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14. ABSTRACT

π-Conjugated molecular systems show attractive semiconducting and optical properties, which makes them highly interesting materials with a great potential for applications in organic electronic devices and molecular electronics. This report covers a thorough investigation into the photophysical properties of various functional π-electronic molecular systems (e.g., expanded and Möbius porphyrins; π-π stacked molecular assemblies) using combined integrated time- and space-resolved spectroscopic methodologies. This study focused on examining π-conjugation pathways and π-π stacking interactions by using highly designed molecules to relate topology with the number of π-electrons of π-conjugated molecules and thus provide a detailed understanding of the relationship between structure and photophysical properties. Control of conformational flexibility was critical to determining the π-conjugation pathway and thus important to understand structure/property relationships in view of three-dimensional aromaticity.

Experimentally, an array of analytical approaches was used in this study, including: 1) Steady-state (UV-Vis-NIR Absorption & Emission; NIR Photoluminescence); 2) time-resolved laser (Time-Correlated Single Photon Counting (TCSPC) Method; Nanosecond Transient Absorption; Femtosecond Transient Absorption; Femtosecond Broadband Transient Absorption; Femtosecond Up-conversion; Femtosecond Broadband Up-conversion; Femtosecond Impulsive Stimulated Raman); and 2) non-linear (Femtosecond Z-scan Method) spectroscopies.Exciton dynamics and excited-species formation processes in columnar, helical stacked H-aggregates of planar perylene bisimides (PBI) were examined by time correlated single-photon counting (TCSPC) and femtosecond pump–probe measurements with anisotropy changes. The photogenerated exciton experiences complicated relaxation processes contributed by excited-state interactions such as exciton delocalization and excimer formation. This indicates that exciton dynamics can occur in whole assembled structures and the coherent exciton can exist beyond the dimeric segments. In certain systems, the estimated certain limit of exciton diffusion process does not exceed about ten repeat units.

Through active control of π-conjugation and π-π interactions this work has explored the structure-property relationships of various π-conjugated molecular systems in conjunction with aromaticity and exciton delocalization dynamics by using ultrafast spectroscopic measurements as well as theoretical calculations (Nuclear-Independent Chemical Shift (NICS) Values; Anisotropy of the Induced Current Density (AICD) Calculation; Molecular Orbitals & Electronic Excited-State Excitation Energies.

15. SUBJECT TERMS

Exciton, Two-Photon Absorption, Materials Characterization, Materials Chemistry, Nonlinear Optical Materials, Spectroscopy

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Time- and Space-Resolved Spectroscopic Investigation on π-Conjugated Nanostructures

30th, July 2014

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Table of Contents

Abstract

π-Conjugated molecular systems show attractive semiconducting and optical properties, which makes them highly interesting materials with a great potential for applications in organic electronic devices and molecular electronics. In this regard, we have investigated the photophysical properties of various π-electronic molecular systems, such as expanded porphyrins and π-π stacked molecular assemblies *etc*. by combining our integrated time- and space-resolved spectroscopic methodologies.

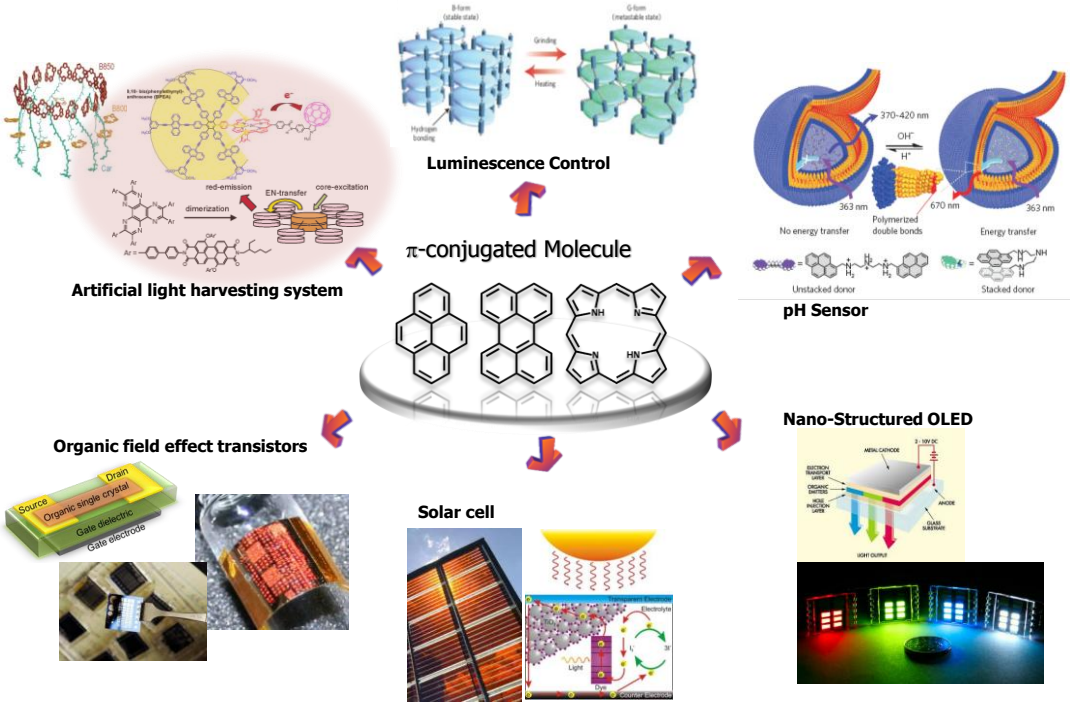


Figure 1. Various applications of π-conjugated molecular systems

Introduction

Over the past few decades, researchers have witnessed a rapid growth in the applications of π-conjugated nanostructured organic materials. This fact has inspired numerous research activities ranging from fundamental studies of their chemical versatility and photophysical properties to practical applications such as molecular photonic devices, artificial photosynthesis systems, and dye-sensitized solar cells. Strenuous research efforts have focused on developing new types of π-conjugated organic molecules that display certain characteristics for applications. In this context, a detailed understanding of the relationship between structure and photophysical properties is crucial for the fabrication of novel π-conjugated systems targeted for specific application.

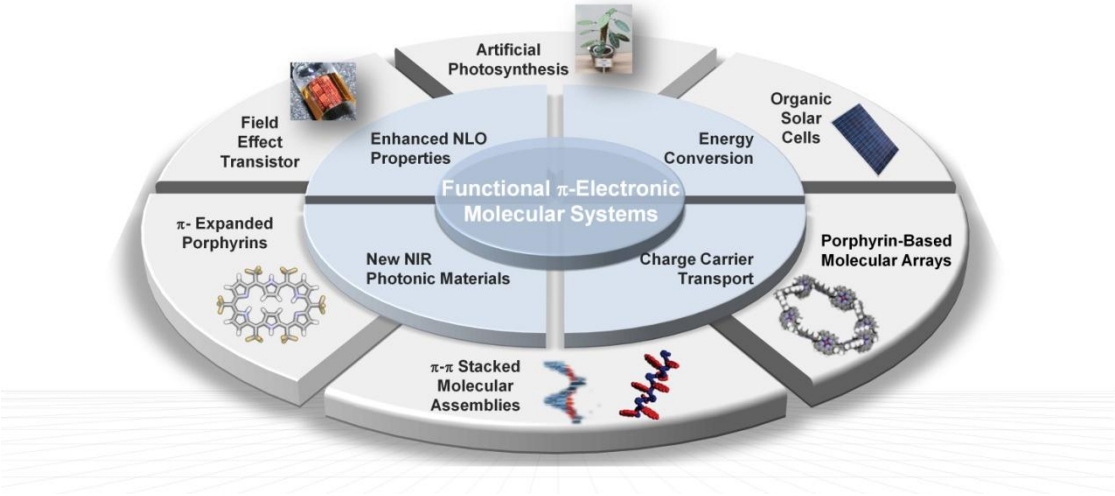


Figure 2 Research areas in π-conjugated nanostructures

In the study of functional π-electronic molecular systems, we have focused on the π-conjugation pathways and π-π interactions. First, the π-conjugation pathway is directly related to the topologies and the number of π-electrons of π-conjugated molecules. Particularly, a control of conformational flexibility is critical in determining the π-conjugation pathway. In this regard, compared with normal all-carbon annulene molecules, expanded porphyrins are best candidates to investigate the structure/property relationship in view of aromaticity and an index for π-conjugation, because a comparable set of [4n] / [4n+2] expanded porphyrin can be systematically prepared due to an easy two-electron oxidation/reduction of pyrroles through a stepwise addition of pyrrole rings into the tetrapyrrolic porphyrin macrocycle. Another important issue in π-electronic molecular systems is π-π interactions in various molecular architectures such as liquid crystals,

supramolecules, molecular aggregates, nanofibers, and so on. In the formation of such molecular structures, the π-π stacking plays a crucial role by providing intermolecular interaction forces between constituent molecular elements. Depending on the distance and orientation between the adjacent constituent molecules as well as π-conjugation associated with molecular topologies, π-π stacking interactions would be different, leading to versatile molecular architectures. Thus we have investigated the extent of π-π electronic interactions in these systems by using time-resolved transient absorption and polarization anisotropy spectroscopy.

Consequently, with an active control of π-conjugation and π-π interaction, this work has explored the structure-property relationship of various π-conjugated molecular systems in conjunction with aromaticity and exciton delocalization dynamics by using ultrafast spectroscopic measurements as well as theoretical calculations.

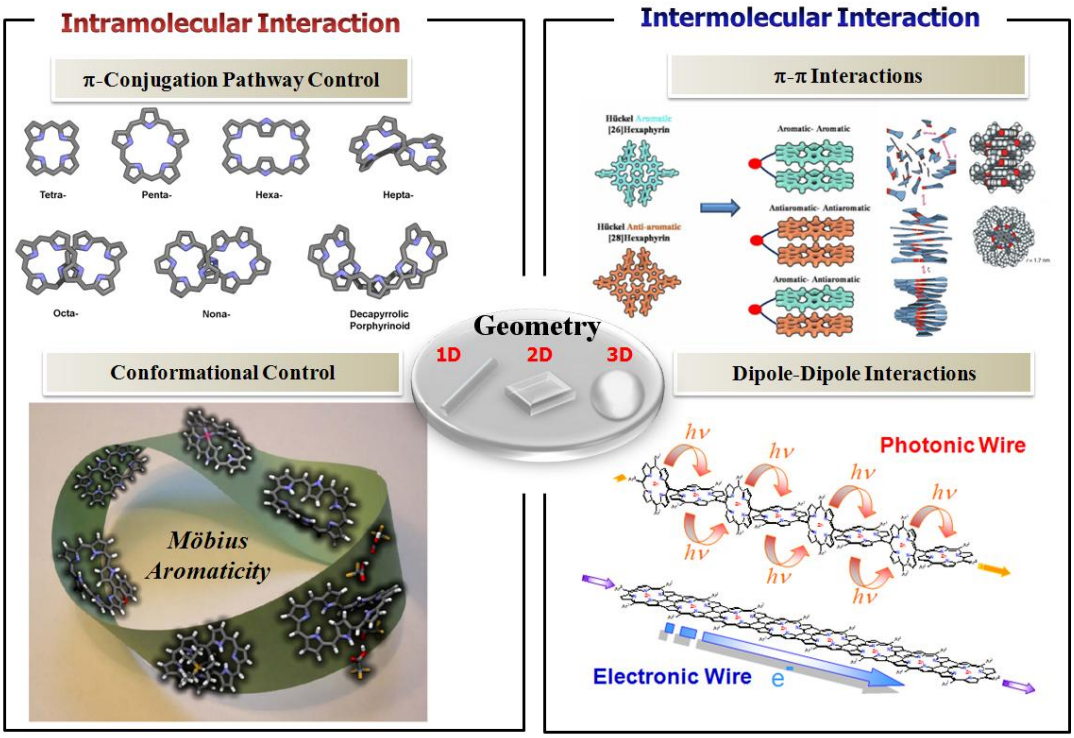
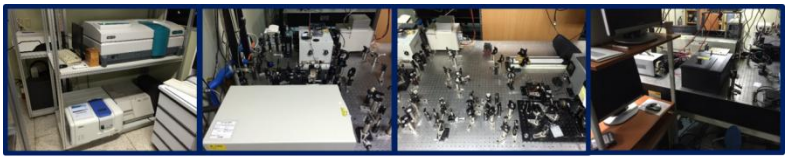
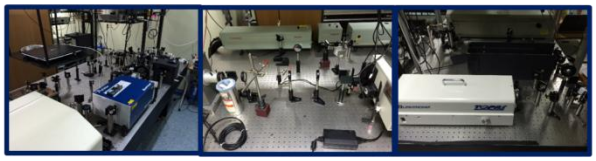


Figure 3. Research contents for functional π-electronic molecular systems

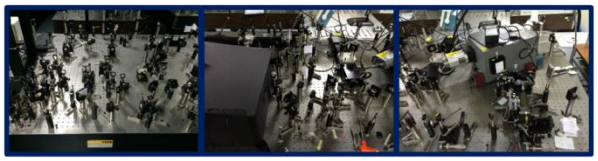
Experiment



Steady-state UV-Vis-NIR Absorption & Emission Measurement | Time-correlated Single Photon Counting Setup | Femtosecond Fluorescence Up-conversion Setup | Near-IR Photoluminescence Setup



Femtosecond Transient Absorption Setup | Nanosecond Transient Absorption Setup | Femtosecond Z-scan experiment Setup



Femtosecond Broadband Transient Absorption Setup | Femtosecond Impulsive Stimulated Raman Setup | Femtosecond Broadband Fluorescence Up-conversion Setup

I. Experimental method

1. Steady-state Spectroscopy

- UV-Vis-NIR Absorption & Emission Steady-state Spectroscopy
- NIR Photoluminescence Spectroscopy

2. Time-Resolved Laser Spectroscopy

- Time-Correlated Single Photon Counting (TCSPC) Method
- Nanosecond Transient Absorption Spectroscopy
- Femtosecond Transient Absorption Spectroscopy
- Femtosecond Broadband Transient Absorption Spectroscopy
- Femtosecond Up-conversion Spectroscopy
- Femtosecond Broadband Up-conversion Spectroscopy
- Femtosecond Impulsive Stimulated Raman Spectroscopy

3. Non-Linear Spectroscopy

- Femtosecond Z-scan Method

II. Quantum Mechanical Calculation

1. Nuclear-Independent Chemical Shift (NICS) Values
2. Anisotropy of the Induced Current Density (AICD) Calculation
3. Molecular Orbitals & Electronic Excited-State Excitation Energies

Results and Discussion

I. New Paradigm in Aromaticity in π-Conjugated Expanded Porphyrins

Aromaticity is regarded as one of the most important concepts in modern chemistry. Although the history of this concept began with the discovery of benzene by Faraday in 1825, there is no simple definition to explain what the aromaticity really is. Most widely-accepted notion is that cyclic conjugated molecular systems with [4n+2] π-electrons have closed-shell electron configurations and reveal aromaticity like benzene. This is known as Hückel's rule. In contrast to the fact that Hückel considered the planar molecular structure, Heilbronner suggested that [4n]π-electron conjugated system can have a closed-shell configuration, namely aromatic property, when the system takes Möbius strip-like topology with a half-twisted π surface in the π-conjugated pathways. This is the key concept of Möbius aromaticity, in which Hückel's rule is adopted inversely; [4n] π-systems are aromatic but those with [4n+2]π-electrons are antiaromatic. For a long time, the Hückel and Möbius (anti)aromaticity theories have enticed many chemists to try to use them as a 'magic rule' that predicts the nature of conjugated molecules using both theoretical and experimental methods. In this section, we would like to report recent progress on the photophysical characterizations of new types of aromaticity in various expanded porphyrins by using steady-state and time-resolved spectroscopy as well as theoretical calculations.

1. Reversal of Aromaticity in the Excited State

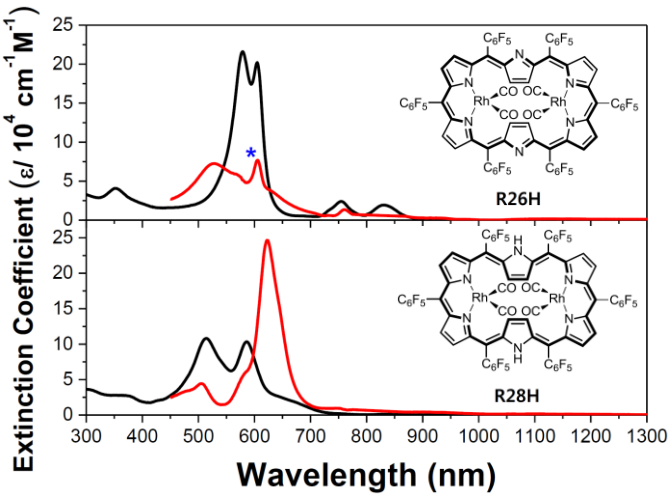


Figure 4. Ground-(black lines) and excited-state (red lines) absorption spectra of **R26H** (top) and **R28H** (bottom).

Reversal of aromaticity in the triplet excited-state, known as Baird's rule, has been suggested by theory. However, to date it has not been experimentally verified. We have now demonstrated the aromaticity reversal in the lowest triplet excited-states (T_1-states) of two bis-rhodium hexaphyrins containing [26]- (**R26H**) and [28]- (**R28H**) π-electron peripheries **(Figure 4)**. In the ground state, **R26H** exhibits a sharp Soret-like band and distinct Q-like bands characteristic of an aromatic porphyrinoid, while **R28H**

exhibits a broad absorption spectrum without Q-like bands as typical for an antiaromatic porphyrinoid. In contrast, the T-T absorption of **R26H** is broad, weak, and featureless, while that of **R28H** displays an intense and sharp Soret-like band. These spectral signatures are diagnostic of antiaromatic and aromatic porphyrinoids, respectively. This provides a direct experimental evidence of aromaticity reversal in the T_1-states of both systems.

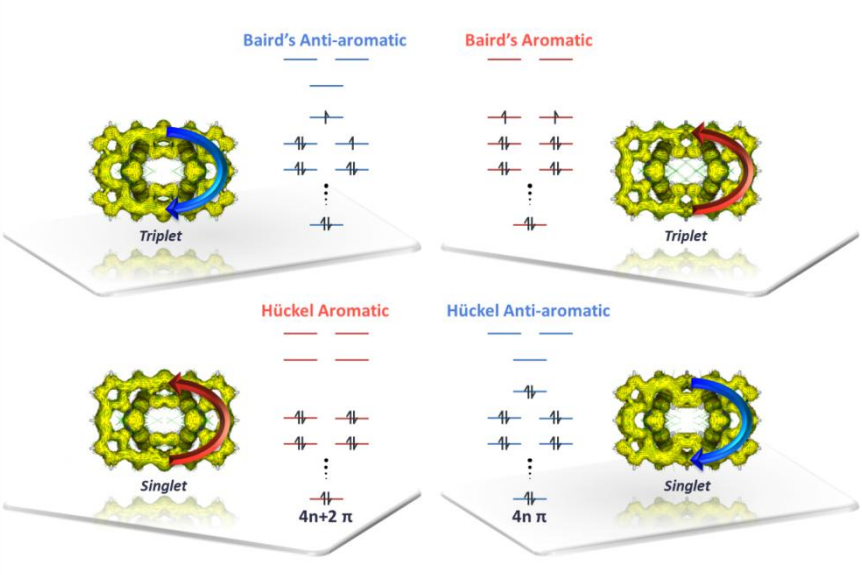


Figure 5 Isosurfaces (yellow) and current density vectors (small green arrows) calculated by ACID for **R26H** (left) and **R28H** (right) in the ground sate (top) and lowest triplet state (bottom).

The experimental results are fully supported by a number of standard calculations of aromaticity and associated indices **(Figure 5)**. Moreover, both sets of findings, namely experimental and theoretical, are in good agreement with the previous theoretical analyses that predicted the reversal of aromaticity in the T_1-states of such simple annulenes as benzene, cyclobutadiene, and cyclooctatetraene. We predict that the ability to manipulate aromaticity or antiaromaticity through selection of the electronic state will provide additional fruitful insights into the relationship between aromaticity and electronic structures and, as a consequence, an increased ability to modulate chemical reactivity. We also believe that an ability to control the spectroscopic features of π-extended chromophores through aromaticity reversal will allow for new promising applications, including the development of saturable absorbers and photo-switchable devices that operate in both the visible and near-IR regions. To the extent this proves true, it could have far-reaching practical applications that complement the advances in theoretical understanding that studies such as the present one are likely to provide.

2. 3-dimensional Aromaticity

Recently, efficient multiple π-electron delocalizations within three-dimensional conjugated molecular framework represent an emerging research frontier for novel properties of both Hückel- and Möbius-type porphyrinoid systems.

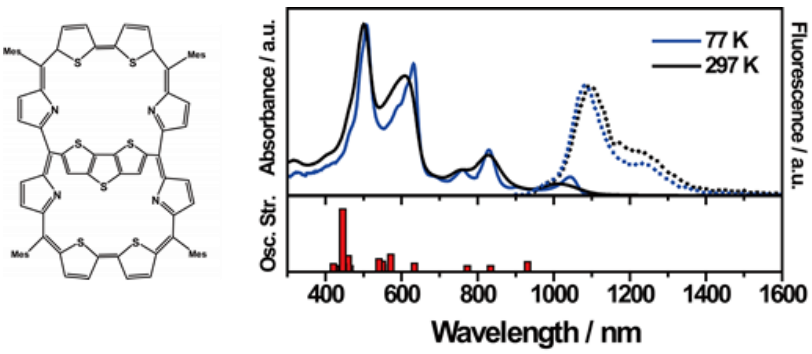


Figure 6 Molecular structure (left), absorption (solid line) and fluorescence spectra (dotted line) at 77 and 297 K, and calculated vertical transitions.

Multiple π-electron delocalizations can occur through multiple conjugation pathways in one molecule, and the development of new topologies that allow effective three -dimensional delocalization confronts a fascinating synthetic challenge. Various modifications have been carried out on expanded porphyrins including core-modification and *meso-meso* connection with aromatic moieties. Throughout the studies on core-modified and *meso*-bridged expanded porphyrins, we have observed the correlations between photophysical properties and three-dimensional aromaticity in measurements of the magnetic indices, temperature-dependent steady-state absorption and emission spectra, time-resolved excited-state dynamics, and computational calculations. The absorption spectrum at 297 K exhibits two B-like bands at 501 and 605 nm **(Figure 6)**. These spectral features largely reflect a summation of those of aromatic [26]hexaphyrin and [34]octaphyrin.

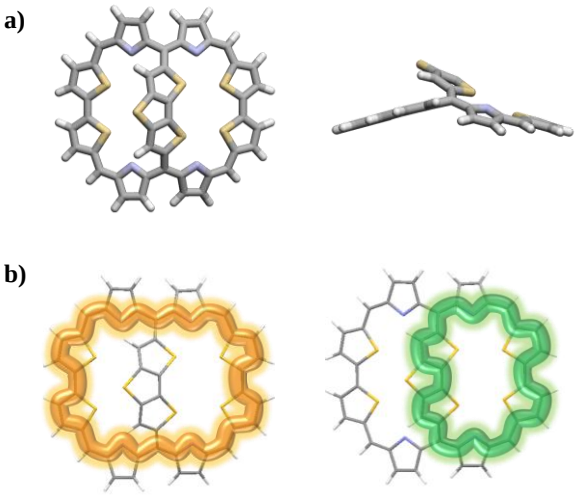


Figure 7. a) Optimized structure and b) expected conjugation networks.

The optimized molecular structure represents that dithienothiophene (DTT) moiety not only acts as a bridge, but also plays an important role in its electronic nature. Because DTT moiety is too large to fit into the molecular frame, the side view of optimized molecular structure reveals two types of slightly distorted planes which allows for effective two directional π-orbital interactions in one molecule as shown in **Figure 7**.

According to the absorption wavelengths of B-like bands and the origins of calculated vertical transitions as shown in **Figure 6**, we suggest that two modes of effective π – conjugation pathways are operative in one molecule encompassing 26 (green color) and 34 (yellow color) π-electron networks, respectively.

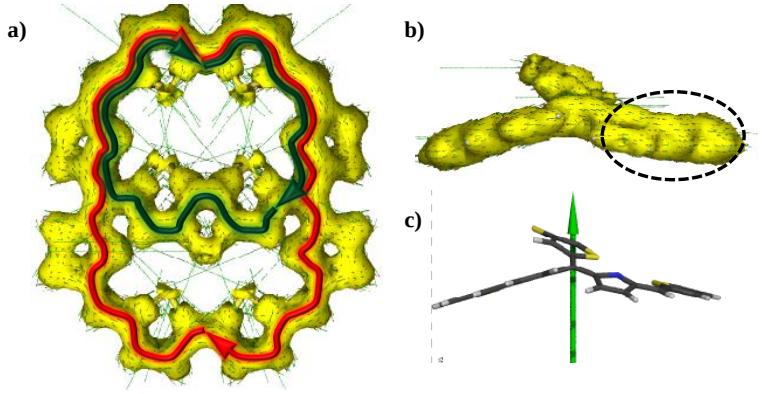


Figure 8. a), b) ACID plots. c) The external magnetic field vector is applied as a large arrow. Isosurface value is 0.045.

To obtain further information on π-electron density distribution along the two directional π-conjugation pathways, we calculated the ACID plots which represent the 3D image of delocalized electron densities with a scalar field and illustrates the paramagnetic term of the induced current density. Definite two π-conjugation pathways which are represented by green and red arrows in **Figure 8a** illustrate nearly the same π-electron densities. Although the molecular framework of 34π conjugation pathway is highly symmetric, the right side of π-electron density (dotted area in **Figure 8b** is thicker than the opposite side, which means that the two types of π-conjugation can be manifested with partially sharing the same π-conjugation pathway. As a result, both 26 and 34π electron systems can produce effective π-conjugation networks through hexaphyrin- and octaphyrin-like molecular framework, respectively.

In conclusion, the DTT-bridged and core-modified octaphyrin was prepared to investigate the three-dimensional aromatic properties in one molecule. Owing to double aromatic characters in one molecule, this molecule exhibits remarkably rigid molecular structure, long excited state lifetime and strong NIR fluorescence emission. Our experimental and computational methods for investigating the three-dimensional aromaticity will be a guideline for continuous efforts on realizing the three-dimensional aromaticity in other types of molecules.

II. The relationship between Two-photon absorption and Aromaticity

We have extensively investigated the relationship between aromaticity and TPA cross-section values for the last few years. Interestingly, two-photon absorption (TPA) cross-section ($\sigma^{(2)}$) values can be correlated with the degree of aromaticity in expanded porphyrin derivatives. The two-photon absorption is a third-order NLO phenomenon, and its

probability of occurrence is closely related to the π-electron behavior. Therefore, the aromaticity is also intuitively associated with TPA phenomena in terms of π-electron delocalization. In previous studies, we have found out that aromatic molecules tend to have larger TPA cross-section values than antiaromatic molecules. These results suggest that the TPA cross-sections can be a semi-quantitative measure of aromaticity. Therefore, we believe that it is possible to roughly evaluate aromaticity character by TPA measurement.

1. Aromaticity enhancement in [26]Hexaphyrin

Throughout the studies on expanded porphyrins, we have consistently observed the correlations between photophysical properties and aromaticity in measurements of the magnetic indices (chemical shift), steady-state absorption and emission spectra, time-resolved excited-state dynamics, and computational calculations. Aromatic expanded porphyrins, regardless of whether they are Hückel- or Möbius-type, exhibit distinct absorption spectra with well-defined, sharp B- and Q-like bands, strong fluorescence, long-lived excited states, and large TPA (two-photon absorption) cross-section values as compared with anti- or nonaromatic expanded porphyrins. As a part of our continuous efforts to explore novel electronic states of expanded porphyrins, we propose a new method for controlling aromaticity in expanded porphyrins by deprotonation with tetrabutylammonium fluoride (TBAF) as an organic base.

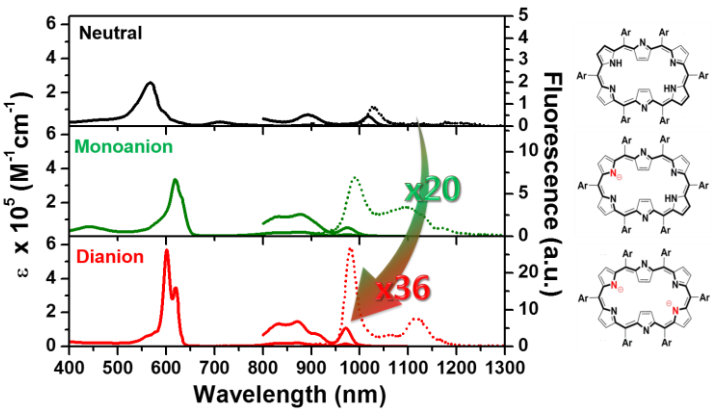


Figure 9. Steady-state absorption and fluorescence spectra of neutral, monoanion and dianion.

[26]Hexaphyrin was selected in our study because it has been recognized as a representative expanded porphyrin with a 26π-conjugated electronic circuit in its planar structure to satisfy Hückel's aromatic [4n+2] rule. A careful treatment with one equivalent of TBAF gave monoanion selectively and the addition of 10 equivalents of TBAF produced dianion exclusively **(Figure 9)**. The formation of monoanion and dianion was probed by ^{1}H NMR spectroscopic measurements and the structure of dianion was unambiguously confirmed by single-crystal X-ray diffraction analysis. In going from neutral to dianion, the extinction coefficients of B- and Q-like bands increased and the overall absorption spectra became increasingly well-shaped.

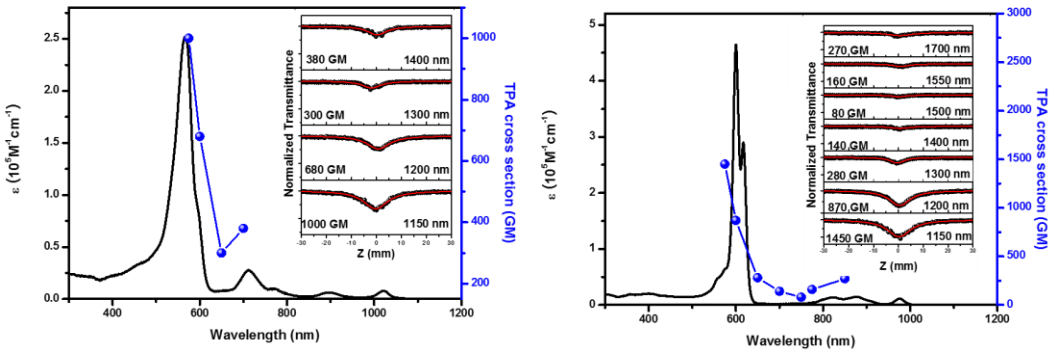


Figure 10. Two-photon absorption spectra (blue) and Z-scan traces (insets) of neutral (left) and dianion (right), respectively. The solid line indicates the steady-state absorption spectrum for comparison, and the solid line in inset is the best curve fit line of experimental data.

More importantly, the fluorescence of neutral [26]hexaphyrin in NIR region was significantly intensified by 20 and 36 times in monoanion and dianion, respectively. The increased fluorescence intensities may be ascribed largely to enhanced aromaticity. Actually, it has been well established that expanded porphyrins exhibit more distinct B- and Q-like bands with larger extinction coefficients and larger fluorescence quantum yields with increasing aromaticity.

The TPA cross-section ($\sigma^{(2)}$) values are largely correlated with the degree of aromaticity in expanded porphyrins but also depend on molecular shape and symmetry. The TPA process is a third-order nonlinear optical (NLO) phenomenon, and its occurrence probability is closely related to π-electron delocalization feature. In other words, the aromaticity is intuitively associated with the TPA phenomena. In our previous works, we have measured the $\sigma^{(2)}$ values of various kinds of expanded porphyrins, and have revealed that aromatic systems show relatively larger $\sigma^{(2)}$ values compared with non- or antiaromatic ones. The $\sigma^{(2)}$ values of neutral and dianion were measured to be 1000 and 1450 GM, respectively **(Figure 10)**. The larger $\sigma^{(2)}$ of dianion seems to support our conjecture that the dianion has a more effective conjugated Hückel aromatic circuit.

2. Formation of Möbius Aromatic [32]Heptaphyrin

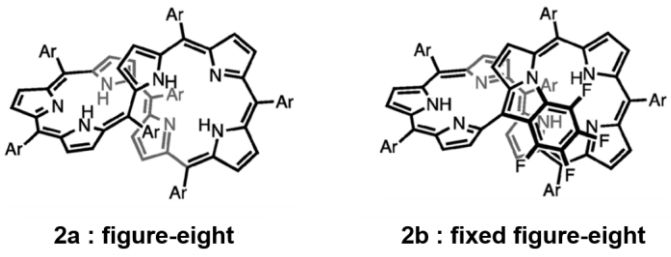


Figure 11. Molecular structures of neutral [32]heptaphyrin **2a** and singly N-fused [32]heptaphyrin **2b**.

Encouraged by the case of [26]hexaphyrin, we have examined deprotonation of [32]heptaphyrins and have found that deprotonation is an effective means to realize Möbius aromatic heptaphyrins.

In this study, we have focused on [32]heptaphyrin **2a** and singly N-fused [32]heptaphyrin **2b** as a conformationally rigid reference molecule **(Figure 11)**.

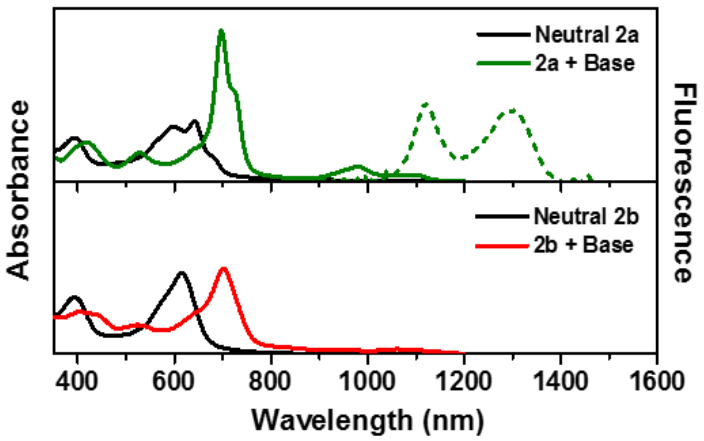


Figure 12. The steady-state absorption (solid line) and fluorescence (dotted line) spectra of neutral and deprotonated **2a** and **2b**, respectively.

Upon addition of an excess amount of TBAF **(Figure 12)**, the absorption spectrum of **2a** changed significantly, featuring a sharp and intense B-like band at 700 nm and Q-like bands at 970 and 1080 nm in NIR region, and relatively strong NIR fluorescence was observed with a small Stokes shift (196 cm^{-1}). The observed small Stokes shift suggests the structural rigidity of the S_1-state of deprotonated **2a**. These spectral properties are characteristic of aromatic expanded porphyrins, hence suggesting that deprotonated **1** takes a twisted Möbius aromatic structure on the basis of our previous observations. It is conceivable that the removal of pyrrolic NH proton leads to a disruption of the intramolecular hydrogen bonding, hence changing the figure-eight conformation to the extended Möbius conformation. The absorption spectrum of **2b** was red-shifted, but definite Q-like bands and NIR fluorescence were not observed, and its ^{1}H NMR spectrum did not show a newly generated diatropic ring current, probably due to its rigidly fixed figure-of-eight structure. Through our continuous efforts, TPA cross-section values have been shown to be a nice measure to evaluate the degree of aromaticity of expanded porphyrins. As shown in **Figure 13**, upon deprotonation, the TPA value of **2a** largely

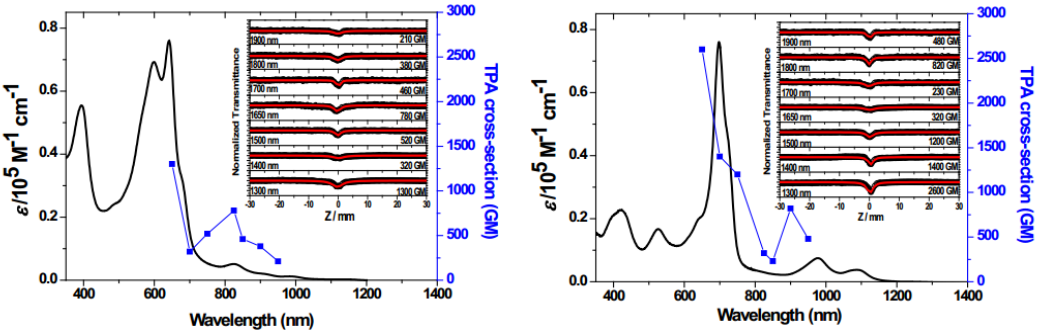


Figure 13. Two-photon absorption spectra (blue) and Z-scan traces (insets) of neutral (left) and deprotonated (right) of **2a**. The solid line indicates the steady-state absorption spectrum for comparison, and the solid line in inset is the best curve fit line of experimental data.

increases, which also supports our conjecture that deprotonation of [32]heptaphyrins gives rise to enhancement of aromaticity of Möbius species.

In conclusion, deprotonation-induced structural changes of **1** and **2a** were accompanied by 1) red-shifted and sharp B-like band, 2) distinct Q-like bands in NIR region, 3) elongated S_1-state lifetime, and 4) enhanced TPA cross section values. Through these works, we have demonstrated that deprotonation can be a new effective means to control the conformation of expanded porphyrins and hence their aromatic characters dramatically.

III. Exciton Delocalization and Dynamics in π-Stacks of Self-Assembled Perylene Bisimides (PBI)

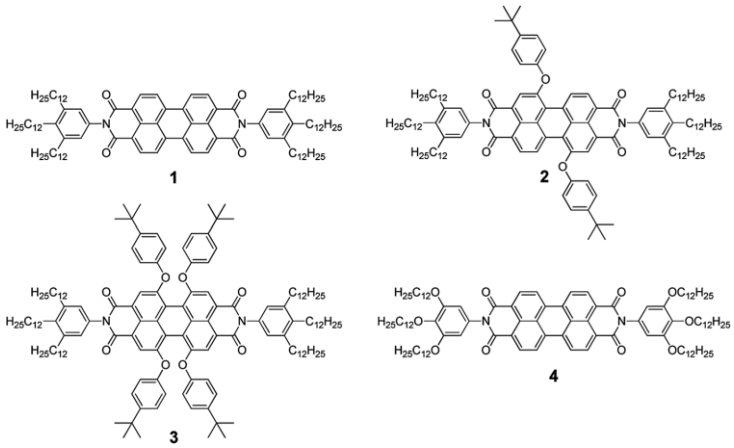


Figure 14 Molecular structures of PBI dyes employed in this study. PBIs **1** and **4** adopt helical aggregate structures in MCH solvent at high concentrations while PBIs **2** and **3** have dimer and monomer forms, respectively. PBI **4** with its electron-donating 3,4,5-tridodecyloxyphenyl substituents shows non-fluorescence behavior.

There are numerous investigations for the photophysical properties in self-assembled molecular aggregates, since they reveal promising characteristics such as high charge carrier mobility. And those researches are mainly concerned with the photophysical properties of slipped stacking structures of J-aggregates or well -arranged self-assembled systems. Whilst the excitonic properties of J-aggregates have been investigated in great detail, those of H-aggregates have not been systematically investigated yet. However, unfortunately, most of self-assemblies exhibit columnar stacked structures with complex interactions among their unit molecules. Thus, in this study, we have investigated the photophysical properties of various aggregates system. We have explored the exciton dynamics and excited-species formation processes in columnar H-aggregates of planar PBI dyes that are stacked in a helical fashion by various spectroscopic techniques such as time correlated single-photon counting (TCSPC) and femtosecond pump–probe measurements with anisotropy changes. By controlling the core PBI structure with bay- and amino alkyl-substituents, we have utilized a series of PBI (**1**, **2**, and **3**) self-assemblies which can

represent monomer, dimer and highly stacked structures, respectively. The photogenerated exciton in helically stacked PBI dyes experiences complicated relaxation processes contributed by excited-state interactions such as exciton delocalization and excimer formation process. For instance, the reduced anisotropy values of the helically stacked aggregates also might be originated from the excited-state interactions. Interestingly, these spectroscopic features were not observed in monomer or dimer states of PBI molecules. These features indicate that the exciton dynamics can occur in the whole assembled structures and the coherent exciton can exist beyond the dimeric segments. Moreover, by utilizing hetero-PBI aggregates with non-fluorescence PBI **4**, we have estimated certain limit of exciton diffusion process that does not exceed about ten PBI units.

To scrutinize the exciton dynamics in the helically stacked aggregates, we have also included PBI **2** and **3**, distorted bay-substituted PBI dyes as reference molecules. PBI **2** exhibit only relatively small-sized dimeric aggregate structures, whereas PBI **3** forms no multimeric structures at all. The comparative study revealed that the excited-state interactions in the large-sized helically stacked aggregates extend beyond two PBI units, leading to a final excimer (here, excimer means not only an "excited dimer" but an "excited multimer") trap state within ~50 ps. Although in competition with this relaxation path into the excimeric trap state, exciton diffusion has been revealed by exciton–exciton annihilation processes, occurring at high excitation power. Whilst the excimer formation process interrupts the direct observation of exciton diffusion in these columnar PBI aggregates, the exciton migration distance could be estimated by the incorporation of non-fluorescent PBI **4** quencher molecules into PBI **1** aggregates. From this analysis we can conclude that the exciton diffusion can reach a length of about 10 monomer units. Although this value appears to be shorter than those values observed for J-aggregates, this result shows that columnar PBI stacks might still be useful for optoelectronic applications if the relaxation process leading to excimer traps is prevented, e.g. by structural modifications of the molecules.

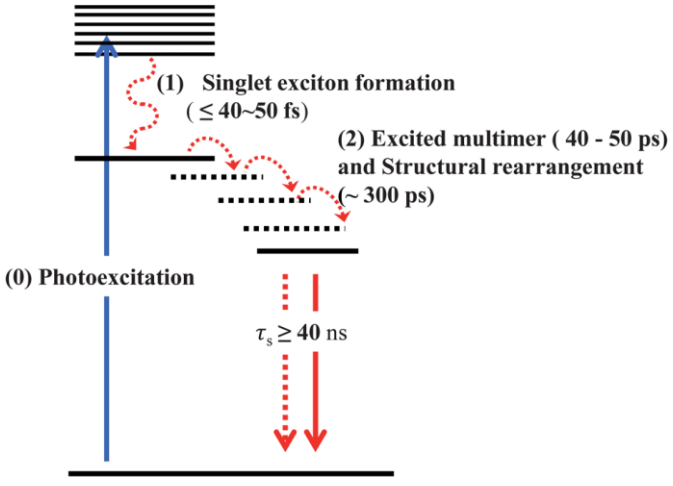


Figure 15 Exciton dynamics in helically stacked aggregates of PBI dyes.

Overall, we have demonstrated the photophysical properties of various PBI molecules. And,

especially, we have focused on the exciton behaviors such as exciton dynamics and excited-species formation processes in helically stacked PBI system. The outcome of this study is that photogenerated excitons in helically stacked PBI dyes experience complicated relaxation processes that involve excited-state interactions such as exciton delocalization and excimer formation. Thus our new findings would give a clue to further understanding of the exciton behaviors in helically stacked self-assembled systems. Moreover, to the best of our knowledge, the systematic photophysical investigations of various aggregates have not been studied.

IV. Femtosecond Pump-Probe Nondegenerate TPA Spectroscopy

The rapid development of applications for photonic device has led to aggressive efforts to find materials with large optical nonlinearities. Many different types of materials have been extensively studied, with organic materials having been identified as being particularly promising due to their ease of processing and large nonlinear figures of merit. Most efficient means of characterizing organics has been to study their optical properties in solutions by using such methods as the Z-scan technique which can simultaneously measure the

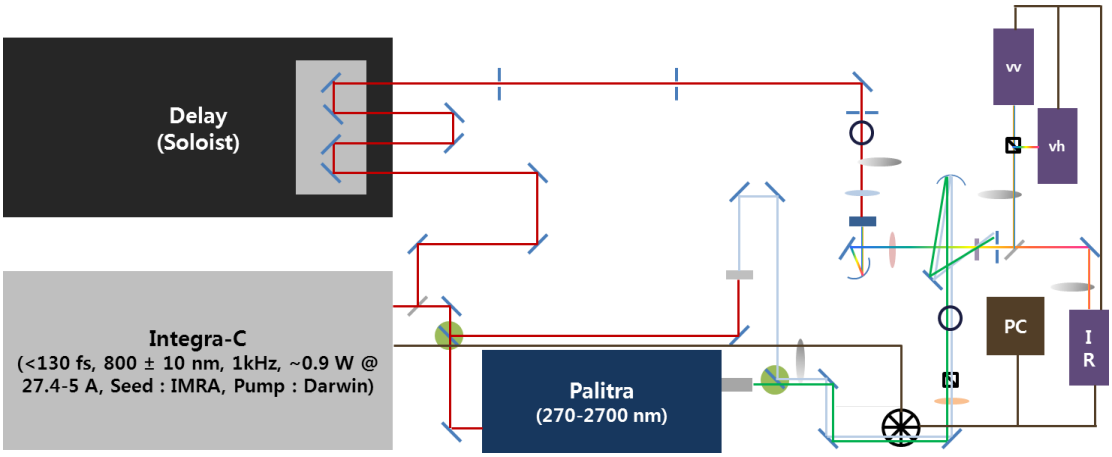


Figure 16. Femtosecond time-resolved pump–probe absorption spectroscopy set-up

two-photon absorption (TPA) cross-section values utilizing a single Gaussian beam. In this technique the sample is scanned along the axis of a focusing beam, while measuring the transmittance through an aperture in the far field. This Z-scan method has proven quite useful in separately measuring nonlinear absorption and refraction at single wavelengths for semiconductor and transparent dielectric materials. However, for materials with more complicated electronic structure, such as complex organic compounds (expanded porphyrin), multiple two-photon bands can occur. To date, no universal theory of structure property

relationships can predict these spectra, and the database of nonlinear spectra is sparse.

To fill this void, a method is needed to rapidly and accurately monitor nonlinear spectra. The method of interest to us is the multichannel detection utilizing the technique of femtosecond time-resolved pump–probe absorption spectroscopy, since the large spectral extent of the probe beam could allow for full characterization of the sample with a pump pulse, where a broadband, weak, white-light continuum (WLC) is used to probe a medium that is subjected to an intense pump pulse **(Figure 16)**.

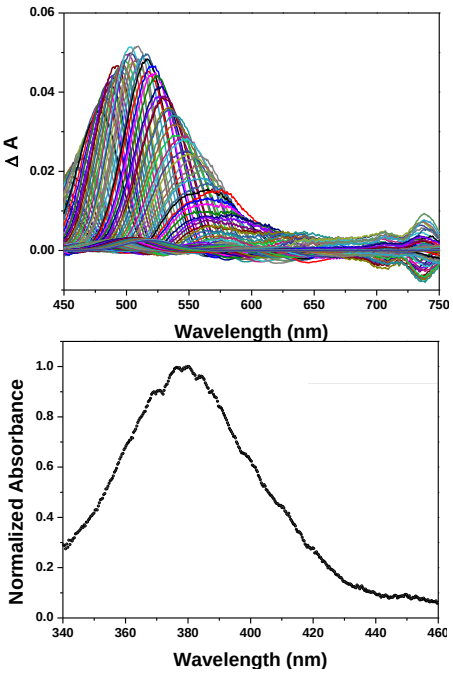


Figure 17. Nondegenerate two-photon absorption spectra of all-trans retinal in hexane (top) and Pump-induced absorption spectra plotted as a function of wavelength corresponding to the sum frequency of the pump and probe pulses (bottom).

The result of this pump-probe technique is the nondegenerate TPA spectrum. Because the TPA process occurs only when the pump pulse and probe beam are temporally overlapped, a TPA spectrum is obtained as a pump-induced absorption spectrum at zero time delay between the two pulses. Technically, the present TPA measurement is very similar to femtosecond time-resolved pump–probe absorption spectroscopy. The difference is that we employ a nonresonant NIR pulse for pumping, instead of a resonant UV or VIS pulse. Taking advantage of well-established techniques for femtosecond time-resolved absorption spectroscopy, we can perform the multichannel detection of pump-induced transmittance changes in the probe beam to obtain the TPA spectra with high S/N ratios **(Figure 17)**. We have installed this rapid characterization technique to accelerate the study in various two-photon absorbing organic compounds. We are currently pursuing a study of NIR-absorbing organic molecular systems. Finally, we are automating both the experimental procedure as well as the data analysis process to truly enhance the speed at which characterization can be performed.

List of Publications

1. Molecular Engineering and Solvent Dependence of Excitation Energy Hopping in Self-Assembled Porphyrin Boxes

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3. Stable Tetrabenzo-Chichibabin's Hydrocarbons: Tunable Ground State and Unusual Transition between Their Closed-Shell and Open-Shell Resonance Forms

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4. Kinetically Blocked Stable Heptazethrene and Octazethrene: Closed-Shell or Open-Shell in the Ground State?

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8. Exciton Delocalization and Dynamics in Helical pi-Stacks of Self-Assembled Perylene Bisimides

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21. Unique Ultrafast Energy Transfer in a Series of Phenylene-Bridged Subporphyrin-Porphyrin Hybrids

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Chem. Commun., 2014, Accepted Manuscript