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14. ABSTRACT
To create synthetic materials with optoelectronic properties two fundamental challenges must be overcome, namely, understanding how multicomponent supramolecular systems assemble into mesoscale structures, and determining how novel optical and electronic properties can emerge by bringing together donor and acceptor components that individually lack the desired properties. Herein we describe the design, preparation, and study of a novel self-assembling system composed of diketopyrrolopyrrole (DPP) electron donors and perylene diimide (PDI) electron acceptors, where multiple, complementary noncovalent interactions direct the assembly of hierarchical

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Report Title

Final Report: Donor-Acceptor Superstructures with Emergent Optoelectronic Properties: Synergistic Approaches to Functional Self-Assembling Aggregates

ABSTRACT

To create synthetic materials with optoelectronic properties two fundamental challenges must be overcome, namely, understanding how multicomponent supramolecular systems assemble into mesoscale structures, and determining how novel optical and electronic properties can emerge by bringing together donor and acceptor components that individually lack the desired properties. Herein we describe the design, preparation, and study of a novel self-assembling system composed of diketopyrrolopyrrole (DPP) electron donors and perylene diimide (PDI) electron acceptors, where multiple, complementary noncovalent interactions direct the assembly of hierarchical superstructures that will undergo efficient charge generation and long-distance charge separation in solution and the solid-state. Specifically, we describe: (1) The assembly of DPP-PDI superstructures in solution and in the solid-state to develop new predictive models that quantitatively explain heteroaggregation with different components, donor-acceptor ratios, and environmental conditions, (2) an understanding how structure and FMO energies interact to produce emergent properties that respond external stimuli, and (3) the production stable solid-state materials that can be incorporated into electronic devices.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
05/30/2014	1.00	David Ley, Carmen X. Guzman, Karin H. Adolfsson, Amy M. Scott, Adam B. Braunschweig. Cooperatively Assembling Donor–Acceptor Superstructures Direct Energy Into an Emergent Charge Separated State, Journal of the American Chemical Society, (05 2014): 0. doi: 10.1021/ja5015053
08/22/2015	2.00	Carmen X. Guzman, Rafael M. Krick Calderon, Zhong Li, Shiori Yamazaki, Samuel R. Peurifoy, Chengchen Guo, Stephen K. Davidowski, Mercedes M. A. Mazza, Xu Han, Gregory Holland, Amy M. Scott, Adam B. Braunschweig. Extended Charge Carrier Lifetimes in Hierarchical Donor–Acceptor Supramolecular Polymer Films, The Journal of Physical Chemistry C, (08 2015): 0. doi: 10.1021/acs.jpcc.5b03713
08/22/2015	3.00	Samuel R. Peurifoy, Carmen X. Guzman, Adam B. Braunschweig. Topology, assembly, and electronics: three pillars for designing supramolecular polymers with emergent optoelectronic behavior, Polym. Chem., (05 2015): 5529. doi: 10.1039/C5PY00420A
TOTAL:	**3**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

[12]Florida International University, Department Colloquium, 23 March, 2016
"On the quantitative determination of binding constants: Implications on supramolecular chemistry, surface science, and solar energy harvesting."
[11] University of Massachussetts, Amherst Chemistry Department Colloquium, 24 February, 2016
"Chasing Emergence: A Supramolecular Approach Towards Optically and Biologically Active Nanosystems"
[10]Tufts University Department of Chemistry Colloquium, 23 February 2016
"Chasing Emergence: A Supramolecular Approach Towards Optically and Biologically Active Nanosystems"
[9]Emory University, Department of Chemistry Colloquium, 15 February, 2016
"Chasing Emergence: A Supramolecular Approach Towards Optically and Biologically Active Nanosystems"
[8] City University of New York, Advanced Science Research Center, 11 February 2016
"Chasing Emergence: A Supramolecular Approach Towards Optically and Biologically Active Nanosystems"
[7]CUNY Advanced Science Research Center Active & Adaptive Materials Symposium, New York, NY, 22-23 October 2015
"Nanosecond Charge Carrier Lifetimes in Hierarchical Donor-Acceptor Supramolecular Polymer Films"
[6]Fusion Functional Polymer Materials Conference, Ascot, UK, 6 August 2015
"Correlated Structure and Photophysics in Supramolecular Polymer Films"
[5] International Mini-Conference on Singlet Fission, Erlangen, Germany, 14 – 16 May 2015
Plenary Lecture: "Competing Charge and Spin Dynamics in Donor-Acceptor Hierarchical Films"
[4]4th Zing Polymer Chemistry Conference, Riviera Maya, 10 – 13 December, 2014
Competitive Electron Spin Dynamics in Multicomponent Hierarchical Donor-Acceptor Films
[3]2nd Targeting and Triggering Basic Research Workshop and Review, Cambridge University, Cambridge, UK, 19-20 August 2014
Emergent Charge Transfer in Cooperatively Assembling Donor-Acceptor Supramolecular Polymers and Films
[2] 247th American Chemical Society National Meeting, Dallas, TX
Polymeric Materials: Science and Engineering Young Investigator's Symposium
"Photochemically- and Force-Initiated Brush Polymer Microarrays and Their Applications in Sensing and Electronic Materials"
[1] Fusion Functional Polymeric Materials, Cancun, Mexico, 12 February 2014
"Emergent Charge Transfer in Cooperatively Assembling Donor-Acceptor Superstructures"

Number of Presentations: 12.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper
09/28/2016 8.00	. Nanosecond Charge Carrier Lifetimes in Hierarchical Donor-Acceptor Supramolecular Polymer Films, Active and Adaptive Materials Symposium. 23-OCT-15, CUNY Advanced Science Research Center, NY, NY. : ,
09/28/2016 9.00	. Nanosecond Charge Carrier Lifetimes in Hierarchical Donor-Acceptor Supramolecular Polymer Films, IX International Congress on Chemical Sciences, Technology and Innovation (Quimicuba' 2015). 14-OCT-15, Havana, Cuba. : ,
09/28/2016 10.00	. Supramolecular Polymers and the Subtleties of Molecular Recognition, 15th European Symposium on Organic Reactivity, Kiel, Germany. 05-SEP-15, Kiel, Germany. : ,
09/28/2016 11.00	. Nanosecond charge carrier lifetimes in hierarchical donor-acceptor supramolecular polymer films, Pacifichem 2015. 17-DEC-15, Honolulu, HI. : ,
TOTAL:	**4**

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Received	Paper
TOTAL:	

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper
TOTAL:	

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Kavli Fellow 2016 • Royal Society of Chemistry Chemical Society Reviews Emerging Investigator 2016
Journal of Physical Organic Chemistry Award for Early Career Excellence in Physical Organic Chemistry 2015
ACS Organic Chemistry Young Innovator 2015
UM Provost's Research Award
Polymer Chemistry Emerging Investigator 2015
ACS PMSE Young Investigator Award 2014

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Xiang Zhong	0.37	
Carmen Guzman	0.02	
Xu Han	0.19	
Yeting Zheng	0.19	
Chuan Liu	0.50	
FTE Equivalent:	**1.27**	
Total Number:	**5**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Adam Braunschweig	0.06	
FTE Equivalent:	**0.06**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
Samuel Peurifoy	0.05	Chemistry and Mathematics
FTE Equivalent:	**0.05**	
Total Number:	**1**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	1.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	1.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:.....	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	1.00

Names of Personnel receiving masters degrees

NAME
Carment Guzman
Chuan Liu
Yeting Zheng
Total Number: **3**

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

FINAL REPORT 15 April 2014 – 31 August 2016 (W911 NF-14-1-0164). Donor-Acceptor Superstructures with Emergent Optoelectronic Properties: Synergistic Approaches to Functional Self-Assembling Aggregates. PI. Adam B. Braunschweig, University of Miami, Coral Gables, FL 33146. Email: a.braunschweig@miami.edu; adam.braunschweig@asrc.cuny.edu

1. Statement of the Problem Studied. The primary aim of the research was to develop a new supramolecular photoactive system with emergent optoelectronic properties that are absent in the individual components and to study how chemical structure, noncovalent assembly, and frontier molecular orbitals (FMOs) can be synergistically designed to control and optimize these properties. Biology abounds with examples of systems where small molecules organize into hierarchical superstructures with important optoelectronic properties that are absent in the individual components. Researchers aim to create synthetic systems with comparably sophisticated stimuli-responses, but for several reasons, these systems do not have the architectural or functional complexity of their biological counterparts. Thus developing synthetic systems with emergent optoelectronic properties could address important DoD needs related to energy harvesting, molecular information transfer (sensing), or camouflage. With these aims in mind, we have developed a novel molecular system composed of diketopyrrolopyrrole (DPP) electron donors and perylene-derived bisdiimide (PDI) electron acceptors that assemble into donor-acceptor helical superstructures as a result of multiple noncovalent interactions operating in unison. These hierarchical assemblies persist in the solid state, where charge carrier lifetimes are improved 1000-fold in comparison to solution. Over the course of the project, we demonstrated that these DPP-PDI aggregates undergo photoinduced electron transfer upon assembly, form highly-ordered films with desirable photophysical properties, including photoinduced charge separation and subsequent charge migration, and have developed quantitative models for explaining assembly and transport across length-scales. Establishing these fundamental relationships will enable the rational control of the structural, electronic, and emergent properties of future organic systems to meet the DoD's forthcoming materials needs.

2. Summary of Most Important Results. During the project period, major advances were made in understanding the organization and photophysical properties of DPP-PDI superstructures in solution and in the solid-state, examining the transport of PDIs in thin films, and in developing methods to control the equilibrium dynamics in solution of DPP homoaggregates. The major advances include demonstrating reversible photoinduced charge transfer in solution following assembly (**Section 2.1.**), confirming that superstructure is conserved in the solid state, resulting in a 1000-fold increase in charge separation lifetimes (**Section 2.2.**), developing a quantitative model for the assembly of the components as a function of binding thermodynamics (**Section 2.3.**), investigating transport and the role of defects in films (**Section 2.4.**), exploring how electron beam damage affects the ability to characterize the structures of soft and hybrid materials (**Section 2.5.**), and using new concepts related to complexity to model charge transport in donor-acceptor superstructures (**Section 2.6.**). Finally, we review the design rules that have developed from this system and similar ones in the literature (**Section 2.7.**). The major scientific advance of these studies is a more complete understanding of how emergent macroscopic properties – such as charge separation or controlled multilength-scale organization – can be achieved by careful

control over molecular design and a thorough understanding of thermodynamically-controlled assembly.

2.1. Solution organization and photophysics. Substituted DPP donors and PDI acceptors were prepared efficiently *via* organic synthesis consisting of only a few steps, and the band gaps and absorption maxima can be tuned by varying the substituents (Figure 1A). Orthogonal noncovalent interactions were programmed into these compounds to drive the supramolecular assembly of DPP and PDI (Figure 1B). We found that the heteroaggregation process occurs following a cooperative assembly path: the DPP units first form disordered homoaggregates *via* π-stacking, while in the next step, PDI units are associated to the DPP stacks by means of triple H-bonding. This binding model allows the preparation of heteroaggregates with a precisely controlled ratio of DPP to PDI. We proceeded to investigate the optoelectronic properties of the system and to assess the ability to undergo photoinduced charge separation and subsequent charge separation to create a long-lived radical pair state, which is a prerequisite for efficient light harvesting. The ground state frontier molecular orbital (FMO) energy levels of the individual compounds were investigated by cyclic voltammetry (CV), UV-Vis, and fluorescence spectroscopy to study whether the system can undergo thermodynamically favored charge separation upon photoexcitation. Our studies revealed that the energetic positions of the FMOs do allow the reduction of the PDI acceptor by the photoexcited DPP donor (electron transfer), or the oxidation of the DPP donor by the photoexcited PDI acceptor (hole transfer). Based on the FMOs of the individual compounds, electron transfer can occur by the transfer of an electron from the upper SOMO (–3.24 eV) of photoexcited DPP into the LUMO (–3.63 eV) of PDI, while the hole transfer route corresponds to the transfer of an electron from the DPP HOMO (–5.98 eV) into the lower SOMO (–5.35 eV) of photoexcited PDI. The driving forces are –0.39 eV for electron transfer from DPP to PDI, and –0.63 eV for hole transfer from PDI to DPP (Figure 1C).

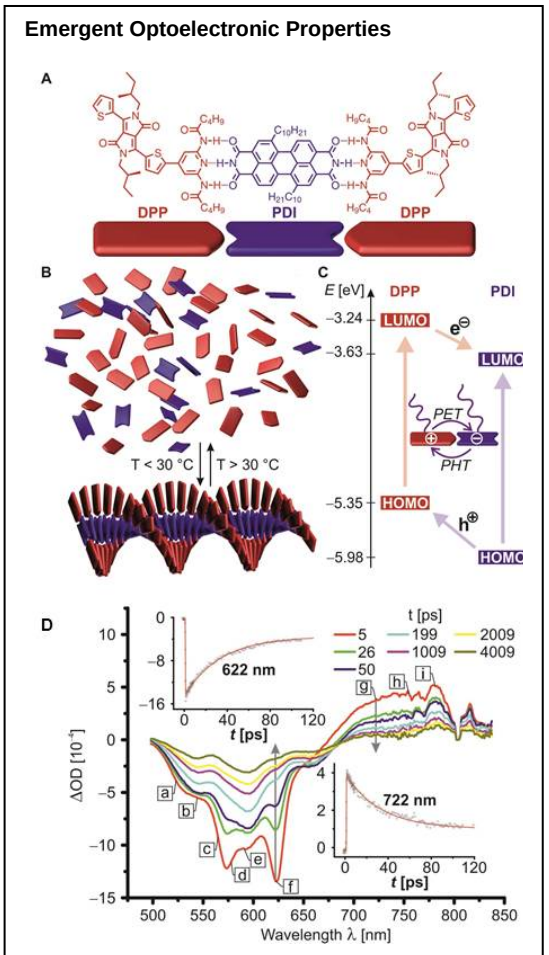

Figure 1. (A) H-bonding brings the DPP donor (red) and the PDI acceptor (blue) together. (B) Upon cooling, superstructures arise from H-bonding and orthogonal π-stacking. (C) Frontier molecular orbital scheme indicating photoinduced electron and hole transfer *via* donor or acceptor excitation. (D) Femtosecond transient absorption spectra of the 2:1 (DPP:PDI) mixture in toluene with absorption *vs.* time profiles of (upper inset) the ground state absorption band of the supramolecular DPP-PDI aggregate at λ = 622 nm and λ = 722 nm.[2]

To take reorganization energies of the ionic species and solvent effects in account, the charge separation energies (ΔG_{CS}) were calculated by performing the Weller correction on the measured reduction and oxidation potentials. With respect to the ground state, the charge separation energy was 2.0 eV (620 nm), which corresponds to the absorption band in the visible spectrum that the aggregate exhibits. This is a new absorption band, which is not present in the individual components, and vanishes upon thermally or chemically induced disaggregation of the supramolecular aggregates. This indicates that the direct excitation of the system into its charge separate state is an emergent property of this donor-acceptor system that comes along with the formation of heterosuperstructures. To investigate the charge separation and recombination dynamics in detail, static reorganization energies λ_S were calculated by invoking the Marcus relation, which is based on the dielectric continuum model of the solvent. As expected for toluene as a low polarity solvent, this static contribution (λ_S = 0.03 eV) is insignificantly small, so that the overall reorganization energy λ is given by the intrinsic value (λ_i = 0.30 eV), which was determined with density functional theory (DFT) computations using the ORCA program package. The charge separation energy of a DPP-PDI assembly is –0.35 eV based on photoexcited PDI, so that the condition $-\Delta G = \lambda$ is fulfilled; so based on the Marcus equation, very fast electron transfer is expected to proceed from photoexcited PDI. As a result of the much larger free enthalpy for charge recombination (ΔG_{CR} = –2.00 eV) that shifts this process into the Marcus inverted regime, so recombination is expected to occur much slower than charge separation so that continuous excitation with visible light would efficiently result in a charge-separated steady-state. This donor-acceptor system therefore exemplifies how supramolecular assembly and FMO tailoring can be combined to achieve emergent charge transfer in hierarchical organic superstructures.

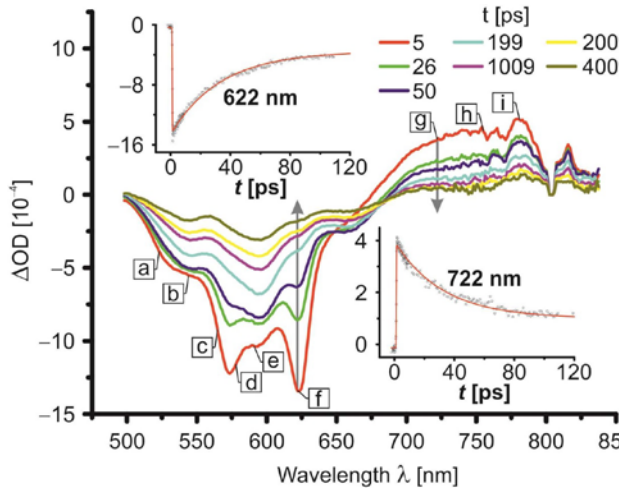

Figure 2. Femtosecond-transient absorption spectra of a 2:1 mixture of DPP and PDI in toluene. With the kinetic traces (denoted by the arrows) of the ground state absorption band of the aggregate at 622 nm (upper inset), as well as that of the radical anion of the PDI (722 nm, lower inset). The accurate matching of the two profiles indicates that they represent the same process, *i. e.*, charge recombination.

Experimental evidence for photoinduced charge transfer within these donor-acceptor superstructures was obtained by performing femtosecond transient absorption (fs-TA) spectroscopy at room temperature in toluene with the individual compounds, and with the 2:1 mixture (Figure 2). Photoexcitation of DPP (83 µM) at 485 nm with ~150 fs laser pulses results in the appearance of ground state bleaching at 544 nm and 594 nm, where the ground state recovers monoexponentially with a time constant around 5 ns. Positive transient features in the range of 700 to 800 nm decay with longer time, which indicates that the S_1 state of DPP undergoes inefficient singlet triplet crossing with a time constant that is approximately two times larger than the fluorescence lifetime. The fs-TA spectrum of the PDI shows a ground state bleaching feature at 523 nm, which is slightly red-shifted compared to the ground state absorption as a result of

convolution with stimulated emission (536 nm), while a negative feature at 578 nm results from stimulated emission alone. The fs-TA spectra of the aggregates are clearly different from those of the individual compounds, as they express very strong ground state bleaches at 622 nm, which is a spectral signature of the aggregate and corresponds to photoexcitation of the system directly into its charge-separated state. The ground state corresponding to the negative feature at 622 nm recovers mainly monoexponentially (~71 %) with a time constant of 33 ± 0.5 ps, and importantly, this recovery is accompanied by the decay of a positive transient feature at 722 nm (33 ± 0.5 ps, ~70 %). With the two time constants – charge separation bleaching and ground state recover – matching each other perfectly, and the positive feature matching the spectral range of the PDI radical anion, we assigned the observed ultrafast process as charge recombination between the PDI radical anion and the DPP radical cation. In accordance with our results from applying the Weller equation and the Marcus relation, the charge separated state constitutes the lowest excited state of this novel donor-acceptor assembly (Figure 3), and its formation is kinetically favored as the respective electron transfer occurs closely between the Marcus normal and inverted region and is therefore very fast. As charge recombination (τ_{CR} = 30 ps) is much faster than fluorescence (τ_{FL} = 5 ps), the photoexcited system mainly relaxes *via* the charge-separated state, explaining our experimental observation that the charge-separated state decays radiationlessly. This understanding of the photophysical processes is a critical step in characterizing these systems and will used to anticipate the photophysics of future donor-acceptor systems composed of different donor and acceptor components.

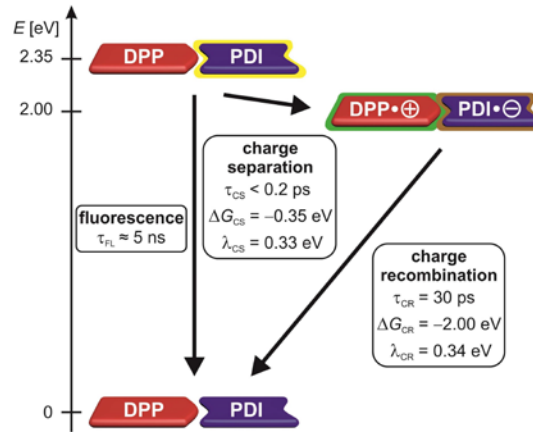

Figure 3. Energy diagram of a DPP-PDI assembly in toluene. The lowest excited state of DPP (2.07 eV) is not shown, as it is almost isoenergetic with the charge transfer state, which is the lowest excited state of the system.

The results of the studies described above are disseminated in detail in: Ley, D.; Guzman, C. X.; Adolffson, K. H.; Scott, A. M.; Braunschweig, A. B.* "Emergent Charge Transfer in Cooperatively Assembling Donor-Acceptor Superstructures" *Journal of the American Chemical Society*, **2014**, *136*, 7809.

2.2. Thin-Film Assembly and Photophysics. To make use of the advantageous emergent properties of the DPP-PDI donor-acceptor system requires that the photophysics observed in solution – which follow from the hierarchical structure – are maintained in the solid state. Our first aim was to prepare films of the supramolecular polymers and determine whether the noncovalent bonding and helical structure observed in solution persisted in the solid-state. The challenge that arises with such hierarchical systems is that no single technique is capable of characterizing structure at the molecular, nanoscopic, and microscopic length scales, and as such, multiple characterization methods were combined to create a holistic picture of the film organization.

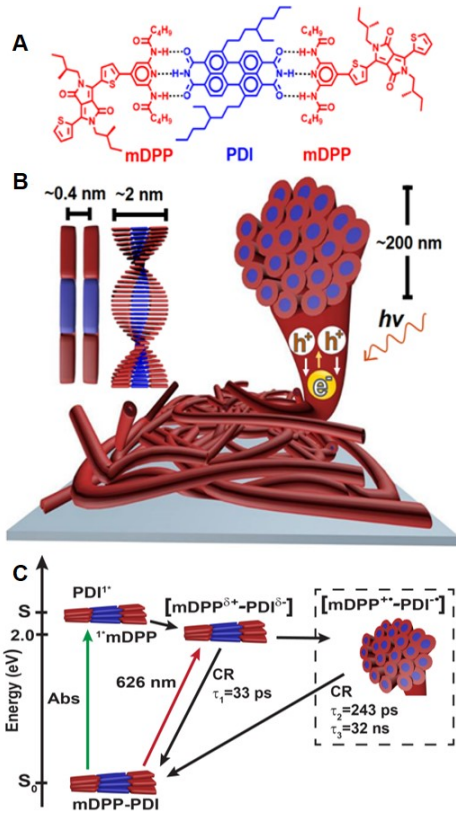

Figure 4. (A) mDPP electron donors and PDI electron acceptors. (B) Thin films preserve supramolecular structure with organization across multiple length-scales. (C) Photophysics of charge separation in mDPP-PDI thin films, whose lifetimes increase 1000-fold compared to solution.

We demonstrated previously that the DPP:PDI mixture forms 2:1 heteroaggregates with characteristic peaks in the UV-Vis spectrum, circular dichroism, and infrared spectra that are indicative of assembly. Upon mixing the donors and acceptors in thin films, a new peak in the UV/Vis spectrum emerges at 626 nm which indicates the existence of a charge-transfer state, therefore implying physical intimacy between the donor and acceptor compounds. In the drop-casted thin films, the monomeric components assemble into a disordered state. In comparison to the solution there is only a bathochromic shift of 4 nm in moving from solution (navy blue) to the solid state, indicating a high degree of consistency between molecular-scale structure in the solution and solid-state.

Attenuated total reflectance (ATR) IR spectroscopy confirms that the H-bonding that drives aggregation in solution persists into the solid state (Figure 5). The IR spectrum of the mDPP donor, red line, displays a sharp peak at 3392 cm^{-1} from the free amine peak of the homoaggregated donor structure and a broad peak at 3276 cm^{-1}, in a region and with a shape that is typically associated with H-bonded amines. Single-crystal X-ray analysis indicates that the mDPP homoaggregate adopts herring bone packing, in which one amine of the DAP group H-bonds with an adjacent mDPP, and the other remains free, and this is also likely occurring in mDPP thin films. In the donor-acceptor films, the peak corresponding to the free amine disappears because the PDI interacts with both amines, and only H-bonded amine peaks are present in the donor-acceptor IR spectrum, consistent with a structure where all DAP amines are involved in H-bonding with PDI diimide carbonyl groups. Circular dichroism spectrsocopy on the mDPP:PDI films confirms the persistence of a hierarchical structure – composed of chiral donor-acceptor helices – in the solid state. Upon aggregation with the achiral PDI, a significant bisignated Cotton effect occurs, further indicative of homochiral helical aggregates. Measurements on the donor-acceptor film confirm that the chiral superstructures are transferred successfully into the solid state.

Femtosecond transient absorption (fs-TA) and nanosecond (ns-TA) experiments were performed at room temperature on films of both the individual components (DPP and PDI) and the 2:1 DPP:PDI film. Photoexcitation of mDPP and PDI resulted in the appearance of a ground state bleach from 523-594 ad a positive excited state feature between 700 and 800 nm. After assembly of the 2:1 mixture, a new negative ground state feature appeared at 622 nm and a

positive excited state peak at 722 nm. The spectroscopic features of the donor-acceptor film are nearly identical to those in solution, with a notable difference: In the organized films, the charge carrier lifetimes increase a thousand-fold to 32 nanoseconds (Figure 4C). The increase of the recombination time is likely due to the delocalization through the long π-channels that form in the solid-state compared to solution, resulting in new electronic states that are inaccessible in solution. This result is significant because having charge carriers that persist is necessary for charges to diffuse to interfaces, which is a prerequisite for using these materials in the context of signaling or energy harvesting. Moreover, the relationship between structure and transport in these films is understood on a fundamental level, which will be used in designing properties in future systems.

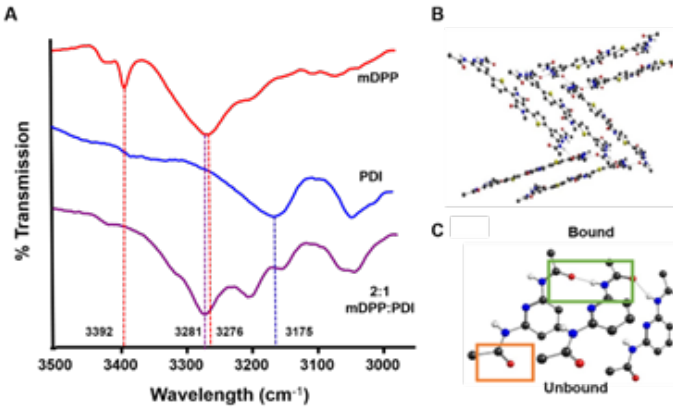

Figure 5. (A) IR Spectra of the donor (red) acceptor (blue) and mixture (purple) on film. (B) Herring bone packing of the homoaggregate of the DPP. (C) A cut out image of figure B with indication of both bound and unbound amines are present in the DAP groups of the DPP in the absence of PDI.

The results of the studies described above are disseminated in detail in: Guzman, C. X.; Krick Calderon, R. M.; Xu, H.; Peurifoy, S. R.; Yamazaki, S.; Guo, C.; Davidowski, S. K.; Rosner, H. F.; Holland, G.; Scott, A. M.; Braunschweig, A. B.* "Competitive Charge and Spin Dynamics in Multicomponent Hierarchical Donor-Acceptor Films," *Journal of Physical Chemistry C,* **2015**, *119*, 19584 – 19589.

2.3. Studies of DPP Aggregation. To control predictably organization – and thereby design properties into supramolecular materials – a fundamental understanding of the relationship between thermodynamics and aggregate size must be established. While for simple complexes, these relationships are well established, surprisingly little is known and few quantitative models exist on how thermodynamic parameters relate to structure of extended aggregates, like the supramolecular polymers studied in the context of this project. We therefore set out to establish fundamental relationships between thermodynamic binding parameters thermodynamic binding parameters (ΔH, ΔS, ΔG^{o}, and K_a) and supramolecular polymer properties, such as aggregate size and optoelectronic properties as a function of controllable solution parameters, such as temperature and concentration. The diketopyrrolopyrrole heterocyclic scaffold with appended thiophenes is an increasingly popular component of polymers, molecular electronics, and organic photovoltaics as a result of its straightforward preparation, stability, and tunable frontier molecular orbitals levels. A less recognized but equally important aspect of DPP that facilitates electronic transport and contributes to DPP optical properties is its ability to form highly ordered films owing to substantial noncovalent contributions that that occur between proximal DPP molecules in the solid-state.

The equilibrium between bound and unbound states is dependent upon both temperature and concentration, and taking spectroscopic data at a sufficient number of points along the range of conditions where the system behaves under equilibrium control can be used to create fundamentally new models that predict the response to external perturbations. To obtain these thermodynamic binding parameters, spectra of each DPP (**1** – **5**, Figure 6) in solution were taken from 300 – 800 nm at temperatures ranging from 10 – 85 °C. For the DPP derivatives that contained the DAP unit, spectra were also taken in the presence of 1% DMSO, that disrupts H-bonding, so that the energetic contributions of H-bonding could be separated from π•••π stacking, and van der Waals forces that accompany the addition of this additional group to the DPP structure. The VT UV-Vis. spectrum of **1** is shown in Figure 7, and displays the spectral features that are common to all of the DPP derivatives studied. The ground state DPP spectra is characterized by maxima at 355, 548, and 586 nm. The relative peak intensities demonstrate a dependence upon concentration and temperature resulting in isosbestic points, which are the hallmark of a thermodynamic equilibrium between two states, at 532 nm. In addition to the isosbestic points, several other aspects of this spectrum are indicative of assembly of the DPPs into *J*-aggregates, including the bathochromic shift, and the increasing absorbance ratio 548 nm/586 nm.

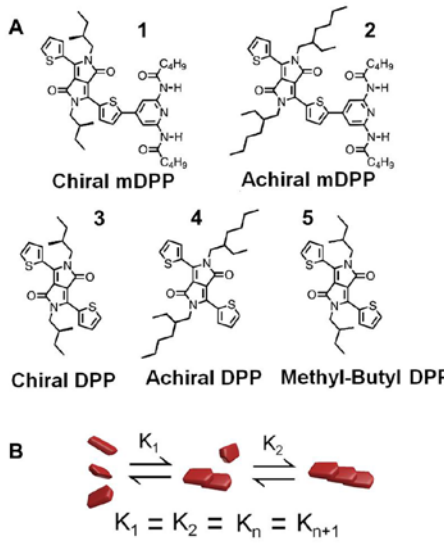

Figure 6. (A) Various DPP derivatives, whose aggregation was studied to determine how structure affects equilibrium thermodynamics. (B) Isodesmic assembly model, which assumes that binding energy is independent of stack size.

To determine the thermodynamic binding parameters for each DPP derivative, the VT UV-Vis data were fit to an isodesmic binding model to solve for ΔH, ΔS, ε_m, and ε_∞ simultaneously at every temperature, concentration, and wavelength by minimizing the sum of square residuals (SSR) between the experimental data and the model.

Briefly, the VT UV-Vis. data for a solution of a given concentration is a 3D surface comprised of a mesh of points that contain the values for temperature, wavelength, and absorbance. Finally, another variable, concentration, is considered to create a hypersurface (Figure 8), which contains all the titration data. The data is fit to the isodesmic model to provide values of ΔH, ΔS, ε_m, and ε_∞. The values obtained for DPP **1** were consistent with our previously determined results, demonstrating the reproducibility of this analytical procedure. Previously, ΔH and ΔS were determined to be −7.4 ± 0.5 kcal/mol and −3.0 ± 2.0 e.u. respectively, compared to −6.4 kcal/mol and −0.31 e.u. determined by our recent fittings. A characteristic of the supramolecular assembly of chromophores that can be used to identify aggregation is a deviation from Beer's law because the extinction coefficient of the aggregates is distinct from the monomer, and this phenomenon is observed in the VT UV-Vis spectra of all the DPP derivatives studied herein. From the fittings of the spectroscopic data, ε_m (extinction coefficient of the monomer), and ε_∞ (extinction coefficient of the supramolecular polymer) at the absorbance maximum were determined to be 1.7 x 10^4 and 2.1 x 10^4 cm^{-1} M^{-1}, respectively. Thermodynamic parameters and extinction coefficients were determined for each of the DPP derivatives to understand how subtleties of molecular structure affect aggregation.

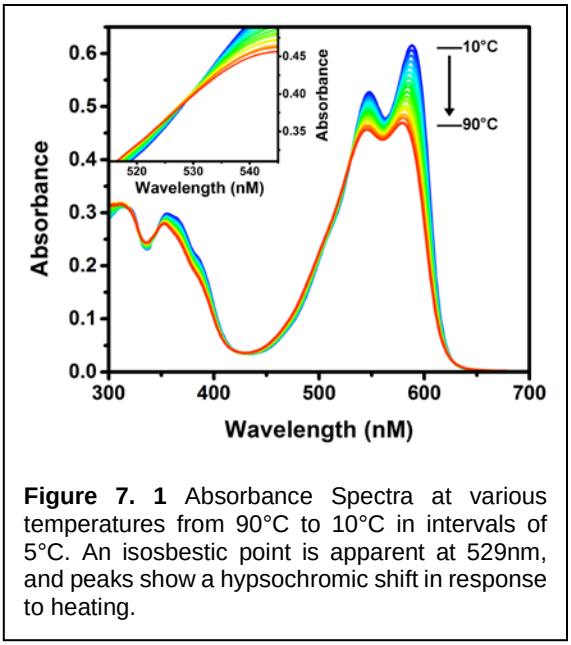

Figure 7. 1 Absorbance Spectra at various temperatures from 90°C to 10°C in intervals of 5°C. An isosbestic point is apparent at 529nm, and peaks show a hypsochromic shift in response to heating.

A major absence in the supramolecular literature that precludes the development of multi-length-scale emergent systems is the lack of mathematical models that relate molecular-level interactions to macroscopic structure. To bridge this gap, we developed a series of new mathematics that relate the thermodynamic parameters obtained through the spectroscopic fittings described above to average stack size with varying temperature and concentration (Figure 9A). Because these are supramolecular systems, their sizes – and as a direct consequence photophysical properties – change in response to these solution variables. In addition, it must be understood that these aggregates are under equilibrium control, so that average stack size is a distribution rather than a single value, and equations have been developed to determine the characteristics of these distributions (Figure 9B). This work represents a major advance in that now macroscopic structure – from whence emergent properties directly arise – can be anticipated from easily acquired thermodynamic assembly parameters.

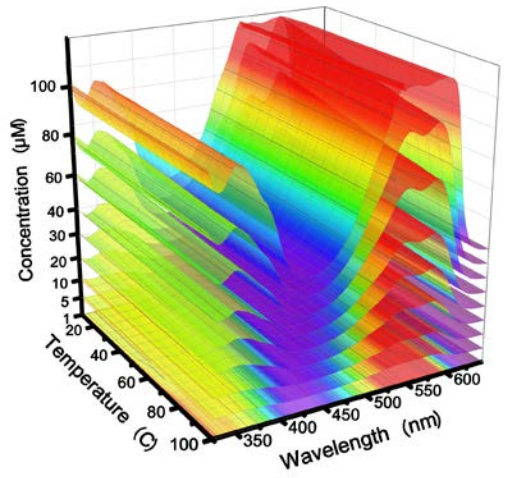

Figure 8. A hypersurface displaying absorbance spectra of **1** at varied concentration. Each surface is a set concentration, with absorbance scaled and displayed along the same axis.

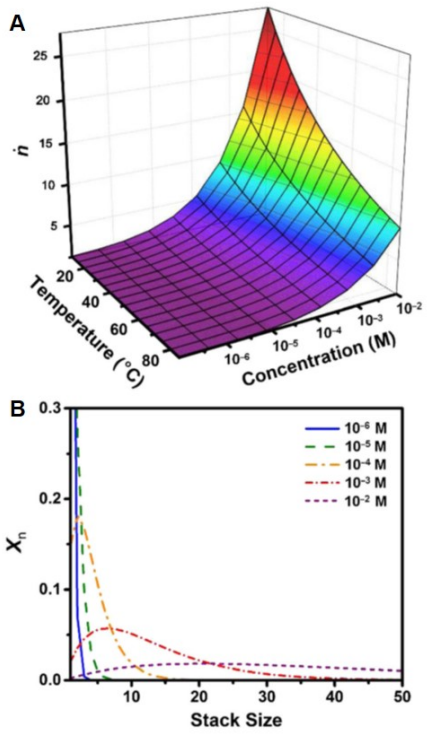

Figure 9. (a) Mean stack size of **1**, n, is displayed at various temperatures and concentrations (b) Mass fraction, Xn of **1** is displayed at 25 °C for various solution concentrations.

The results of the studies described above are disseminated in detail in: Zhou, Y.; Guzman, C. X.; Helguero-Kelley, L.; Captain, B.; Braunschweig, A. B.* "Isolating Structural Effects on Diketopyrrolopyrrole Aggregation" *Journal of Physical Organic Chemistry*, **2016**, DOI: 10.1002/poc.3548.

2.4. Film Transport Properties of PDI Derivatives. A goal of this project involves translating advantageous optoelectronic properties observed in solution of DPP and PDI derivatives to the solid-state, where the emergent phenomena could be explored in the context of sensing, computing, communication, and energy harvesting. To this end, we explored the properties of PDI derivatives, in collaboration with the Marohn Group at Cornell University, by carrying out surface potential measurements using frequency-modulated Kelvin probe force microscopy (FM-KPFM, Figure 10).For electron conductors like PDIs, the major source of charge trapping is expected from thermodynamics to be reaction of the anion radical ($PDI^{\bullet-}$) with water and oxygen to form shallow, reversible traps. We examined charge trapping in transistors fabricated with "high-LUMO," thermodynamically unstable PDI derivatives. We demonstrate through maps of trapped charge that trapping reactions take place throughout the channel upon a positive gate bias. We also present the first trap-clearing spectra measured in n-channel organic semiconductors. We found that some PDI traps are cleared upon exposure to light, but we find no LUMO-level trend in trap-clearing behavior. In one PDI derivative, we observe possible spectroscopic evidence for different trapping mechanisms on bare versus HMDS-passivated SiO_2. These fundamental studies assist us in understanding how the film morphology and defects in that morphology – driven by supramolecular forces – governs how charges move through the film.

Films of the PDIs were prepared, and a positive gate bias was applied for two minutes, followed by FM-KPFM imaging of residual trapped charge with the gate set to zero volts. The gate must be set to zero in order to image trapped

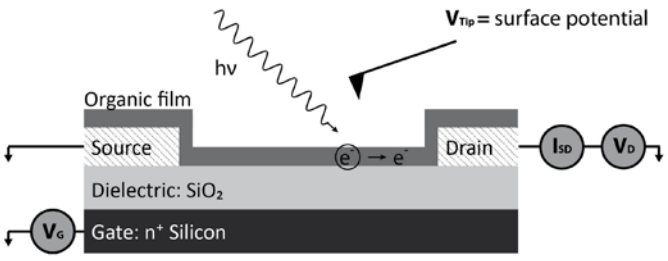

Figure 10. Sketch of trap-clearing spectroscopy experiment. Trapped charge is induced in a PDI film by applying a positive gate bias to the bottom-contact transistor substrate. Trapped charge in the semiconductor film (circled e^-) is converted to free charge (free e^-) under visible light. The progress of this trap-clearing is monitored by tracking the surface potential versus time with FM-KPFM.

charge, since free charged induced by the gate will screen the trapped charge. The source and drain were grounded during the measurement. Trapped charge appears as regions of negative potential (blue), while the more positive source and drain electrodes are visible above and below the transistor channel. As the scans progress from left to right in the dark, trapped charge is cleared thermally. The most negative regions at left are not trapping "hot spots" but rather represent the initial concentration of trapped charge after the gate is turned off. Transient surface potentials obtained by averaging several rows of potential data in the channel are plotted below each transistor map (Figure 11e-h). For the PDI derivatives studied, traps clear thermally in 5-10 minutes. Traps can be cleared by visible light through two possible processes: excitation of the neutral semiconductor or excitation of the trap. In both cases, after excitation, the trapped electron is transferred to the neutral PDI. These light enhanced trap-clearing processes compete with the thermal trap-clearing process, where the electron is transferred directly from the trap to a neutral PDI molecule with no additional optical excitation. When the PDI anion radical is formed ($PDI^{\bullet-}$, final state), the charge is mobile again and can be transported to an electrode and out of the film.

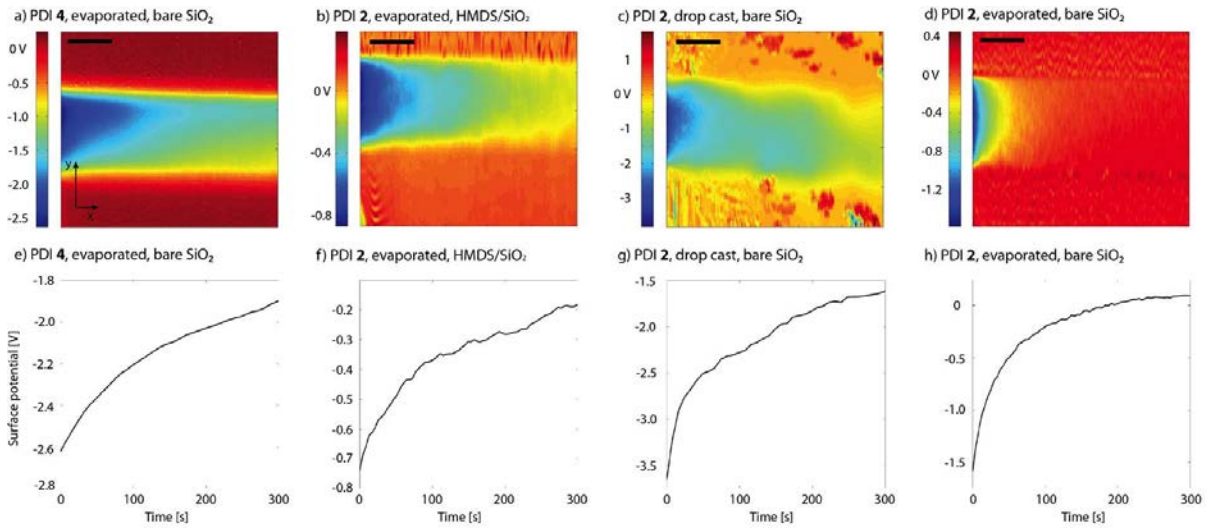

Figure 11. Long-lived electron traps in PDI thin-film transistors. Top row: FM-KPFM images of trapping in the transistor channel after a 2 minute positive gate bias of (a,b,d) +5V or (c) +15V. The traps clear over time as each scan progresses from left to right. Bottom row: Several rows of data in the center of each channel were averaged to produce surface potential transients of thermal trap-clearing. (a,b) PDI 4 (dibromo PDI) thermally deposited on bare SiO_2. (c,d) PDI 2 (dipyrrolidine PDI) thermally deposited on HMDS-treated SiO_2. (e,f) PDI 2 drop cast on bare SiO_2. (g,h) PDI 2 thermally deposited on bare SiO_2.

We find that electron traps in four high- LUMO PDI derivatives exhibit a wide range of responses to visible light that do not track with the LUMO level. In one PDI derivative studied on bare and HMDS-treated SiO_2, we found that trap-clearing rates were enhanced by visible light, but that the highest rates of trap-clearing were observed at different wavelengths in the two samples. Trap-clearing on HMDS-treated SiO_2 was consistent with excitation of the neutral PDI, but a different trap-clearing mechanism, possibly involving the PDI radical anion, appears to be dominant for traps on bare SiO_2. We concluded that thermodynamic stability alone does not predict the behavior of electron traps in PDI thin-film transistors, and we anticipate that our observations will serve as a foundation for further microscopic studies of trap-formation and trap-clearing mechanisms in these materials.

The results of the studies described above are disseminated in detail in: Smieska, L. M.; Li, Z. Ley, D.; Braunschweig, A. B.; Marohn, J. A. “Trap-Clearing Spectroscopy in Perylene Diimide Derivatives” *Chemistry of Materials*, **2016**, *28,* 813 – 820.

2.5. Complexity Transport Model of Donor-Acceptor Superstructures. The current ability to synthesize polymer materials from the size of molecular aggregates up to two or three dimensional crystals, offers a new area of common interest for chemistry and solid state physics, as well as novel potential optoelectronic applications to light harvesting devices. In addition to the materials challenge, however, there is a need for simple yet plausible models which can span the spectrum of length-scales being fabricated and examined, in order to help guide future design. We developed a simple stochastic model, based on the DPP-PDI donor-acceptor superstructures, which can cover such a length-scale range. It incorporates the dynamics of charge transfer and electron/hole recombination in arbitrarily complex polymer networks. As a test of the model’s predictive power, we compared it to experimental data on hierarchical donor-acceptor supra-molecular polymer films composed of a 2:1 mixture of mDPP electron donors and PDI electron acceptors. Using realistic parameter values from the literature, we obtain good agreement with experiments: in particular, it provides an explanation for the 1000-fold increase in the electron-hole recombination time for this structure when it is measured in solution as compared to its solid state form. This new model is a major fundamental advance because it bridges molecular- and micro-scale models of charge separation and transport to explain macroscopic conductivity.

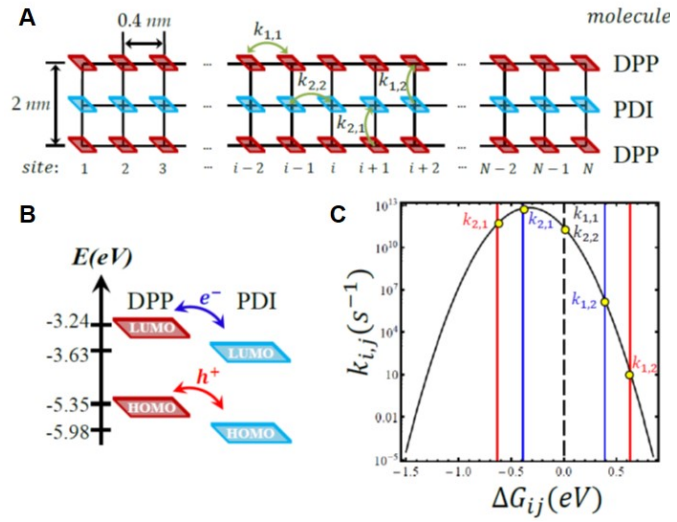

Figure 12. (Color online) Supra-molecular polymer modeling. (A) Network structure for a single chiral supra-molecular polymer of 3 × N sites according to π-stacking and H-bonding molecular assembling. Dark red and cyan squares represent DPP and PDI molecular sites, respectively. Transfer rates from DPP to PDI is referred as $k_{2,1}$ and back transfer $k_{1,2}$, as illustrated by green arrows. The transfer rate from molecule **1**(**2**) to DPP (**1**) or PDI (**2**) is referred as $k_{1,1}$($k_{2,2}$). (B) HOMO/LUMO energy levels associated to each molecule type. (C) Transfer rates as a function of Gibbs’ free energy according to Marcus theory for a reorganization energy of λ = 0.33eV and transfer integral |V | = 35meV. Vertical lines point to the transfer rates values for electrons (blue) and holes (red).

The 2:1 mixture of mDPP electron donors and PDI electron acceptors assemble into helices at room temperature as a result of from H-bonding and π-π stacking. We modeled a single helical polymer with a simple two dimensional network with 3 × N molecular sites as shown in Figure 12A. Given that there are two types of molecules, there are four different transfer rates; from DPP to PDI (i.e., $k_{2,1}$), from PDI to DPP (i.e., $k_{1,2}$), from DPP to DPP (i.e., $k_{1,1}$) and from PDI to PDI (i.e., $k_{2,2}$). These rates are calculated by means of Marcus theory with overall reorganization energy λ = 0.33 eV, free energy change equal to $\Delta G_{i,j} = h\omega ij = E_i - E_j$, for energy values as given on Figure 12B. Transfer integrals were estimated from naphthalene dimers to be |V | = 35meV.

Figure 12C illustrates the transfer rates for the different electron (blue) and hole (red) transitions, where we consider electron transfer through LUMO and holes through HOMO. Interestingly, in both cases $k_{2,1} >> k_{1,2}$, hence the probability for a charge carrier to transfer from DPP to PDI is much larger than its back transfer. Therefore, we can effectively describe the 3 × N network into a linear chain with the respective transfer rates $k_{1,1} = k_{2,2} = 0.23$ ps^{-1} at room temperature (T = 303 K).

The manuscript reporting this work is currently under preparation.

2.6. Understanding TEM Induced Damage in Biohybrid Systems. In an effort to characterize the donor-acceptor systems using transmission electron microscopy (TEM), we found that beam damage affected our ability to characterize these structures that are comprised of both “hard” and “soft” organic components. Thus, in an effort to understand beam damage, we attempted understanding dose-rate effects on imaging of more traditional hard/soft materials, namely peptide coated Pd/Pt nanoparticles. In this work, we showcase that through precise control of the electron dose rate, state-of-the-art large solid angle energy dispersive x-ray spectroscopy mapping in aberration-corrected scanning transmission electron microscope is capable of faithful and unambiguous chemical characterization of the Pt and Pd distribution in a peptide-mediated nanosystem. This low-dose rate recording scheme adds another dimension of flexibility to the design of elemental mapping experiments, and holds significant potential for extending its application to a wide variety of beam sensitive hybrid nanostructures, including the DPP-PDI donor-acceptor supramolecular polymers that were the focus of this project.

In an attempt to avoid electron beam introduced compositional artifacts, we carefully monitored the changes of the less stable small nanoclusters in the simultaneously obtained STEM image. The acquisition was immediately terminated once detectable structural alterations emerge. Under this acquisition scheme, the low accumulated electron dose results in a poor SNR in the integrated energy dispersive X-ray (EDS) maps, and is unable to produce reliable image features above background noise. Furthermore, we noticed that despite the electron dose of the second set of EDS maps being about an order lower than the first one, they share a similar dose rate. Previous studies of beam-sensitive nanocatalysts and 2D materials using TEM in-line holography suggested that electron dose rate, instead of the total dose, is important for obtaining high SNR images even at atomic resolution. They proposed that as long as it is working under a structure-reversible dose rate, the specimen recovers before the next electron hits it; meanwhile, signals add up to provide a reasonable SNR. Here, we tested this ‘divide-and-conquer’ philosophy in STEM-EDS mapping.

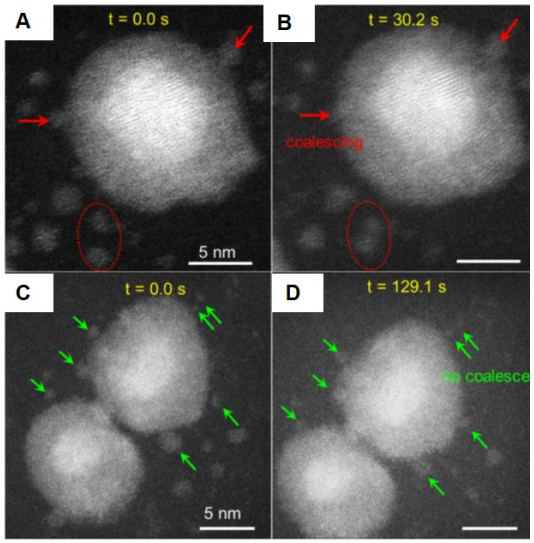

Figure 14. Time sequence annular dark field scanning-transmission electron microscopy (ADF-STEM) images of the peptide-mediated PdPt nanoparticles under dose rate of (a) and (b) 1.4 × 10^4 e Å^{-2}s and of (c) and (d) 1.8 × 10^3 e Å^{-2} s.

Firstly, to establish a safe electron dose rate for this peptide-capped bimetallic nanoparticle sample during the EDS chemical analysis, the effect of different dose rates on the specimen was tested in STEM imaging mode by varying the probe current, magnification and scan duration. As demonstrated in Figure 13, we found that it is the high electron dose rate rather than the accumulated dose that induces visible structural alterations to the nanoparticles. Under a relatively high dose rate of 1.4×10^4 e $Å^{-2}$ s in Figures 13A and 13B, coalescing of nanoparticles is observed at the surface of the large nanoparticle shell as well as at smaller less stable nanoclusters after only 30 s imaging; however, no obvious coalescing was observed for the positions of the nanoclusters at a lower dose rate of 1.8×10^3 e $Å^{-2}$ s even after a prolonged scan of over 2 min (Figures 13C and 13D). We also noticed that a very low dose rate such as below 10^2 e $Å^{-2}$ s could also be problematic, for it requires even longer scanning time that is challenging for both specimen drift and accumulated carbon contamination. On the other hand, it is interesting to note that the large nanoparticles sometimes show clear lattices (on-zone) especially at the core, while this is not the case for the small clusters. This suggests that it is likely the large nanoparticles are more crystalline than the smaller clusters, however, one cannot rule out that the small clusters may not be in a zone axis orientation or perhaps are more mobile than the larger particles.

Based on the above, electron dose rates in the order of 10^2 e $Å^{-2}$s were adopted for STEM-EDS mapping (in contrast to, for example 2×10^3 e $Å^{-2}$s used for inorganic bimetallic nanoparticle systems). Comparing with the non-controlled acquisition, the low dose rate at each pixel allows a much longer integration and thus maintains good EDS signal statistics, while effectively preserving the sample integrity. From these EDS elemental maps with excellent SNR we can then conclude that the large nanoparticles are indeed core/shell structures consisting of Pt at the core, agreeing well with the prediction from the ADF-STEM contrast, and Pd mainly dominates the shell, whereas the small nanoclusters are mainly monometallic Pt. If we put the three EDS mapping schemes of the same biomediated bimetallic nanoparticles side-by-side, it is clear that neither of the two high-dose-rate approaches can provide a reliable answer to the nanoparticle metallic composition. Without going through the dose rate test and working under a safe rate, we may draw wrong conclusions, such as that the large nanoparticles have an alloyed structure, as suggested by the intermixed Pt and Pd distributions. This can further mislead the development of synthesis-structure correlation and hinder our understanding on inorganic–organic interactions. With this improved understanding of dose-rate on hybrid hard/soft materials, we can now approach the problem of imaging DPP-PDI supramolecular polymers with the aim of achieving sub-1 nanometer resolution.

The results of the studies described above are disseminated in detail in: Zhu, Y; Munro, C; Olszta, M. J.; Edwards, D. J.; Braunschweig, A. B.; Knecht, M. R.; Browning, N. D. “Dose-rate controlled EDX mapping of biohybrid nanoparticles” *Semiconductor Science and Technology,* **2016**, *31*, 084002*.*

2.7. Overview of Design Rules. In an effort to fulfill the mission of dissemination of the fundamental science developed in the context of this project, we have published a review article describing how molecular topology, supramolecular assembly, and electronic structure work synergistically to create emergent properties in multi-length-scale materials. Living systems produce materials with complex structures and useful optoelectronic properties by bringing

together simple organic components such that the resulting nanoscale organization triggers new interactions with electromagnetic fields, ions, and charges. Some particularly elegant examples include green fluorescent protein, rhodopsin, and the bacterial reaction center that possess order on the molecular and nanometer scale and whose responses to external stimuli include switchable fluorescence, signaling, and conversion of light to chemical energy, respectively. Two noteworthy attributes that these materials share are that they are composed almost entirely of organic matter and possess the characteristic of emergence-upon-assembly – in which new properties are only observed upon the formation of hierarchical order, whose structure across the molecular-to-macroscopic continuum is dictated by noncovalent interactions programmed into the individual molecular components. As a result of this spatial arrangement, new electronic interactions arise that enable remarkable functionality, such as the conversion of light to chemical energy in photosynthesis. Current synthetic routes are unable to reproduce such multi-length-scale order and advanced function with artificial materials because the large sizes and the complex assembly processes involved exceed the limits of modern manufacturing capabilities. Despite the prevalence of the elegant and functional optoelectronically active structures found in Nature, the materials that continue to dominate the optics and electronics industries are crystalline and inorganic, and are not competitive with natural systems in terms of cost, toxicity, and weight, but the drawback of using biomaterials as replacements is that their lack of stability and poor processiblity has precluded their device integration. So for both industrial applications and to gain fundamental insight into the complex machinery of life, it is important to continue developing

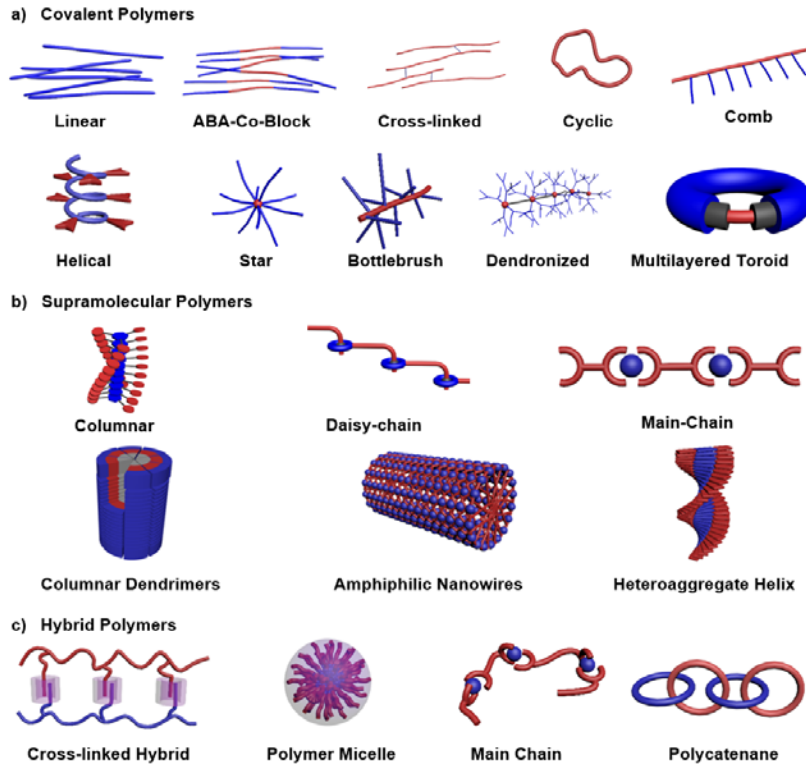

Figure 14. Polymer topology. Polymers derive their properties from the monomer composition, sequence, and arrangement in space (topology). Polymers can be classified in terms of the types of bonding that hold the monomers together, which include covalent, noncovalent, or a hybrid of both. (a) Covalent polymer topologies, where monomers are held together by covalent bonds, are broadly studied in the following categories: cyclic, helical, star, bottlebrush, dendronized, and multilayered toroid. (b) Supramolecular polymer topologies, where monomers are brought together by noncovalent bonds, are broadly studied in the following categories: columnar, daisy-chain, main chain, columnar dendrimers, amphiphilic nanowires and heteroaggregate helices. (c) Supramolecular-covalent hybrid polymers possess functional groups capable of noncovalent recognition appended to covalent polymers, and are studied in the following categories: cross-linked hybrids, polymer micelles, linear hybrids, and polycatenanes.

organic materials that possess hierarchical order and stimuli-responsive optical and electronic behavior.

By adopting a biomimetic design approach where hierarchical assembly and emergent behavior are equally important goals of molecular design, researchers have successfully developed organic materials with impressive optical, mechanical, and electronic properties. Building blocks of both biological and synthetic origin have been leveraged to achieve diverse molecular architectures and functions, and the common element among all these components is that reversible, noncovalent bonding directs superstructure formation. A particularly noteworthy subset of these bioinspired materials, and the subject of this minireview, are the supramolecular polymers, which are macromolecules whose monomers are held together principally by noncovalent bonding through either H-bonding, π•••π stacking, metal coordination, or mechanical bonding (Figure 14). Like oligonucleotides and oligopeptides, they combine the benefits of polymer chemistry and supramolecular chemistry to achieve properties that are absent in the individual components. The benefits of supramolecular polymers include their ease-of-preparation from simple building blocks, dynamic macromolecular composition, and hierarchical structure. The remarkable new emergent properties can include the ability to embed information within molecular scaffolds, impressive mechanical performance, structural changes in response to biological stimuli, and beneficial interactions with electromagnetic fields. Thus, many compelling reasons exist to continue developing new supramolecular polymer-based solutions to address pressing research challenges.

Supramolecular polymers have been explored in the context of medical, electronic, energy, and environmental applications, and several excellent reviews exist already related to this rapidly growing research field. Rather than providing another comprehensive article, our aim was to highlight a few exemplary supramolecular polymers and related systems that achieve one particularly important photophysical property, namely photoinduced charge separation, which is a critical step in artificial photosynthesis. By highlighting their commonalities, we derived design principles for creating new organic materials for energy harvesting, signaling, and sensing. Supramolecular polymers with emergent optoelectronic properties are achieved when considerable attention is given to the three pillars of photoactive supramolecular polymer design, which are topology, noncovalent assembly, and electron and spin dynamics. This minireview discussed the design of artificial supramolecular polymers with emergent optoelectronic properties, where the three aforementioned criteria have been successfully employed to create materials that collect photons and convert them to charges that can be subsequently collected. Particular attention was devoted towards the multicomponent supramolecular polymer prepared in our group composed of a DPP electron donor and a PDI electron acceptor that, following assembly into superstructures with a 2:1 donor-acceptor ratio, produces long-lived charge carriers following irradiation with visible light.

The results of the studies described above are disseminated in detail in: Peurifoy, S. R.; Guzman, C. X.; Braunschweig, A. B.* “Topology, assembly, and electronics: three pillars for designing supramolecular polymers with emergent optoelectronic behavior” *Polymer Chemistry,* **2015**, *6*, 5529 – 5539.

3. Outlook. Over the course of this project, we have advanced significantly our fundamental understanding of the assembly and emergent optoelectronic properties of the unique,

supramolecular DPP-PDI donor-acceptor superstructures in solution and in thin films. Specifically, we have quantified assembly thermodynamics, characterized multi-length-scale structure in solution and the solid state – confirming that supramolecular structure is maintained in this transition – and characterized how photophysical processes change in different states. Beyond the context of this particular supramolecular system, these studies have resulted in quantitative models relating thermodynamic assembly parameters to aggregate size, thereby providing a bridge for predicting structure across the molecular-to-macroscopic continuum that match closely experimental data. With regards to the emergent photophysics, we have mapped how energy levels at the molecular level can be used to produce photoinduced electron transfer upon assembly, and subsequently we used a complexity-based model to describe how molecular structure and electronic-coupling describe transport across macroscopic distances. Thus these studies have laid out fundamental and quantitative models for predicting behavior of supramolecular systems across length scales, and these advances will lead to new structures with emergent properties for addressing forthcoming DoD needs related to sensing, energy, and materials.

Several major questions remain that we continue to address. Namely, we have limited out studies to mDPP-PDI, but we have not yet investigated how subtleties in molecular structure affect film structure, stability, and photophysics. Thus, we intend to investigate how small changes to molecular structure affect macroscopic film structure. In addition, how do these changes in molecular structure affect film stability and transport properties? Finally, we will address whether these studies lead to more sophisticated design rules that enable the control of electronic transport across macroscopic scales based solely upon the molecular structure and frontier molecular orbitals of the individual components that comprise supramolecular systems.

4. Publications

[6] Zhu, Y; Munro, C; Olszta, M. J.; Edwards, D. J.; Braunschweig, A. B.; Knecht, M. R.; Browning, N. D. “Dose-rate controlled EDX mapping of biohybrid nanoparticles” *Semiconductor Science and Technology,* **2016**, *31*, 084002*.*

[5] Smieska, L. M.; Li, Z. Ley, D.; Braunschweig, A. B.; Marohn, J. A. “Trap-Clearing Spectroscopy in Perylene Diimide Derivatives” *Chemistry of Materials*, **2016**, *28,* 813 – 820.

[4] Zhou, Y.; Guzman, C. X.; Helguero-Kelley, L.; Captain, B.; Braunschweig, A. B.* “Isolating Structural Effects on Diketopyrrolopyrrole Aggregation” *Journal of Physical Organic Chemistry*, **2016**, *In Press.* DOI: 10.1002/poc.3548
• Early Career Excellence in Physical Organic Chemistry Award Paper

[3] Guzman, C. X.; Krick Calderon, R. M.; Xu, H.; Peurifoy, S. R.; Yamazaki, S.; Guo, C.; Davidowski, S. K.; Rosner, H. F.; Holland, G.; Scott, A. M.; Braunschweig, A. B.* “Competitive Charge and Spin Dynamics in Multicomponent Hierarchical Donor-Acceptor Films,” *Journal of Physical Chemistry C,* **2015**, *119*, 19584 – 19589.

[2] Peurifoy, S. R.; Guzman, C. X.; Braunschweig, A. B.* “Topology, assembly, and electronics: three pillars for designing supramolecular polymers with emergent optoelectronic behavior” *Polymer Chemistry,* **2015**, *6*, 5529 – 5539.

[1] Ley, D.; Guzman, C. X.; Adolfsson, K. H.; Scott, A. M.; Braunschweig, A.B.* “Emergent Charge Transfer in Cooperatively Assembling Donor-Acceptor Superstructures” *Journal of the American Chemical Society,* **2014**, *136*, 7809 – 7812.