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Photoactive organic material discovery with combinatorial supramolecular assembly

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Organic semiconductors have received substantial attention as active components in optoelectronic devices because of their processability and customizable properties. Tailoring the organic active layer in these devices to exhibit the desired optoelectronic properties requires understanding the complex and often subtle structure–property relationships governing their photophysical response to light. Both structural organization and molecular orbitals play pivotal roles, and their interactions with each other are difficult to anticipate based upon the structure of the components alone, especially in systems comprised of multiple components. In pursuit of design rules, there is a need to explore multicomponent systems combinatorially to access larger data sets, and supramolecularly to use error correcting, noncovalent assembly to achieve long-range order. This review will focus on the use of supramolecular chemistry to study combinatorial, hierarchical organic systems with emergent optoelectronic properties. Specifically, we will describe systems that undergo excited state deactivation by charge transfer (CT), singlet fission (SF), and Förster resonance energy transfer (FRET). Adopting combinatorial, supramolecular assembly to study emergent photophysics promises to rapidly accelerate progress in this research field.

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1. Introduction

Organic materials are increasingly investigated in solar energy harvesting devices,^{1–3} sensors,^{4–6} field effect transistors,^{7–9} and

catalysts.^{10–13} The active components that drive these applications are organic semiconductors—small molecules or polymers that are conductive following charge injection or upon photoexcitation. Organic semiconductors offer several potential

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focuses on supramolecular organic semiconductors and their fabrication into photovoltaic devices. Outside of lab he enjoys cooking, playing soccer, gardening, and astrophotography.



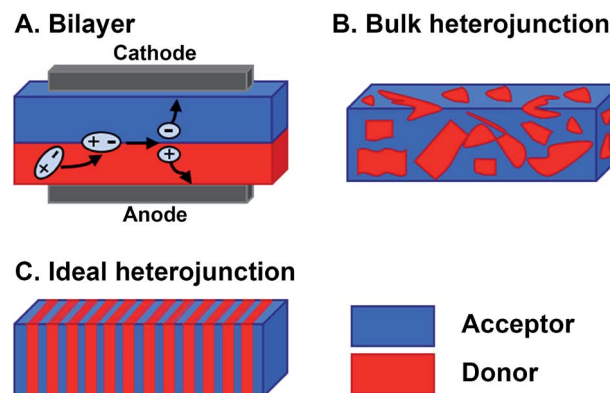
Sankarsan Biswas obtained his B.Sc. in Chemistry from University of Calcutta, India and M.Sc. in Chemistry from Indian Institute of Technology Madras (IIT Madras). After his M.Sc., he joined the PhD program in Chemistry at the CUNY Graduate Center. He is currently working under the guidance of Professor Adam B. Braunschweig and Professor Rein V. Ulijn at the Advanced Science Research

Center (ASRC). Sankarsan's research focuses on self-assembly of supramolecular organic semiconductors, covering fundamental studies to materials design for various applications.



A portrait of Dr. David A. Clark, a middle-aged man with a shaved head and a light beard, wearing a light blue button-down shirt. He is smiling slightly and looking directly at the camera. The background is a blurred outdoor scene with trees and a brick building.

These operational criteria for organic photovoltaics dictate that the FMO energy levels and electronic coupling, which govern the dynamics of charge transfer, and film morphology are treated as equally important considerations in the design of the components of the BHJ layer, but this is not commonly reflected in practice. Rather, the donor and acceptor components are typically designed such that upon photoexcitation, the relative energies of the FMOs favor electron transfer from donor to acceptor, while morphology is an afterthought that is optimized *via* trial and error.^{20,23,24} Typically, two component systems are spin-coated together to create blended active layers, and the most common strategies for improving the mixing of donors and acceptors during this process include installing



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Combinatorial approaches are used extensively to address some of the most vexing challenges in drug discovery,³⁸ material science,³⁹ and nanotechnology.⁴⁰ Combinatorial science involves synthesizing libraries of components that differ in some key structural aspect, and screening them for a particular property.³⁸ This strategy results in large data sets that are used

Homoaggregates

to unearth trends and outliers without devoting exorbitant resources to time-consuming design, and, as a result, naturally lends itself to solving complex scientific challenges. Combinatorial approaches have been increasingly adopted for understanding subtle structure–activity relationships in photoresponsive organic materials, where the ability to rationally design ensemble properties continues to elude researchers.^{41–43} Deactivation pathways such as charge transfer (CT),^{44,45} singlet fission (SF),^{46,47} and Förster resonance energy transfer (FRET)^{48,49} are all in competition following the photoexcitation of organic donor–acceptor mixtures, and the factors that determine whether one occurs preferentially over another is the result of an interplay between kinetic and thermodynamic driving forces as well as the orientation of the components and the long-range film order. Here, we focus on

the use of supramolecular ordering with combinatorial approaches to achieve and optimize CT, SE, and FRET in hierarchical, photoactive, organic semiconductor materials.

2. Combinatorial supramolecular photoactive assemblies

This review will present several recent examples of combinatorial, supramolecular photoactive systems that undergo CT, SE, or FRET following assembly. This section describes how chromophores were chosen to promote certain deactivation pathways and the role of combinatorial, supramolecular assembly in controlling and understanding their deactivation. In doing so we hope to show the value of adopting this approaches to study and optimize photoactive organic materials as active elements in various emerging optoelectronic applications.

2.1 Charge transfer

CT involves the transfer of an electron from an electron donor to an electron acceptor (or a hole from an acceptor to a donor) upon photoexcitation, and is the most common strategy for harvesting energy from light in OPVs (Fig. 3C). Ground state CT is also possible if the electron donor and the electron acceptor sufficiently mix orbitals to produce a partial CT state.^{50–52} The charges generated from CT must then have contiguous pathways to diffuse to electrodes before being lost to geminate (exciton electron–hole pair) and non-geminate recombination if they are to be collected.⁴⁴ This phenomena is governed by factors described in the Marcus equation,⁵³ whose major considerations are donor–acceptor distance, electronic coupling, and the thermodynamic driving force of charge transfer. As such, designing FMOs to favor charge separation and creating ordered pathways for charge diffusion are critical considerations of donor and acceptor design.⁵⁴

FMOs can be tuned by functionalizing the organic semiconductors with electron donating or withdrawing substituents,^{55,56} however, changes to molecular structure en route to tailoring FMOs will inevitably affect packing geometry, and, consequently, the electronic coupling between donors and acceptors. There are many examples of organic donor–acceptor systems that undergo photoinduced CT, and the ways in which they bring together the components involve noncovalent assembly,⁵⁷ polymer blending,^{58,59} covalently linking,⁶⁰ and inorganic bonding to form covalent organic frameworks (COFs).^{61,62} An example of a combinatorial system in which forming contiguous conduction pathways is also considered in conjunction with charge transfer to create active layers for OPVs as critical design criteria is the work of Jin *et al.*⁶³ In this study, they describe a system in which metallophthalocyanine donors and diimide acceptors (Fig. 3A) are joined *via* the formation of boronate esters to form a COF with emergent photoinduced CT following assembly. This system is also significant because there has also been a push for more cost-effective, air-stable, and FMO-tunable electron acceptors because fullerenes, which are typically used as acceptors in

A. Molecular structures of active components



B. Assembly driven photoinduced charge-delocalization



C. Photophysics for charge transfer



Fig. 3 Charge transfer (CT) in a covalent organic framework (COF). (A) Metallophthalocyanine donor and diimide acceptor components. (B) Assembly into columnar arrays with emergent CT behavior. (C) Photoinduced CT mechanism *via* excitation and photoinduced electron transfer (PET).⁶³

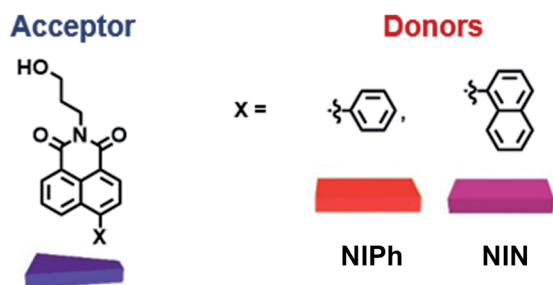
OPVs, degrade relatively quickly in ambient conditions, absorb visible light weakly, and their isotropic structure makes using them for creating hierarchical order challenging.^{16,64} The donors and acceptors in these COFs assemble into columnar arrays *via* $\pi\cdots\pi$ stacking. These stacks promote charge migration and increase the lifetime of charges produced following photoinduced CT by providing contiguous pathways for migration (Fig. 3B). This system is combinatorial in that Cu, Ni, and Zn are explored as different metal centers in the phthalocyanine (Pc), and the three diimides have different extents of π -conjugation, but they all organize as a result of the same conserved boronate ester formation. As such, the six components produce nine donor–acceptor systems that can be formed and screened for their ability to separate charges upon photoexcitation (though only six were actually investigated). Crystal structures resolved by XRD confirm slipped stacked



Another example of achieving CT with a combinatorial, supramolecular library of donor and acceptor components was reported by Mallia *et al.* who studied a series of nonparallel stacked dyad chromophores.⁶⁵ A Suzuki–Miyaura cross-coupling reaction was used to bring together covalently naphthalimide (NI) acceptors with either naphthalene (N) or phenyl

2.2 Singlet fission

A. Molecular structures of active components



B. Assembly driven photoinduced charge-delocalization

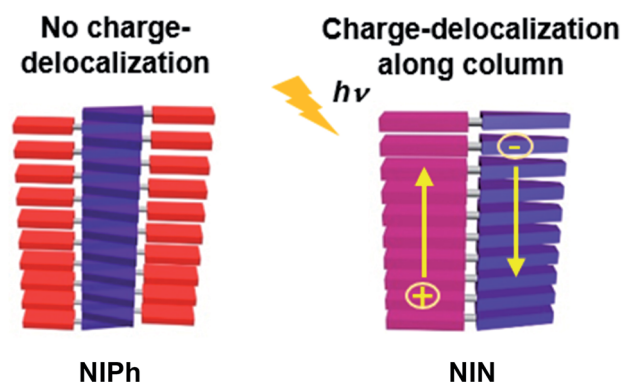
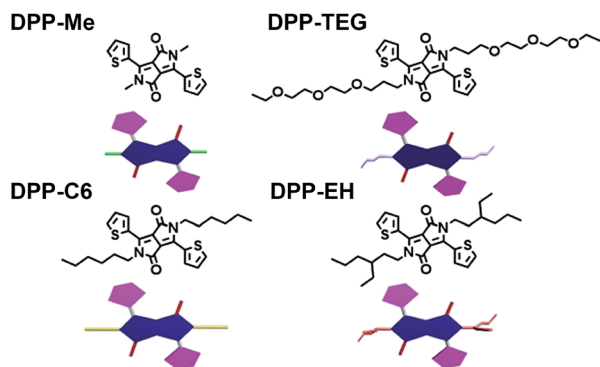
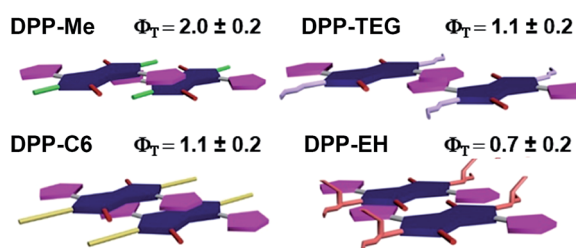


Fig. 4 Charge transfer (CT) in a supramolecular dyad system. (A) Naphthalimide (NI) acceptor with either naphthalene (N) or phenyl (Ph) appended donors. (B) Emergent photoinduced charge separation occurs in NIN superstructures but not NIPh.⁶⁵

A. Molecular structures of the components



B. Assembly induced singlet fission



C. Photophysics for singlet fission



Fig. 5 Singlet fission (SF) in self-assembled diketopyrrolopyrrole (DPP). (A) Methyl (Me), *n*-hexyl (C6), triethylene glycol (TEG), and 2-ethylhexyl (EH) substituents appended to the DPP core nitrogen. (B) Varying slip-stack geometries caused by sterics, which affect intermolecular orbital coupling and ultimately SF yields (Φ_T) and lifetimes. (C) SF mechanism, where one photon generates two excitons.⁷³

maximize coupled triplet formation, but also promote their decoupling—a necessary event for harvesting these excited states without losing them to recombination. For harvesting decoupled triplets, fullerenes have been used with pentacene, essentially promoting CT after the SF event, to make solar cells.⁷⁸ Control over the heterojunction organization and overall active layer morphology, and stability in ambient conditions, however, are still ongoing challenges whose resolution could lead to higher SF yields as well as greater collection of decoupled triplets.

Mauck *et al.* used a combinatorial approach to study SF kinetics and triplet yields in DPP by installing different side chains off the DPP core nitrogen (Fig. 5A).⁷³ This is

a combinatorial, supramolecular system in that in their work, DPP derivatives with methyl (Me), *n*-hexyl (C6), triethylene glycol (TEG), and 2-ethylhexyl (EH) substituents on the nitrogen of the DPP core are prepared using the same straightforward chemistry. These DPPs assemble into stacks, and crystal structures of these materials show that the side chains alter the DPP stacking torsion angle offset along with transverse and longitudinal displacement with the thiophene substituent of one molecule over the DPP core of its neighbor. This slip-stack geometry is known as *J*-aggregation and is preferable for SF over *H*-aggregation, where molecules are stacked parallel, because of the antisymmetric orbital overlap between coupled neighbors.⁷³ This $\pi \cdots \pi$ stacking geometry is altered by the sterics imposed by side chains off the core, and these relatively subtle offsets in packing geometry play critical roles in orbital overlap, and thus, SF yields and lifetimes (Fig. 5B). Increased sterics of the side chains separates the DPP cores and leads to slower formation (τ_1) of an intermediate state that precedes the formation of (T_1T_1) *via* SF (τ_2). The Me, C6, and TEG systems demonstrate SF yields over 100%, although τ_2 increases with increasing side chain size of 22.1 ± 0.9 , 336 ± 7 , and 195 ± 8 ps, respectively. The bulkier EH system, however, presents a τ_2 of 1600 ± 500 ps and is the only system with <100% triplet yield. This longer deactivation lifetime is assigned to fluorescence, and based on the 70% triplet yield, τ_2 is calculated to be 1.2 ns. This work demonstrates precisely the importance of control over molecular packing geometry in promoting SF, and because of DPP's structural customizability, this study showed how supramolecular assembly with combinatorial components leads to insight into how structure affects the complex photophysics of SF.

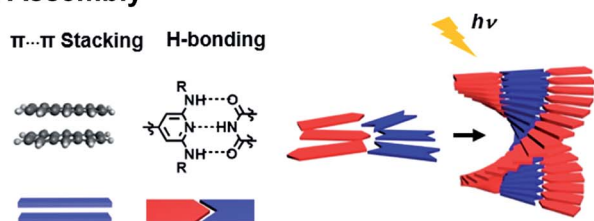
We have also recently developed a supramolecular system to explore how SF yields and lifetimes are affected by subtle changes in stacking geometry.⁷⁹ The active component that undergoes SF is based upon a DPP core that is substituted with diamidopyridine (DAP) H-bonding moieties (Fig. 6A). In addition, orthogonal $\pi \cdots \pi$ stacking between the cores of the aromatic DPP dyes drives organization into hierarchical structures. The appended DAP groups form H-bonds with rylene diimides, which serve as scaffolds for altering relative DPP orientations in the stack. Both DPP and rylene structures are easily modified, providing a lever for altering superstructure geometry in the solid state (Fig. 6B). In our system molecular and long-range geometry were affected in two ways: (1) DPP was monodentate (mDPP) or bidentate (dDPP) depending on the number of DAP groups appended to the DPP core, or (2) core and bay substitution of rylenes were varied to affect their packing geometry, and, as a result, the way they scaffold DPP in the superstructures. From two DPPs and three rylenes, six superstructures with fiber, sheet, and scroll morphologies (Fig. 6C) in the solid state were obtained, and these were all interrogated with fs- and nsTA spectroscopy. Compared to samples composed solely of DPP, some heterosuperstructures show increased decoupled triplet yields and lifetimes. In the case of monodentate mDPP, most decoupled triplet lifetimes from SF were longer (as long as 9.2 μ s) in combinatorial, supramolecular thin films compared to films composed solely of mDPP (1.9 μ s). And in the case of dDPP, most decoupled



A. Molecular structures of the components



B. Assembly



C. Combinatorial library



Fig. 6 SF in combinatorial, supramolecular DPP–rylene superstructures. (A) DPP SF components and rylenes used for scaffolding. (B) Noncovalent interactions lead to cooperative assembly for forming hierarchical superstructure. (C) Different superstructure morphologies including fibers, sheets, and scrolls. Scale bars are 200 nm.⁷⁹

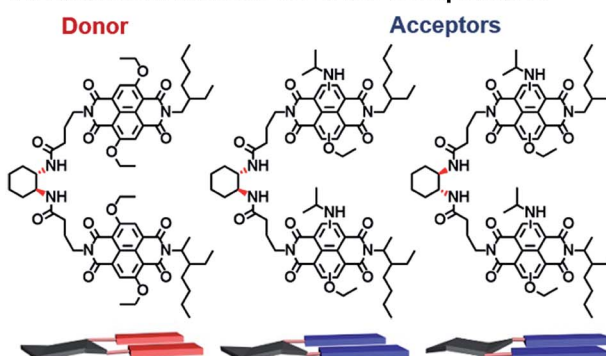
triplet yields were higher in mixed films (as high as 28%) compared to films of dDPP (23%). To date, the most common approaches to explore and optimize SF focus solely on dye structure, and orientation of dyes in films is an afterthought. As such, very few groups use secondary components to control their geometry, despite the importance of packing on SF yield. Our work showed that subtle changes in DPP geometry that result from controlled noncovalent binding manifest as changes in SF yields and lifetimes.

2.3 Förster resonance energy transfer

FRET occurs when the energy released nonradiatively by an excited chromophore is absorbed by a neighboring molecule

(Fig. 7C). This happens when donor and acceptor are in close proximity, $\sim 10\text{--}100\text{ \AA}$, and the absorbance of the acceptor overlaps with the emission of the donor.⁸⁰ The nonradiative transfer of energy manifests as a decrease in the donor's fluorescence and an increase in the acceptor's. FRET is not as sensitive to electronic coupling as CT or SF and is less affected by orientation changes, but is highly sensitive to chromophore distance and spectral overlap. Therefore a wider range of modifications can be done to donors and acceptors to better control FMOs without as much concern for how the changes in structure affect neighbor orientation with respect to the FRET partner. FRET has many applications including sensitizing triplet oxygen into its excited singlet state, which can be used for photodynamic cancer therapy,⁸¹ as a photocatalyst for synthesis,⁸² and for solar energy harvesting.⁸³

A. Molecular structures of the components



B. Assembly driven photoinduced energy transfer



C. Photophysics of FRET

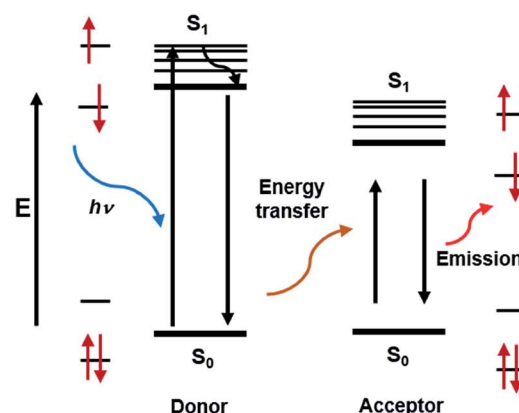
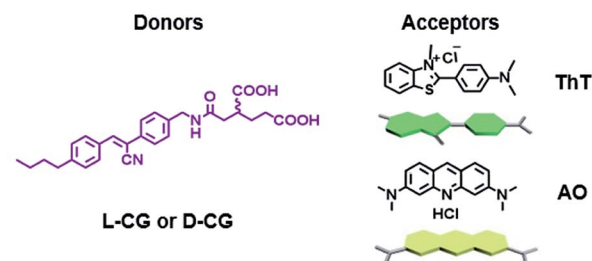


Fig. 7 Förster resonance energy transfer (FRET) in assembling naphthalene dimers. (A) Donors and acceptors synthesized by varying core substitution. (B) Chiral linkers promote either co-assembly or self-sorting structures. (C) FRET mechanism showing energy transfer from donor to acceptor.⁸⁴



A. Molecular structures of the components

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ChT: Chirality transfer **FRET:** Förster resonance energy transfer
S-FRET: Sequential Förster resonance energy transfer

peptide assembly that's used to create nanotube scaffolding in this study, or DNA assembly⁸⁶ used in other photoactive systems, can be combinatorial given the diverse library of components, their ease of fabrication into oligomers, and their chirality can be used for investigating emergent deactivation pathways in combinatorial, supramolecular systems.

3 Conclusion and outlook

Optimizing the photophysical deactivation pathways of organic semiconductors requires understanding their structure-property relationships. The packing geometry of the molecular components can be tailored using programmed supramolecular assembly to form self-assembled and co-assembled materials to achieve emergent photophysics that are absent in individual components. Understanding the subtle and complex relationships that govern how hierarchical structure affects overall device performance can be accelerated by adopting a combinatorial approach where libraries of components assemble by error-correcting, noncovalent assembly that can be screened quickly and in parallel to reveal trends that would otherwise be difficult to derive. Here we show how CT, SF, and FRET were studied and the insights revealed by adopting this strategy. Although we have only selected a few examples, this approach is being increasingly adopted to understand complex photoactive organic systems and promises to rapidly accelerate progress in

this important research area. Combinatorial, supramolecular libraries can have orders of magnitude more components, and it will be then that we have truly tapped into its potential for material discovery. To do so, however, will require concomitant advances in how we study and understand complex photo-physics in hierarchical organic systems.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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