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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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advantages over their inorganic counterparts. First, they can be cheaper to prepare because the expensive, high-energy annealing processes needed for inorganic semiconductors are not required for organics.^{14,15} Second, their structures can be altered to vary their frontier molecular orbital (FMO) energies, shapes, absorptions, and solid-state packing, thereby providing a degree of tailorability not available with inorganics.¹⁶ This is a major potential benefit of organic semiconductor systems because systematically altering their substituents could ideally produce relationships between their molecular structures and their responses to light and charge in solution and in films. In reality, however, deriving these relationships is far more complex than this description suggests. The optoelectronic response of organic semiconductors, and particularly multicomponent materials that are often composed of mixtures of n-type and p-type molecules, remains difficult to predict if one were to consider only the molecular structures of the components.^{17,18} The reason is that many important properties, such as the photophysical deactivation pathway—the way in which photoexcited electrons relax through various excited states and intermediates back to the ground state—excited state lifetimes, film conductance, and light absorption, are ensemble properties that are dependent upon the interactions between two or more molecules. As such, the properties of organic semiconducting films are sensitively dependent on the relative orientations and spacing of the components. So, predicting and optimizing the optoelectronic responses of organic semiconductors so they can realize their promise as active elements for various devices and advanced applications remains a particularly unwieldy problem. This is primarily because of the sensitive dependence of their ensemble properties on Ångström-scale perturbations and the necessity of reproducing these orientations across micrometer or even millimeter length scales. Meeting the structural and electronic requirements of organic optoelectronic devices becomes even more challenging in multicomponent active layers where different constituent molecules must be brought together in a specific geometry to achieve a desired function.

The magnitude of the challenges involved in optimizing the photoresponse of a multicomponent organic system can be understood by considering the active layer of bulk

heterojunction (BHJ) organic photovoltaics.^{19,20} The BHJ is an OPV device geometry where organic electron donor molecules and electron acceptor molecules are blended together into a film that is sandwiched between two electrodes (Fig. 1B). In this layer, electrons in the donor or acceptor chromophores are photoexcited to create coupled electron-hole pairs (excitons). These excitons migrate to a donor-acceptor interface where they charge separate—electrons are thermodynamically driven into the acceptor phase and holes into the donor phase.²¹ Following this charge separation event, charge carriers must migrate to the opposing electrodes so that they can be harnessed as electricity (Fig. 1A). When the films are cast from solution, the donor and acceptor components tend to phase-segregate,^{3,19,22} reducing heterojunction (*i.e.* donor-acceptor contact) area. As the amount of heterojunction interface decreases, the number of charge separation events decrease and/or pathways to electrodes do not form so the charges cannot be collected. Alternatively, too much mixing increases unproductive recombination events because the length of the percolation pathways to the electrodes can exceed charge carrier diffusion lengths. Ideally, the active layer could adopt a geometry (Fig. 1C) that maximizes the donor-acceptor interface, while providing contiguous and short pathways for charge migration to the electrodes.

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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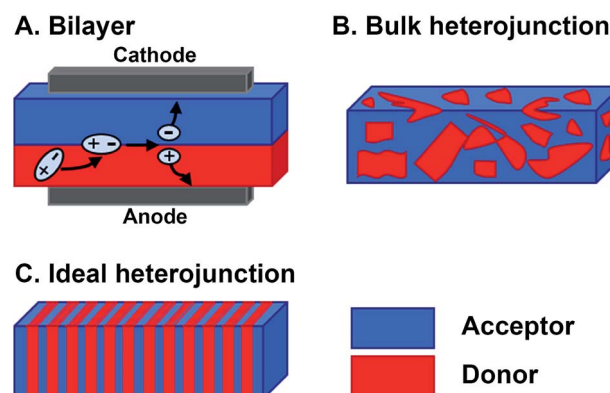


Fig. 1 Donor-acceptor heterojunction morphologies. (A) Bilayer structure showing process of charge collection in OPV devices. (B) Bulk heterojunction (BHJ) and (C) heterojunction optimized to increase junction area, while providing contiguous pathways for charges to migrate to the electrodes.



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

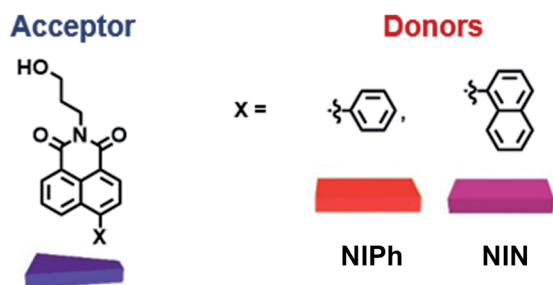
OPVs, degrade relatively quickly in ambient conditions, absorb visible light weakly, and their isotropic structure makes using them for creating hierarchical order challenging.^{16,64} The donors and acceptors in these COFs assemble into columnar arrays *via* $\pi\cdots\pi$ stacking. These stacks promote 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



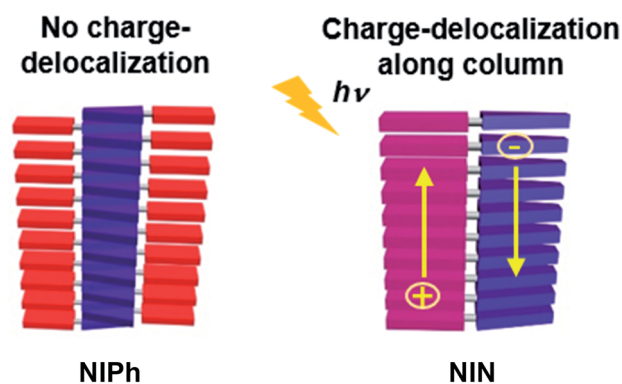
Another example of achieving CT with a combinatorial, supramolecular library of donor and acceptor components was reported by Mallia *et al.* who studied a series of nonparallel stacked dyad chromophores.⁶⁵ A Suzuki–Miyaura cross-coupling reaction was used to bring together covalently naphthalimide (NI)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

2.2 Singlet fission

A. Molecular structures of active components



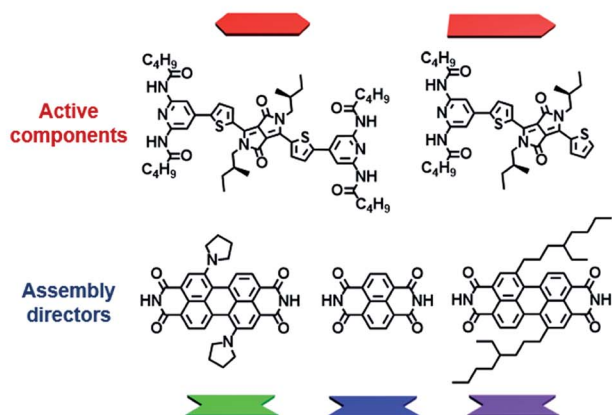
B. Assembly driven photoinduced charge-delocalization



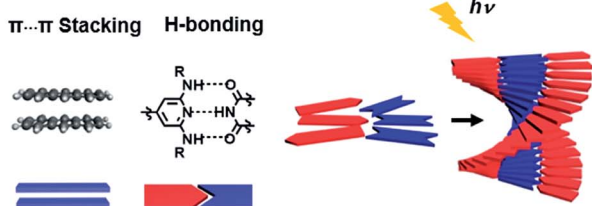
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Nanoscale Adv., 2019, 1, 3858–3869 | 3863

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

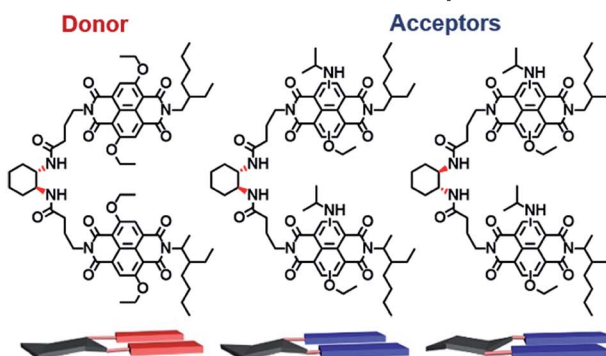
triplet yields were higher in mixed films (as high as 28%) compared to films of dDPP (23%). To date, the most common approaches to explore and optimize SF focus solely on dye structure, and orientation of dyes in films is an afterthought. As such, very few groups use secondary components to control their 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

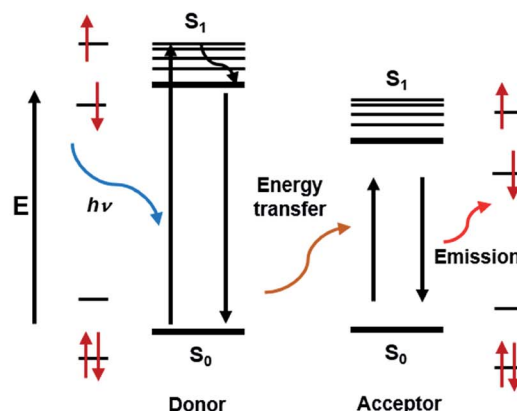


Fig. 7 Förster resonance energy transfer (FRET) in assembling naphthalene dimers. (A) Donors and acceptors synthesized by varying core substitution. (B) Chiral linkers promote either co-assembly or self-sorting structures. (C) FRET mechanism showing energy transfer from donor to acceptor.⁸⁴



Ji *et al.* have recently reported chiral light-harvesting nanotube antennas and studied cooperative assembly and energy transfer amongst its water soluble donor and acceptor components.⁸⁵ In their work, cyanostilbene-appended glutamate (CG) self-assembled into helical nanotubes, as seen in SEM and TEM, whose chirality was controlled by switching between L-CG and D-CG (Fig. 8A). This CG bilayer structure, which was substantiated with XRD, is the basic building block that formed lamellar structures, which then roll into chiral nanohelices and nanotubes (Fig. 8B). When achiral acceptor components thioflavin T (ThT) and/or acridine orange (AO) acceptors were inserted into the L-CG or D-CG to form superstructures, FRET occurs where the CG is the FRET donor. This system is combinatorial because of the variety, and multitude, of acceptors that can be incorporated into the superstructure resulting in 14 possible combinations from five components. Co-assembly was confirmed by emergent signals in circular dichroism (CD) measurements. CG emission overlaps with ThT absorption, making them a suitable FRET pair, and ThT emission overlaps with AO absorption, but CG emission does not overlap with AO absorption. As such, FRET can be seen in CG/ThT dyads but not CG/AO dyads. In CG/ThT/AO triads, ThT absorbs energy from CG, which is then transferred to AO, essentially acting as a bridge, resulting in two sequential FRET (S-FRET) events. In addition to transferring chirality from donor to acceptor, circularly polarized luminescence (CPL)—the circularly polarized emission of light—is also amplified through CG/ThT and triads. All three components in the CG/ThT/AO triad were independently excited and CPL was measured for chirality transfer (ChT) and compared to solutions of the individual components. In the co-assembled superstructures, a CPL signal was seen when only exciting AO, which was attributed to the chirality imparted by the superstructure. AO CPL further increased when directly exciting ThT, and even more so when directly exciting CG. As such, CPL was enhanced for each additional FRET event in the triad system. More generally, this is an elegant example of how biopolymer assembly, like the

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.

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