 23Aa and 23Ab, respectively. Calculated reflection coefficient changes (Δ dB) between $R_{0\text{min}}$, $R_{1\text{min}}$, and $R_{2\text{min}}$, were expressed by $R_{1\text{min}} - R_{0\text{min}}$ (the middle plot of Fig. 23A) and $R_{2\text{min}} - R_{0\text{min}}$ (the bottom plot of Fig. 23A).

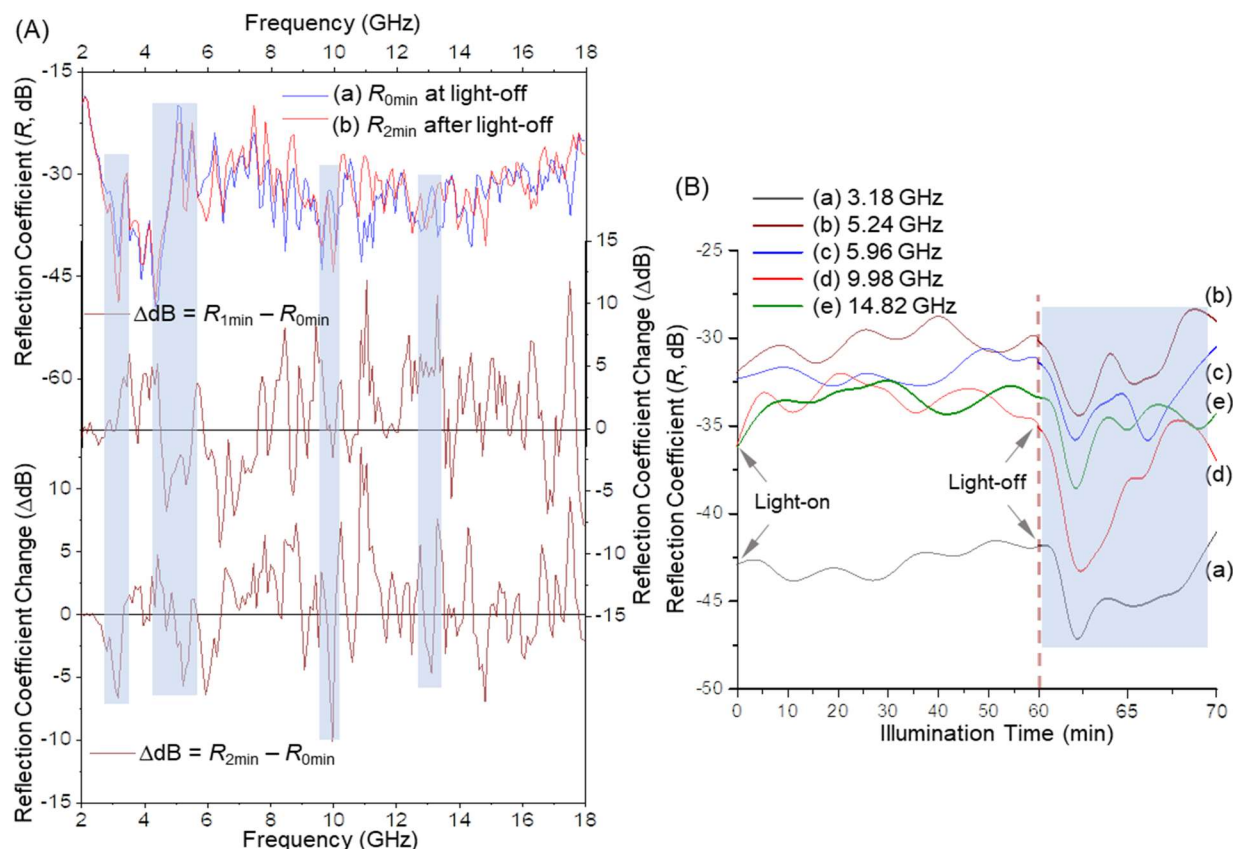


Figure 23. (A) Frequency-dependent reflection coefficient (R , dB) of GN@(FeAuF_n) nanosheets in PDMS polymer by coating in a rectangular pattern on a glass plate with the data collection (a) $R_{0\text{min}}$ immediately at the light-off after the 60-min back-illumination (10.6 J/cm^2) by a white LED light and (b) $R_{2\text{min}}$ at 2.0 min after light-off. The light-induced differences or changes (Δ dB) was calculated by $R_{1\text{min}}$ (at 1.0 min after light-off) – $R_{0\text{min}}$ (the middle plot) and $R_{2\text{min}} - R_{0\text{min}}$ (the bottom plot). (B) Irradiation time-dependent curve profiles of reflectivity at five specific frequencies to show the signal changes (marked by light blue shadow) at the light-off stage at 60–70 min.

Five frequencies at 3.18 (Fig. 23Ba), 5.24 (Fig. 23Bb), 5.96 (Fig. 23Bc), 9.98 (Fig. 23Bd), and 14.82 GHz (Fig. 23Be), as marked by the blue shadow, were selected for the evaluation of irradiation time-dependent reflection coefficient measurements. All frequencies were found to exhibit moderate fluctuation over the entire illumination period up to 60-min. Upon the light being switched off, a sharp fluctuation of reflection coefficients in a higher magnitude to a more negative value ($-dB$) to as much as $R = -45$ dB for 9.98 GHz (Fig. 23Bd), for example, was observed in the first 2.0–4.0 min at the light-off stage. The phenomena were agreed well with the large increase of relative dielectric constant (ϵ_r' , Fig. 18) at the light-off stage, indicating the plausible close relationship between $R_{62-63min}$ and ϵ_r' .

5.0 CONCLUSION

We demonstrated that the fabrication of tetralayered e^- -polarizable core-shell nanostructures was capable of inducing photoswitchable dielectric property (permittivity) amplification at the microwave frequency range of 1.0–4.0 GHz. Configuration of the nanostructure consisted of a magnetic nanospherical center core of γ -FeO_x NP encapsulated sequentially by one plasmonic gold subshell, one middle layer of e^- -polarizable C₆₀(>DPAF-C_n)_x-derived fullerosome membrane, and one outer shell of e^- -donors, as an example. This class of multilayered core-shell nanospherical materials were reported recently to be excellent microwave absorbers over 1.0–18 GHz with the reflectivity loss reaching -28 to -36 dB at 6.0, 8.0, 12.0, 15.2, and 15.5 GHz, using S_{11} scattering parameter measurements, and over -60 to -75 dB at higher frequencies of 17–18 GHz using angle-dependent S_{21} scattering parameter measurements.

We also demonstrated an efficient stepwise fabrication technique to prepare RF-responsive multilayered GN@(FeAuFn) nanosheets. By the use of sequential TEM micrographic evaluations, it is possible to quantify the amount of C₆₀> derivatives necessary to provide a monolayer coverage on graphene nanosheets. These GNs consisting of monolayered [60]fullerosome-grafting on both sides of GNs giving sandwiched nanostructures was applied as a key intermediate in the tunable dielectric nanomaterials preparation. Following subsequent deposition of magnetic (γ -FeO_x@AuNP) nanoparticles and C₆₀(>DPAF-C₉) conjugates as the shell layers, resulting multilayered core-shell nanosheets were capable of inducing a reversible photoswitchable amplification effect of dielectric properties at the RF frequency range of 1.0–18 GHz.

Contribution of surface plasmon resonance energy within the core-shell nanoparticle structure was the critical factor to the observed results. We hypothesized that the release of accumulated SPR energy at the near-field from the intermediate AuNP layer sandwiched between the layer of fullerosome membrane and the core γ -FeO_x NP induced the molecular polarization of C₆₀(>DPAF-C₉)_x moieties to their transient charge-separated (CS) states. This CS state consisting of a positively charged e^- -donor moiety (DPAF)⁺·-C₉ and a negatively charged e^- -acceptor moiety (C₆₀>)⁻· provided the foundation of observed dielectric property amplification. The phenomena were further enhanced by separate applications of additional organic molecular e^- -donors or conducting conjugate polymers deposited at the most outer shell layer. These e^- -donors served as the supply of photoinduced transferrable electrons that increased largely the number of polarized charges on nanoparticles, leading to a maximum of 387% amplification of the relative dielectric constant (ϵ_r') value or a 159%-additional increase from that of the parent trilayered nanoparticles. These results were contributed from the use of organic e^- -donor HMTSF molecules.

Based on the results of facile photoswitchable tunability of reflective microwave signals using monostatic and angle-dependent bistatic synthetic aperture techniques on casted thin films in the frequency range of 0.5–18 GHz, we expect better performance given by the new tetralayered core-shell NPs. As the Wi-Fi wireless network communication being operated at either 2.4 or new 5.0 GHz frequency band, they are within the frequency range of this investigation. Therefore, our results may lead to future implication on the feasibility in modulation or tuning microwave signals to provide photoswitchable interference for the security protection purpose.

6.0 REFERENCES

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