REVIEW

Energy transfer in supramolecular materials for new applications in photonics and electronics

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Supramolecular materials use self-assembly of molecular components to form complex architectures that may otherwise be extremely difficult to prepare. One of the fundamental aspects of this approach is that relatively weak intermolecular forces are used to direct the assembly of the subcomponents. An important point is how to achieve strong electronic communication throughout the material in view of the 'looseness' of the molecular constituents, which interact only weakly. This is particularly important for applications in molecular electronics where exciton delocalization and charge transport generally limit the overall device performance. This review focuses on recent advances in supramolecular materials and architectures that are engineered to possess efficient energy transfer between the self-assembled component in view of new applications in photonics and electronics.

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INTRODUCTION

Supramolecular self-assembly is the process by which two or more molecular components spontaneously organize into an ordered architecture, and is routinely used by nature to build up the molecular machinery used to perform the complex tasks necessary in living organisms. From a practical perspective, it provides an elegant solution to explore the limits situated between the top-down technological miniaturization approach and the bottom-up construction of single-molecule devices. Its principal advantage arises from the use of smaller subunits that can be more easily prepared, characterized and tuned. This also opens up prospects for materials that self-repair or that autonomously regulate their function in response to the operational conditions.^{1–6}

Aside from the complexity of designing molecules that spontaneously self-assemble into ordered structures, the issue of obtaining a functional response from the supramolecular architecture that presents an added value with respect to the properties of the individual molecular constituents must be considered. In its absence, there may be no need or benefit in using self-assembly in the fabrication of a molecular device compared with the use of a mixture of the individual components. To elicit a collective response in a molecular assembly, the notion of molecular communication has been introduced in order to quantify the extent of the electronic and/or steric interactions between molecular subunits. As molecules possess a localized electron density distribution, they exhibit relatively sharp electronic transitions and reduced intermolecular electronic overlap integrals except in specific cases, for example, when π -stacking is important. As a result of this, molecule-based electronic materials are inherently much less susceptible to defects and impurities as their effect is localized to nearby molecules only. However, the lack of

intermolecular electronic communication also reduces the charge carrier mobility and exciton delocalization. Supramolecular interactions, as shown in the following pages, can be used to direct how molecules self-assemble and thus enhance (or reduce, as needed) electronic interactions.

The underlying principle behind the use of designed intermolecular interactions in organic devices is to dissociate the fundamental electronic properties of the molecular component from its self-aggregation properties that drive nonspecific association and would otherwise control the morphology of the aggregates and the active layer. The latter are important in determining energy and electron transfer as a consequence of through space interactions between molecules in the solid phase. Thus, independent control of the morphology and the electronic properties of the molecular subunits will make their optimization possible by considering each process separately. As a result of the dynamic nature of the self-assembly process, the deposition and post-deposition treatment (annealing) can have profound influence on the overall properties.⁷ Depending on the degree of order within the material, different theoretical models can be used to describe energy transfer processes and the mobility of charge carriers, from band theory for structurally ordered materials, to tight-binding models for weakly disordered systems, and hopping models for localized charges in strongly disordered materials. Grozema and Siebbeles⁸ provided an overview of charge-transport models applicable to self-organizing molecular materials.

Supramolecular interactions can benefit from any combination of intermolecular forces, ranging from weak hydrophobic/dispersion forces, to hydrogen-bonding (H-B) or relatively strong metal ion coordination. The energies of these interactions span a wide range, from <1 to 4 kJ mol⁻¹ for relatively weak hydrophobic or aromatic

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π -stacking interactions and single-point H-B, to $>250\text{ kJ mol}^{-1}$ for very strong coordinative bonds. Besides the free energy, other factors such as kinetic lability and directionality are also important in characterizing supramolecular forces. For example, some (for example, H-B and coordination bonds) are directional, others only partly directional (for example, π -stacking), while others are non-directional (dispersive forces). Clearly, directionality is desirable in cases where a bottom-up design is expected to lead to the formation of precise, well-defined architectures. For these applications, the use of H-B and coordinative bonds has been privileged, with H-B interactions being particularly well-suited toward the construction of photoactive supramolecular assemblies as they do not absorb in the ultraviolet and visible range. Aromatic π -stacking, a principal driving force behind the formation of discotic liquid crystals, ensures moderate to good electronic communication between the molecular components.^{9,10} To build complex assemblies comprising several distinct subunits, it can be necessary to combine different supramolecular interactions that can operate independently. These should be orthogonal in their binding to allow sequential assembly with error correction as the system explores all possible low energy architectures.¹¹ When the electronic interactions are sufficiently strong or driven by external forces,¹² the formation of *J*- or *H*-type aggregate structure and their subsequent effect on the electronic absorption and emission spectra is observed. The scope of this article is to discuss the more recent advances in the use of supramolecular architectures to controlling energy transfer in organic self-assembled materials, with particular emphasis on the development of new applications such as sensing and electroluminescent materials. Other potential uses, such as electron transfer for solar energy conversion, have been the subject of numerous recent reviews.^{13–16}

ENERGY TRANSFER IN ORDERED SUPRAMOLECULAR AGGREGATES

Energy transfer, also known as exciton hopping in the solid, involves the transfer of electronic excitation energy from one chromophore to another. Two principal mechanisms, one based on resonance between the electronic transition dipole moments of the donor and the acceptor (Förster energy transfer) and the other on an electron exchange mechanism (Dexter energy transfer) are possible. Both require spectral overlap between the emission of the donor and the absorption spectrum of the acceptor and, whereas the latter relies on close contact between the donor and the acceptor, the former is still efficient even at longer distances. In extended supramolecular aggregates, such as micelles, vesicles or gels, the molecular components are organized in a solid or semisolid framework, akin to a solid environment. In this case, long-range energy transfer (several nanometers) can take place by hopping between chromophores. This phenomenon is also operational in organic photovoltaic materials, where hopping distances of *ca* 10 nm have been determined,¹⁷ and similar hopping distances were found in helical π -stacks of perylene tetracarboxydiimide (PDIs).¹⁸ The dynamic nature of supramolecular assemblies further allows their interconversion between distinct morphologies by external stimuli¹⁹ and allows the formation of hybrid inorganic–organic frameworks.²⁰

Molecular gels are formed by strongly anisotropic growth along a preferential direction during self-assembly, leading to an intertwined fiber network, which traps solvent molecules to form a gel. As unidirectional growth can often be achieved by the incorporation of a linear geometry of complementary supramolecular interactions (for example, H-B), gel materials have been a common scaffold used to induce ordering of π -functional materials.^{21,22} This area has been the

topic of recent thorough reviews by Babu *et al.*^{16,23} and will not be discussed in detail except for the generation of white light from aggregates using energy transfer where it can be sometimes possible to follow the energy transfer across multiple chromophores in the assembly. This is the case in an acene-based organogel composed of a blue light-emitting anthracene donor co-assembled with tetracene and rubrene acceptors emitting in the green and red region, respectively.^{24,25} Upon excitation of the anthracene donor, energy transfer populates the excited states of green and red emitters that are dispersed into the matrix (1.2% red and green acceptors), which contribute to the emission. Despite their low concentration, energy transfer from the green to the red component was also evidenced, supporting a previous observation of long (>100 chromophores) energy hopping in such materials.²⁶ Similar results were achieved in a bi-component system using charge-transfer interactions between naphthalene and 1,2,4,5-tetracyanobenzene to assemble rigid tubes. Addition of a small amount of pyrene affords white light emission through energy transfer (Figure 1).²⁷ A selection of representative systems operating along such lines have been recently reviewed by Armaroli and co-workers,²⁸ and the occurrence of long-range excitation energy migration in self-assembled fibers opens up new opportunities in the construction of amplified molecular sensors.²⁹ Their operation would be similar to the quenching mechanism in fluorescent conjugated polymers, whereby the exciton migrates along a polymer chain to explore multiple binding sites.³⁰ This approach was used by Ajayaghosh and co-workers³¹ to propose a fluorescent molecular gel capable of detecting electron-deficient aromatics (such as TNT) with attogram sensitivity. The scaffold of the material is composed of a π -conjugated tri-alkoxyphenylene-vinylene, appended with pentafluorophenyl groups that impart phase separation through hydrophobic forces and C–F...H–C interactions. X-ray diffraction patterns confirm a regular packing of the chromophores that is maintained upon exposure to nitroaromatic compounds. This point is essential as the packing is crucial for long-range exciton diffusion, which allows the amplification of the signaling ability of the material.

Energy transfer between two compartments in an aggregate was demonstrated by Würthner and co-workers³² by placing a pH-sensitive fluorophore in the interior of a vesicle comprising a luminescent shell. The latter was polymerized to maintain the structural rigidity of the assembly, thus locking the PDI red light emitters in place. A bis-pyrene chromophore whose emission can be switched from monomer (blue emission) to excimer (green emission) by the pH was sequestered inside the vesicle with the aim of absorbing incident radiation and emitting blue-green fluorescence. Förster radiative energy transfer from the fluorophores inside the vesicles to the chromophores located on the peripheral shell thus results in aggregates whose emission envelope is pH-tunable and, at pH = 9, the emission from the single aggregates appears white to the eye. This system therefore displays emission that can be localized with submicron precision and that is responsive to outside stimuli. There is great appeal for the use of vesicles (or micelles)³³ as adjustable point light sources, but their preparation can be cumbersome and not easily compatible with the fabrication of luminescent devices. Generally, long alkyl chains and a water-soluble segment are required for inducing amphiphilicity and controlling the surface curvature of the aggregates, which are formed by dispersion of an organic solution into an aqueous phase.³⁴

To circumvent problems associated with the amphiphilic nature of the supramolecular assembly components in micelles and vesicles, it is possible to use polymeric assemblies (polymersomes) or compounds specifically designed to adopt vesicle-like architectures based on

Figure 1 In acetonitrile solution, naphthalene and 1,2,4,5-tetracyanobenzene form charge-transfer (CT) complexes that self-assemble into hollow rods when the solution is dispersed in an ethanol–water mixture (a). Scanning electron microscope image of the rods (b) evidences their hollow nature. Upon excitation (330–380 nm), blue emission from the CT complex is observed (c). Addition of pyrene (0.015%) results in the emission of white light through an energy transfer process in the self-assembled rods (d, scale bars are 30 μm). Adapted with permission from reference Lei *et al.*²⁷

designed supramolecular interactions. For example, it is well known that urea and bis-urea, as well as analogous ureopyrimidones self-assemble into fibers because of the unidirectional nature of their binding site. Instead, biuret adopts a cyclic structure to expose two H-B sites that are orthogonal to each other, and hence assembles into H-B sheets (Figure 2a). In solution, such sheets are subjected to continuous fluctuations and possess vacant peripheral binding sites. They eventually fold into spherical assemblies to reduce exposed vacant H-B sites (Figure 2b). In fact, the directionality of H-B interactions allows a relatively straightforward interpretation and projection of possible architecture topologies, including switching between the formation of fibers and spheres³⁵ or crystals and vesicles³⁶ or spheres.³⁷

Many rigid luminescent chromophores can be substituted for the photoactive core in Figure 2b without altering the formation of the vesicle-like assemblies. This allows tailoring of the photophysical as well as the photochemical properties of the material independently and of the final morphology of the aggregates. In fact, such hollow spheres were shown to form spontaneously upon dissolution of the solid into an aprotic solvent that does not impede H-B. In such cases, the presence (or absence) of water does not influence the formation of the artificial vesicles as their molecular components are pre-programmed to self-assemble according to specific interactions and do so in solution before casting onto various substrates. Indeed, the presence of hollow spherical aggregates possessing similar size as the aggregates observed by microscopy could be evidenced by small-angle neutron scattering.⁴⁰

By tailoring the absorption and emission envelope of the lumino-phore, it is possible to obtain luminescent spheres that emit light of a given wavelength. In the case of oligo-fluorenes (BU-1), the resulting emission is not affected by aggregation through π -stacking, which

would otherwise induce a strong red shift in the emission spectrum because of the formation of *J*-aggregates. Rather, the emission is strongly dependent on the presence of small amounts of dopants that can be excited through energy transfer processes. By using dopants consisting of a chromophore whose absorption envelope overlaps with the emission envelope of the donor, and that also respects the supramolecular algorithm for incorporating into vesicles (that is, a rigid core appended with biuret units on either end), the materials can be dispersed in the aggregates without disrupting the supramolecular topology. In this case, the dispersion of colors obtained was found to be very uniform and not to vary between aggregates as would be expected for an anisotropic distribution of acceptors. Even for small quantities of dopants (for example, 0.20 mol% of BU-2 and 0.25 mol% of BU-3), the emission from the donor is substantially decreased (only accounting for 85% of the global emission despite accounting for *ca* 99.9% of the absorbed light) and emission from the acceptor components is strong (5% and 10% for BU-2 and BU-3, respectively).

Stable lamellar assemblies of organic chromophores can be readily obtained by grafting them onto flat nanoscopic inorganic structures. Rao *et al.*⁴¹ thus showed that it is possible to use a cationic clay to assemble anionic fluorophores in an ordered architecture. The chromophores were carboxylic or sulfonic acid derivatives of coronene or sulforhodamine G, which were assembled onto an amino-functionalized clay based on an layered magnesium phyllo(organo)silicate having a 2:1 trioctahedral smectite-like structure. The coronene was used as the blue-emitting donor component, whereas the rhodamine G acted as the energy-accepting yellow emitter. Soft gel-like aggregates are formed at total concentrations of donor and clay components greater than *ca* 8 wt.%. Upon inclusion of a small amount of acceptor component (0–

Figure 2 (a) It is often the case that two urea residues appended to a π -conjugated core, such as a phenyleneethynylene unit (UPT), induce the formation of stacked assemblies and the formation of fibrillar gels (crystal structure and atomic force microscopy image below). Adapted with permission from reference Dautel *et al.*³⁸ (b) The use of two biureted hydrogen-bonding (H-B) units code for the spontaneous formation of hollow spheres in solution that persist upon solvent evaporation (scanning electron micrograph, bottom). This is attributed to the existence of two H-B sites on each biureted unit that are orthogonal to one another (labeled A and P). Compounds BU-1, BU-2 and BU-3 emit in the blue, yellowish green and red region of the spectrum and can be combined in a single vesicle to produce light of any color contained in the dashed triangle. Adapted with permission from reference Tseng *et al.*³⁹

1 mol%), the emitted light gradually changes from blue to yellow, and white light is obtained for a concentration of acceptor = 0.65 mol%. The gels thus obtained are stable and free-standing, making the system interesting for lighting applications. H-B between complementary recognition sites can also be used to prepare extended assemblies by using ditopic subunits to allow the formation of extended architectures, such as for cyanurate–melamine ribbons appended with PDI chromophores.⁴²

It is quite reasonable to assume that intra-aggregate energy transfer occurs non-isotropically within the sample, and that this can also depend on the presence of islands of acceptors because of microscopic phase separation within an individual aggregate. To investigate this point, Schenning, Herz and co-workers⁴³ investigated energy transfer efficiency as a function of donor/acceptor ratios and found that this is non-linear for acceptor ratios $> ca$ 0.5% because of clustering of the acceptors within the nanoparticles. It should be noted that this value is likely to depend on the molecular constituents, but that the approach used to highlight acceptor separation within the aggregate is quite general.⁴⁴ The availability of a confocal microscope with which to examine the emission from individual aggregates further enables the investigation of variability between different single aggregates that may arise from non-equilibrium dynamics during aggregate formation. An analogous situation was encountered in surface-grafted polymer particles appended with fluorescein fluorophores, where excitation migrates between identical fluorophores until it is trapped by a non-fluorescent aggregate.⁴⁵ In the case of PDIs, a well-known class of chromophores that are prone to forming π -stacked aggregates, relaxation of the molecules surrounding the localized excited state can provide stabilization that leads to the formation of a potential energy well at that location.⁴⁶ Localization of the excitation

energy onto a single chromophore effectively traps the exciton and reduces energy transfer.

Understanding intra-aggregate energy migration and Förster Resonance Energy Transfer processes is also of interest in cases where such processes are undesirable. This would be the case in spatially colocalized distribution of emitters of different colors, such as in the voxels (volumetric pixels) used in color display devices. In these systems, the individual primary colors are turned on to produce a composite color as perceived by the human eye and it is important that cross-contamination of the primary colors is avoided. This problem is particularly acute in organic light-emitting diode displays, where the chromophores are evaporated through a mask. By taking advantage of the large Stokes shift induced by an excited-state proton transfer process in a series of ortho-hydroxyphenylimidazoles, Park and co-workers⁴⁷ showed that it is possible to impede energy transfer by reducing the spectral overlap between the molecular component in a multichromophoric assembly and were able to produce a mixture of individual molecular producing RGB emission without cross-talk (Figure 3).

ENERGY TRANSFER IN MULTICOMPONENT MOLECULAR CRYSTALS

Energy transfer in organic crystals is a wide topic spanning chemistry and physics that is much too broad to be discussed in detail here. Instead, attention will be focused on examples of systems able to use supramolecular interactions to combine several chromophores in a regular 'crystalline' arrangement in the solid. For comparison, in an archetypical organic crystal such as rubrene, exciton delocalization was estimated by Moran and co-workers⁴⁸ to be ca 18 molecules through a combination of spectroscopic techniques and modeling of

Figure 3 Excited-state intramolecular proton transfer (ESIPT) in a series of o-hydroxyphenylimidazoles (a) induces a large Stokes shift in these materials, which effectively reduces the overlap integral between the emission of the donor and the absorption of the acceptor components. This turns off energy transfer, making these materials interesting for obtaining colors that are the binary mixture of the chemical components (b). Adapted with permission from reference Kwon *et al.*⁴⁷ Copyright 2013 the American Chemical Society.

the spectral densities. These techniques allow the determination of the electronic relaxation dynamics, which in turn govern coherent energy transfer within the crystal. Hayward and co-workers⁴⁹ reported the self-assembly of crystals of poly(3-hexylthiophene) onto perylene tetracarboxydiimide (PDI) crystals. The former grows as small hairs onto the larger fiber-like crystals and acts as quenchers of the intense PDI emission. It is proposed that the thiophene polymer behaves as an additive to enhance the PDI solubility and reduce the lateral dimensions of the PDI crystals, which can be tuned from 25 to

200 nm. A qualitative comparison of the emission from the PDI nanocrystals with and without thiophene polymer crystals shows that the fluorescence is nearly completely quenched, as would be expected for efficient energy transfer within the PDI crystals.

The use of designed supramolecular interactions (as opposed to, for example, intrinsic crystal packing forces) can be applied to favoring the formation of otherwise hard-to-reach polymorphs. When growth along with one of the crystal axes is privileged, then fibrillar or needle-like crystals are obtained. Spontaneous branching then leads to the formation of arborescent architectures, such as those reported by Nabiev and co-workers⁵⁰ for core-shell nanoparticles. Time-resolved photoluminescence studies indicated that some of these structures show energy transfer from the periphery to the interior of the dendritic core. Chain branching was also evident in soft C₆₀ fullerene-based materials reported by the Nakanishi group.⁵¹ In this case, the formation of various fullerene morphologies, including lamellar structures conducive toward two-dimensional energy and electron transport, were obtained by the use of branched alkyl chains (Figure 4).

As an alternative to hydrophobic forces, H-B can be used to induce formation of well-defined fullerene assemblies. These may (or not) also possess saturated hydrocarbon chains to assist the self-assembly and improve solubility, although a high proportion of saturated hydrocarbon chains can be deleterious to energy and electron transport. Barbituric acid derivatives possess two H-B sites, which are partially self-complementary through the formation of two N-H...O H-bonds. Thus, a fullerene-barbituric acid adduct was found by Chu *et al.*⁵² to self-assemble into H-bonded ribbons in which the fullerenes are in close contact along the H-bonded tape-like architecture (Figure 4b).

In the supramolecular fullerene material depicted in Figure 4b, there are two equivalent fullerene molecules per unit cell, and it would be reasonable to assume that energy transfer processes are limited to exciton diffusion amongst identical sites. However, the particular photochemical behavior of fullerenes, along with the specific molecular arrangement directed by the H-B interactions of the barbiturate motif, can strongly influence the photophysical properties of the material. In crystalline C₆₀ samples, excitons formed upon absorption of light by a single fullerene are delocalized over two (or more) fullerenes.⁵² The resulting excimer (for excited state dimer) is slightly stabilized with respect to the locally excited state, and therefore emits at a longer wavelength than is observed for an isolated C₆₀ molecule. However, when a fullerene pair is excited, photoinduced dimerization across the proximal 6,6 double bonds is possible. This can take place in the solid, but also in solution when two fullerenes are held in proximity due to supramolecular interactions as barbiturate H-B motifs are well-suited to promoting [2 + 2] photocycloadditions.⁵⁴

Fluorescence from isolated fullerenes is not polarized because of the high symmetry of the sphere (*I_h*), unlike what is usually observed for aromatic hydrocarbons that emit light, which is polarized along the long and short axes of the chromophore. In the solid, emission from fullerene excimers can be polarized because of their reduced symmetry with respect to fullerene. In the case of emission from the fullerene ribbons in Figure 4c, the emission was found to be polarized with a maximum intensity at 60° with respect to the long axis of the H-bonded ribbon.⁵⁵ This was interpreted as arising from fast exciton migration to populate the lowest energy of the three possible distinct fullerene excimer pairs that can form in the solid state. Interestingly, this excimer is also photoreactive and undergoes photoinduced dimerization upon prolonged irradiation. As a consequence, the electronic energy of this state is raised above that of the other

Figure 4 (a) The presence of branched alkyl substituents can generate lamellar structures in which the fullerene moieties are in closed contact as evidenced by the X-ray diffraction (XRD) spectrum. Reproduced from reference Li *et al.*⁵¹ with permission of The Royal Society of Chemistry. (b) A similarly linear arrangement of fullerenes can also be obtained by designed hydrogen-bonding (H-B) interactions as observed in the crystal structure of a fullerene–barbiturate derivative in which energy transfer is particularly efficient. Reproduced with permission from reference Chu *et al.*⁵² Copyright 2010 the American Chemical Society. Upon irradiation, the polarized emission from this material undergoes a switch in direction (c) of *ca* 60° without any changes in the emission spectrum, intensity or lifetime. This process, termed photopolism, can be used to write information that can only be read out through the polarization component of the emission (d). Reproduced with permission from reference Raffy *et al.*⁵³

excimer pairs, and energy transfer now populates a different excimer whose electronic transition dipole is oriented differently from that of the first. The result is that of a material that emits polarized light, which, upon excitation, undergoes a rotation of the polarization without any changes in its emission spectrum, intensity or lifetime. This process was termed *photopolism* by the authors, and relies on the combination of efficient energy transfer and photoinduced reactivity in the solid.⁵³ The process is diffraction limited and can be used to write information on the material that can only be detected by the use of fluorescence polarization.

ENERGY TRANSFER IN WELL-DEFINED SUPRAMOLECULAR ASSEMBLIES

Supramolecular fullerene assemblies have attracted considerable interest in view of their use in solar energy conversion.^{56,57} In this case, it is charge separation (that is, electron transfer) that is pursued, but energy transfer processes are often also present as either preceding charge separation or as a competitive process.⁵⁸ For example, intramolecular energy transfer in a zinc-phthalocyanine/porphyrin dyad was found to be extremely fast, occurring on a sub-picosecond time scale.⁵⁹ This allowed light harvesting by the phthalocyanine, which powered the subsequent electron transfer from the excited porphyrin to the phthalocyanine. The overall result is an accrued efficiency of photocurrent when the dyad was self-assembled on a transparent TiO₂ electrode by slowing charge recombination on the electrode surface as previously suggested by Imahori and co-workers.⁶⁰ Sequential energy–electron transfer was also observed when the phthalocyanine–porphyrin dyad was non-covalently

attached to a fullerene by axial metal ion coordination,⁶¹ and in an analogous system using an additional bodipy fluorophore.⁶² Control over energy vs electron transfer processes in the well-studied porphyrin–fullerene architectures can generally be obtained by varying the solvent polarity, with non-polar environments favoring energy transfer whereas more polar solvents will accelerate electron transfer by stabilizing the ensuing radical ion pair that is generated. Three-point H-B was used by Rotello and co-workers⁶³ to assemble fullerenes on the periphery of suitable modified quantum dots. The photophysical properties of the material evidence ultra-fast charge separation, but it is reasonable to assume that it is also possible to steer the system toward energy transfer by adjusting the relative energy levels of the donor and acceptor.

PDI is known for their propensity to aggregate, as mentioned in the section on supramolecular aggregates, but they can also be used in structurally well-defined assemblies. Thus, in a large molecular square comprising 16 pyrene donors and 4 PDI acceptors (Figure 5a), a fast energy transfer rate of $5 \times 10^9 \text{ s}^{-1}$ is observed. This process is followed by charge separation to yield the oxidized pyrene and reduced perylene chromophores.⁶⁴ The situation is somewhat similar in a supramolecular porphyrin assembly (Figure 5b) reported by Kim and co-workers.⁶⁵ It consists of a tetrameric assembly of pyridine-appended porphyrin dyads giving a box composed of eight porphyrin chromophores arranged in a perpendicular geometry. Excitation of any one of the chromophores results in energy transfer occurring intramolecularly (through the alkyne bridge) or intermolecularly through axial ligand coordination. The former is about 10 times faster and it could be shown that the dihedral angle

Figure 5 (a) A supramolecular square assembled from four Pt(II) metal centers (green) and four perylene bisimides (red), each of which bears four pyrene units (blue, 16 pyrenes total) shows both photoinduced electron and energy transfer. Reprinted with permission from reference Sautter *et al.*⁶⁴ Copyright 2005 American Chemical Society. (b) A self-assembled porphyrin cube in which both intramolecular (red arrows) and intermolecular (green arrows) energy transfer is possible. The two differ by *ca* one order of magnitude in rate. Reprinted with permission from reference Kim *et al.*⁶⁵ Copyright 2010 American Chemical Society.

Figure 6 At low concentrations, an iridium complex bearing two crown ether macrocycles (Ir-MC) forms a bis pseudo-rotaxane in the presence of a bis-ammonium guest (G), whereas a supramolecular polymer is obtained at high concentrations. The system displays efficient electroluminescence thanks to intermolecular energy transfer and can be modified with a third component (G') possessing similar or different electronic properties. Adapted with permission from reference Liang *et al.*⁷² Copyright 2013 American Chemical Society.

between the porphyrin units is a decisive factor in determining the excitation energy migration.

Energy transfer in metallo-supramolecular assemblies has been widely used in the construction of photoactive assemblies. In particular, it is of interest for the enhanced excitation of lanthanide luminophores whose absorption cross-section is too low for direct excitation.^{66–70} Iridium complexes are widely used as phosphorescent emissive components in organic light-emitting diode devices, and an elegant approach toward blending them in a solution processable supramolecular polymer was reported by Huang and co-workers.^{71–73} Their approach relies on the reversible formation of pseudo-rotaxanes that are obtained from a bis-macrocyclic iridium complex (Figure 6) and a bis-ammonium terfluorenyl emissive guest (G). At low concentrations, a discreet 1:1 assembly is obtained, whereas a supramolecular polymer is formed at high concentrations. The possibility of adding other components (G') is a particularly appealing advantage of these materials, which afford organic light-emitting diode devices displaying high efficiencies.

Ruthenium polypyridine complexes are another class of metallo-supramolecular assemblies that have been the focus of considerable attention as they combine the luminescent properties of ruthenium(II) centers and good kinetic and thermodynamic stability.^{74,75} Pioneering work on rigid bridges⁷⁶ and dendrimers⁷⁷ rely on an energy gradient to move excitation across the bridge or from the periphery to the core of the dendrimer and are relevant to artificial light-harvesting assemblies. In specific cases, the energy level of an organic excited state is near to that of an inorganic excited state, and equilibration between the two is observed. This is a form of energy transfer that has a result similar to that of delayed luminescence if the two excited states possess widely different decay rates.⁷⁸ By adjusting the energy level of the organic chromophore, it is possible to tailor the system for various metal centers, including more abundant ones that otherwise possess short-lived excited states, such as copper (I).⁷⁹

CONCLUSION AND PERSPECTIVES

Energy transfer is a fundamental process that is exceedingly well suited to supramolecular architectures, both in view of harnessing the organization they induce and in view of probing it using well-known rate–distance relationships. Controlling the directionality of multistep energy transfer processes within a single architecture remains a challenge. Recent work by Puntoriero *et al.*^{80,81} in BODIPY assemblies provides an elegant example of ultrafast vectorial energy transfer that occurs on the picosecond time scale. Polysaccharides⁸² and porous silicate frameworks^{83,84} may yet prove to be abundant sources of multivalent scaffolds, which bind chromophores for the construction of light-harvesting architectures. In the assembly of molecular nanowires containing both donor and acceptor fragments, Zhang *et al.*⁸⁵ showed directionality in the electron transport process, opening the way toward self-assembled molecular rectifiers. Another potential route to well-defined architectures grafted onto solid substrates has been developed by the Matile group, and consists of the surface-initiated supramolecular polymerization process.^{86–89} It has been successfully applied to obtaining redox gradients, and energy transfer across such structures comprising multiple chromophores is expected to be particularly efficient.

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