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Abstract

Self-assembling peptides with covalent pi-electron functionality offer new ways to create delocalized conduits within protein-based nanomaterials. My group's recent research is summarized in this regard, detailing foundational self-assembly and photophysical characterizations that validate the electronic couplings existing within the resulting peptidic nanomaterials. Using these initial studies as a benchmark, ongoing studies to create even more complex photonic energy delocalization schemes are presented, spanning excitonic and Förster energy transfer to low-bandgap dopant sites (whereby 46% of the observed photoluminescence could be quenched by the addition of 1 mol% of an energy acceptor), the creation of charge separated states following photoinduced electron transfer that persisted for over a nanosecond, and use of kinetic control to dictate self-sorting (at long time scales, ca. several hours) or intimate coassembly (at short time scales, ca. several seconds) of multiple peptide components. Peptide coassemblies are described that exhibit both directed exciton migration to low-energy sites and follow-up charge separation events, very much in mimicry with relevant photosynthetic processes.

Nature is rich with examples of organisms and structures that can manage the flow of photons. The physical principles at play in these biological examples have been exploited quite elegantly over the past two decades in the construction of functional materials. In some cases, these functions involve purely optical phenomena, whereby the size scales of the photonic structures are in regimes that enable physical manipulation of light (e.g. diffraction and scattering) [1–6]. In other cases, photons interact resonantly leading to an absorption of an incoming photon and/or a subsequent emission. For example, vision is predicated on the absorption of incident photons by retenoid dyes leading to photoisomerizations that trigger the light perception processes that we ultimately decode as color, while in bioluminescence, enzymatic reactions lead to the formation of metabolites in electronically excited states that subsequently emit photons. Even more complex schemes can be found in photosynthetic organisms, entailing exciton creation via incident solar radiation, exciton migration among chlorophylls of different energies, and exciton dissociation via electron transfer, in an orchestrated flow of energy that leads to productive chemical reactions.

The mimicry of photosynthetic processes presents a particularly challenging puzzle with great contemporary implications for photovoltaic or solar fuel technologies [7]. On the molecular side, it requires a careful choice of suitable donor and acceptor chromophores that can facilitate energy migration, both of excitons and electrons [8]. On the supramolecular side, it requires non-covalent associations to put these chromophores into proper positions to facilitate the desired energy migration events [9]. Furthermore, the photosynthetic machinery is in a constant state of flux, being continually re-assembled, thus posing an attractive element of dynamic self-healing often sought after in artificial assemblies. Supramolecular chemistry coupled with proper donor–acceptor relationships thus provides a compelling approach to realize photosynthetic mimics that may find use in biomedicine, catalysis or electronics, provided the development of strategies to engineer photon flow through photophysically resonant and non-resonant processes.

The use of peptides functionalized with suitable chromophores has emerged as a popular route to construct electronically delocalized supramolecular assemblies (figure 1) [10, 11]. With suitable composition, the peptides promote self-assembly into

higher-order structures including nano- to meso-scale tapes, ribbons and tubes. These assemblies also promote intermolecular interactions among the pi-units that lead to the necessary energy transporting conduits analogous to those found in the photosynthetic machinery. My research group has contributed to this area through the development of general synthetic strategies that yield peptide-pi-peptide triblock architectures whereby peptide-driven assembly forces the embedded pi-electron units into pi-stacked configurations [12]. We studied a wide variety of pi-electron systems in the context of biologically relevant electronics, and we explored how peptide sequence composition influences the extent of the intermolecular electronic delocalization. This report will briefly summarize the foundational photonic properties of the specific assemblies studied in our laboratory and then discuss our more recent research on controlling energy migration through sequence design and through co-assembly approaches.

Benchmark photophysical properties

Our synthetic strategies allow for a diverse palate of pi-electron inclusion, and the molecular platforms thus formed are designed to have tunable solubility as a function of solution pH or ionic strength [13–15]. We typically include carboxylic acid residues (presented by glutamic or aspartic acid) that are effectively deprotonated under a basic pH (above pH 10 for example). These ionized peptides present Coulombic repulsions that frustrate intermolecular associations, and we consider these peptides in solution to be molecularly dissolved. At lower pH (below pH 4 for example), the carboxylates are protonated, and the more charge neutral structures can engage in intermolecular interactions more effectively. The presence of the transition dipoles associated with the embedded pi-electron units provides a photonic reporter of the pi-electron interactions that exist within the self-assembled structures due to these intermolecular electronic couplings [16, 17]. UV–vis, photoluminescence and circular dichroism spectroscopies provide critical information about supramolecular electronic assemblies [18–20].

The photophysical properties of the molecularly dissolved molecules and the resulting self-assembled structures depend on the nature of the pi-electron unit, and a representative example for the well-established distyrylbenzene chromophore (OPV3) is shown in figure 2. In general, the oligo-aromatic character of the typical pi-systems that we investigate in their molecularly dissolved states leads to broad UV–vis absorptions and notable Stokes' shifts in the associated photoluminescence at wavelengths comparable to what would be expected for the same chromophores in organic solvents without the peptide substituents. Furthermore, the CD spectrum reveals information about the peptide conformations (alpha-helix, beta-sheet) in the high energy UV region corresponding to the coupled interactions of the amide *n*–pi* transitions (190–250 nm) but shows no differential absorption in the lower energy visible region corresponding to the pi–pi* chromophore transitions (400–800 nm). The latter point is not unexpected because the achiral pi-systems are not undergoing any exciton coupling, whereas the chirality of the oligopeptide segments leads to distinct high-energy CD signals. For a given chromophore, these properties were essentially invariant to the compositional nature of the attached peptides.

Upon triggering the assembly via solution pH change, notable features are observed that are consistent with an H-like exciton coupling process [21]. The absorption λ_{max} is blue-shifted while the resulting photoluminescence is dramatically quenched. In addition, a strong bisignate Cotton response is found in the CD spectra indicating that the achiral chromophore is being held in a local chiral environment, as expected from the natural handedness associated with the curvature of the peptide beta-sheet motif. In addition, subtle variations of the component amino acid residues led to variance of the nature of this intermolecular exciton coupling. The photonic and electrical properties of supramolecular pi-electron polymers are known to be quite sensitive to variations in peptide sequence, length, and even local chirality expression [22–24]. One notable example from our research was revealed in a systematic variation of the residue directly attached to the pi-electron core [25]. As these flanking positions were changed from the smaller glycine and alanine (DFAG and DFAA, figure 2(c)) to the larger phenylalanine and valine (DFAF and DFAV, figure 2(c)), a distinct shift from weakly-coupled low-energy excimer states (λ_{max} ca. 515 nm) to tightly-coupled high-energy exciton states (vibronic progressions with absorptions at ca. 425 and 450 nm) was apparent. This was further validated with atomistic molecular dynamics simulations in collaboration with Andrew Ferguson at the University of Illinois that suggested the smaller residues had more contribution from aqueous solvation whereas the larger hydrophobic sequences promoted a greater extent of self-solvation [26]. Another example comes from altering the 'polarity' (that is, the nature of the N-to-C directionality) of the oligopeptides expressed on the pi-electron unit that can further alter the strength of the electronic coupling on the basis of the nature of the hydrogen-bonding networks thus formed (being formally parallel or anti-parallel beta-sheet architectures) [27].

Unfortunately, the interpretation of the extent of electronic coupling is not as easy as simply assigning a red or blue-shift to an observed absorption profile. Within an assembled aggregate, it is likely that the oligoaromatic chromophores could be planarized (thus leading to a UV–vis red-shift) or could be subject to restricted torsional rotation (thus possibly leading to more resolved vibronic features). These non-res-

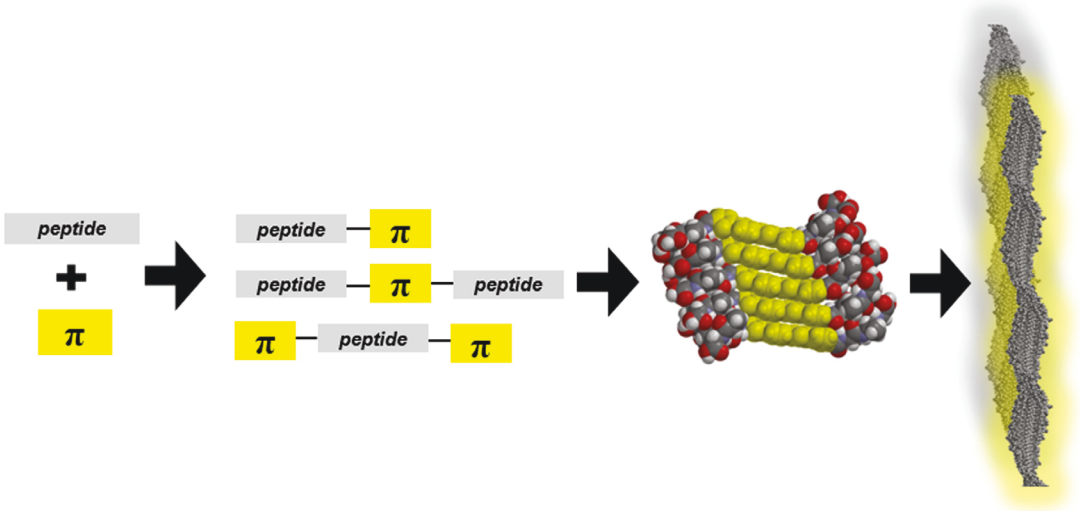

Figure 1. Conceptual merger of peptides and pi-electron units to create self-assembling molecules with photonic function that mimic several key aspects of natural protein aggregation, from intermolecular hydrogen-bonding to extended fibrillization. Reprinted with permission from [10]. Copyright 2015 American Chemical Society.

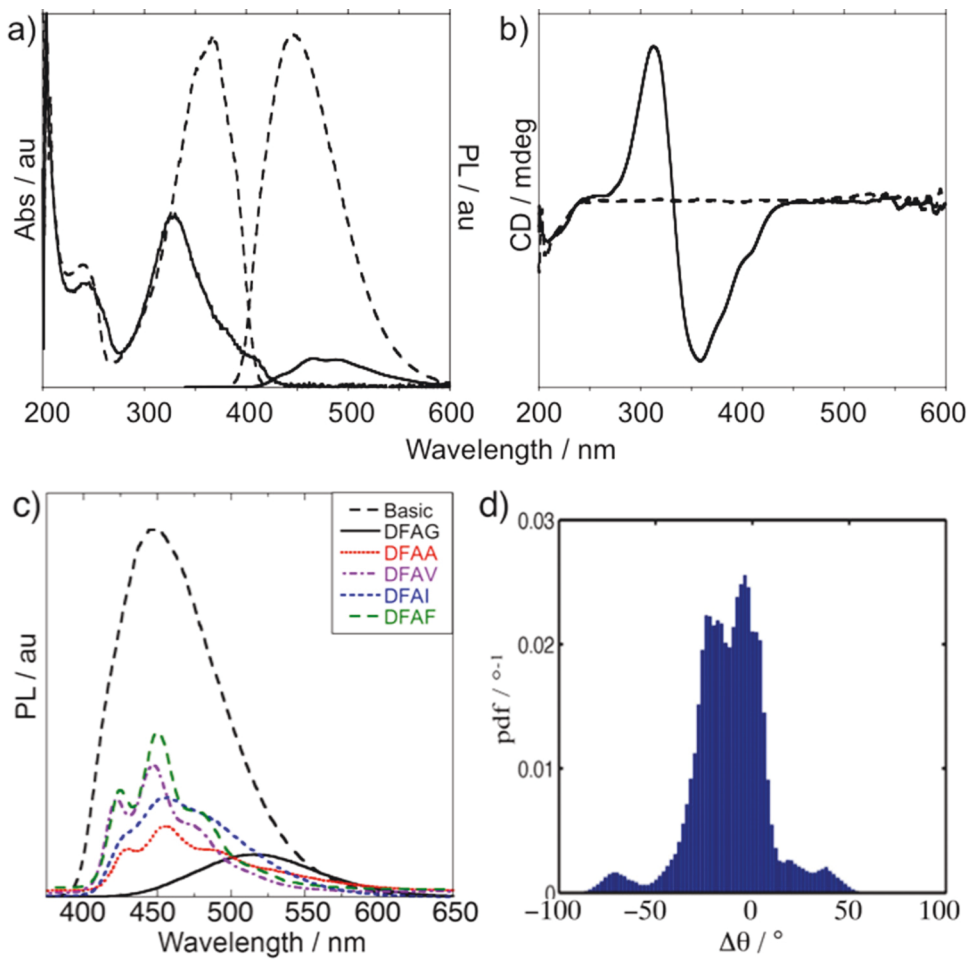

Figure 2. Representative spectral ((a)–(c)) and computational geometric (d) data for OPV3-based peptide nanomaterials, including absorption and photoluminescence spectra (a) and circular dichroism spectra (b) recorded at basic pH ('molecularly dissolved', dashed lines) and at acidic pH (self-assembled, solid lines). Photoluminescence variations amongst OPV3 peptides (c) span from broad excimer-like states (DFAG, solid black trace) to the vibronic progressions associated with strong exciton coupling (e.g. DFAV and DFAF). The disorder within the nanomaterials is depicted by atomistic molecular dynamics simulations (d) where the histogram shows the deviation after relaxation from an initial angle offset of 10° between nearest neighbors in a stacked peptide tape. Data taken from [14, 27].

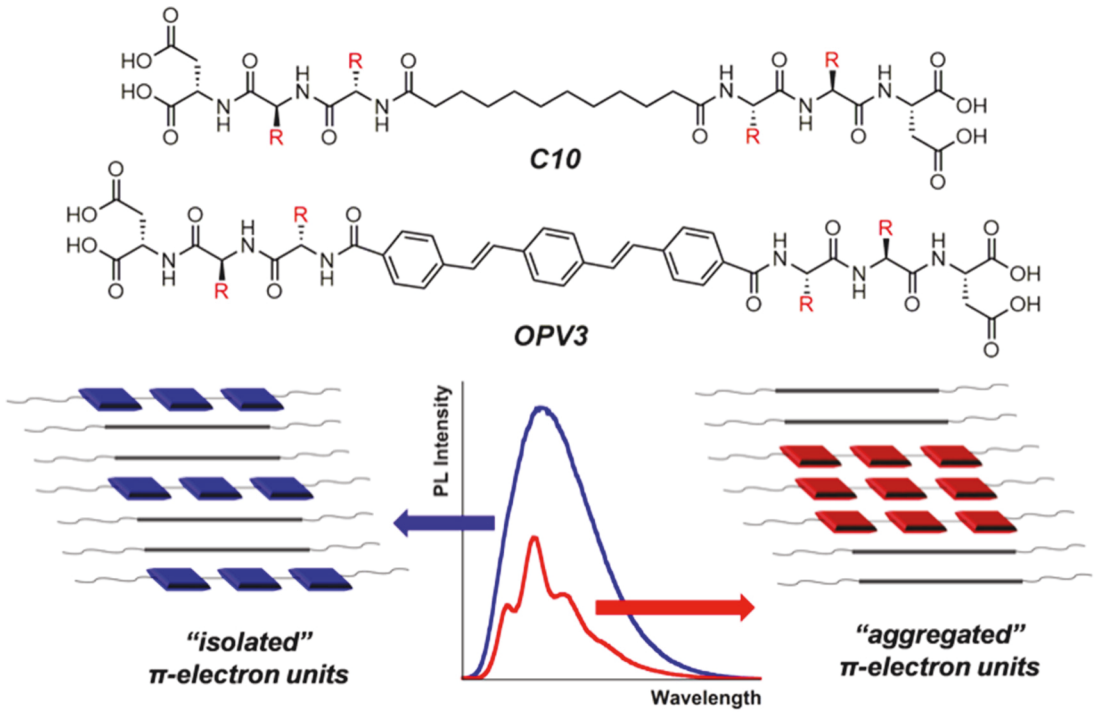

Figure 3. Structures of 'spectrally silent' peptides (C10) and pi-electron peptides (OPV3) where $R = -CH_2COOH$ or $-CH(CH_3)_2$ (top), along representative spectra corresponding to the extreme situations of intimate coassembly (bottom left) and self-sorting (bottom right). Adapted with permission from [29]. Copyright 2017 American Chemical Society.

onant influences are in addition to the exciton coupling influences that would lead to the blue-shifted UV–vis features [28]. In the absence of corroborating electronic structure calculations, a careful consideration of the observed spectral outcomes is necessary to gain insight about the nature of the intermolecular interactions within the peptidic nanomaterials. In order to probe these competing influences, we diluted an OPV3-containing peptide within a nanomaterial matrix that was comprised of optoelectronically silent alkyl peptides (C10, figure 3) [29]. Therefore, the pi-electron unit was blended as a minority component within the alkyl-rich nanomaterial. In principle, this allowed us to remove the influence of the exciton coupling (resonant influence) from the inherent change in local viscosity that would impact the chromophore's ability to undergo torsional rotation relative to the molecularly isolated case in solution (non-resonant influence), although the coincidence of the spectral windows where these signatures are manifested posed another challenge in the data interpretation. This was not a clear-cut study, as some peptide sequences promoted self-segregation (figure 3 bottom right) within the nanomaterials while others promoted the minority dilution (bottom left). This study further highlights the importance of sequence considerations when engineering a specific photonic outcome into peptidic nanomaterials.

Electrical transport

Based on the intermolecular electronic delocalization observed within the peptide nanomaterial assemblies, we envisioned their potential as biologically relevant semiconductors. Over the past decade, charge transport has been revealed in natural sequence oligopeptide fibrils as well as in artificial peptides bearing pi-electron semiconductors [30, 31]. In collaboration with Howard Katz at Johns Hopkins, peptide nanomaterials containing embedded quaterthiophene units (OT4, figure 4) were used as the semiconductive active layers in field-effect transistors that demonstrated charge carrier mobilities on the order of 10^{-4}–10^{-2} cm V^{-1} s^{-1} (top) [13, 32]. Although these are far from record-breaking values, they are remarkable coming from non-crystalline materials made up primarily of 'insulating' peptide sequences, and they are among the highest values reported for supramolecular peptide materials. Attempts were made to correlate peptide structure to the electrical performance (both in terms of sheet resistance and semiconductive behavior), but no definitive trends were found that could be correlated directly to the molecular composition. The surface roughness and overall packing densities of the active layers played a much greater role to optimize electrical transport [33]. We also studied the potential for these materials to transmit voltages, whereby we

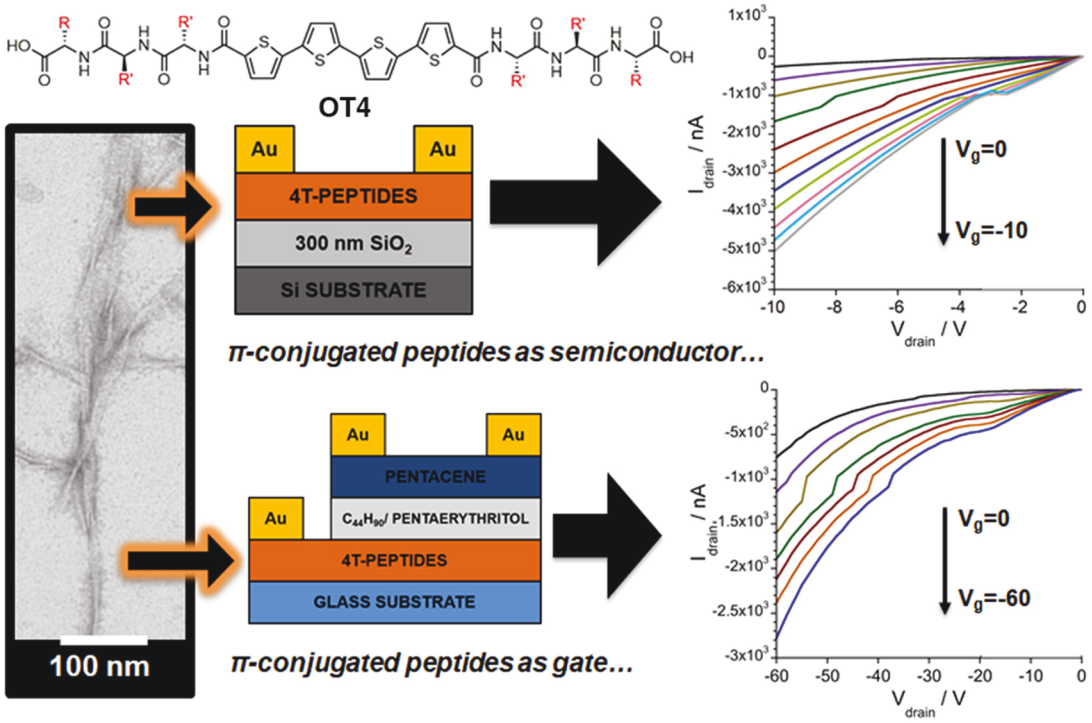

Figure 4. Schematic transistor architectures using OT4 peptide nanomaterials as an active semiconductor layer (top) and as an addressable gate electrode (bottom), along with their respective output curves (at right) showing the modulation of the drain current with applied gate voltages. Adapted with permission from [32]. Copyright 2015 American Chemical Society.

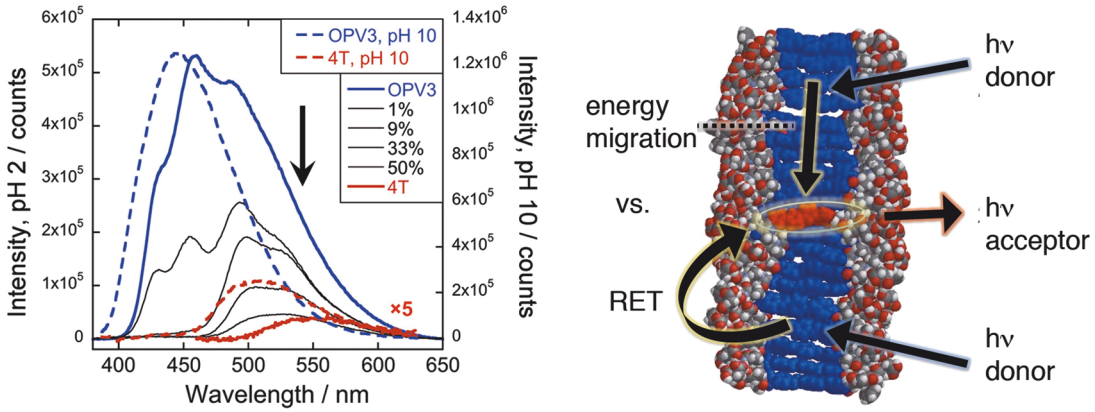

Figure 5. Pi-embedded peptides with energy donating (OPV3) and accepting (OT4) chromophores were mixed in varying ratios prior to photophysical measurements, leading to a dramatic shift to OT4 emission upon dilution within a matrix of OPV3 peptides (left) indicating the efficient energy transfer (right: OPV3 in blue, OT4 in red). Data taken from [38].

fabricated devices that used the peptide nanomaterials as a device gate electrode (rather than as the active layer, figure 4 bottom). The peptide nanomaterials were able to support the creation of electric fields that could be perceived by the device active layer even when insulated with up to 70 nm of dielectric material.

Photonic transport

Many materials sets generating current interest in bioelectronics are operative under electrical transport mechanisms. Although the impact of electrical signals on many cellular processes is well-established, generating such signals typically requires external power sources that must be implanted for *in vivo* use (e.g. pacemakers). A less explored aspect of bioelectronics involves using photonic stimuli to change materials properties or even create electric fields *in vitro* or *in vivo*. Excitonic migration and fluorescence resonance energy transfer processes are well established in supramolecular nanomaterials of interest for optoelectronics [34–37], and we turned our attention to similar photonic energy migration schemes within the peptide nanomaterials towards these more biomedical goals. In these cases, we move beyond the steady-state characterization of a single chromophore system to more complex coassemblies composed of chromophores poised for gradient

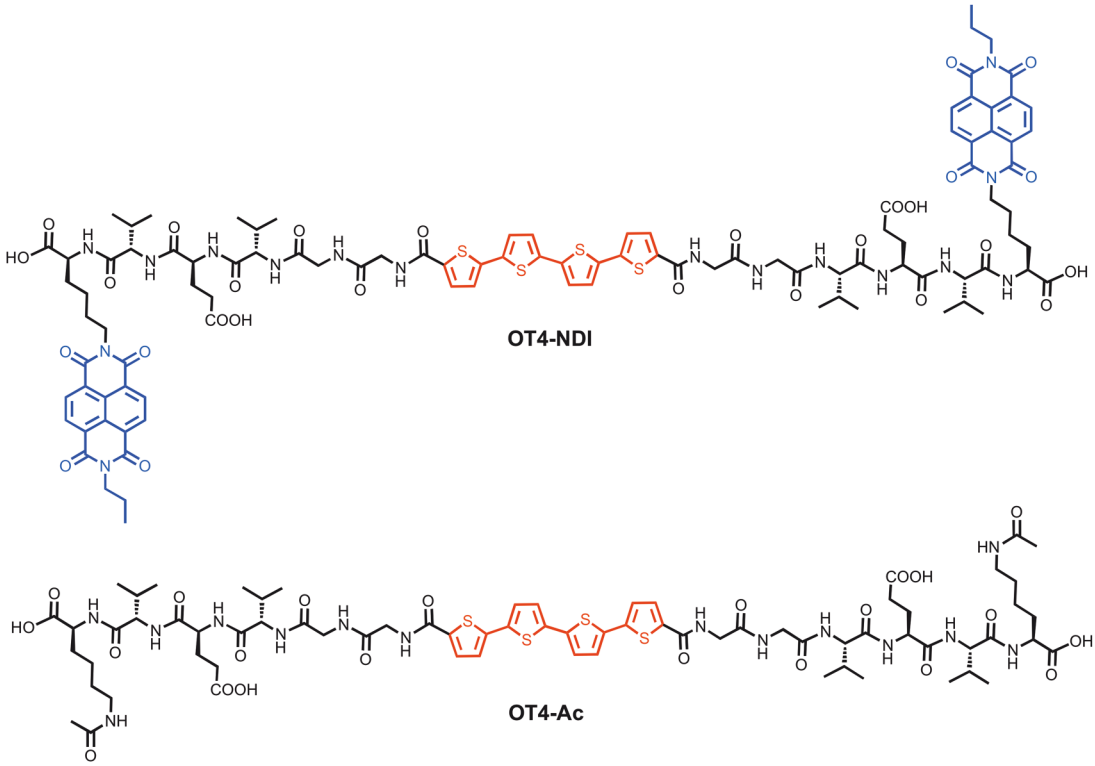

Figure 6. Structures of peptides with covalent electron donor–acceptor pairs (OT4-NDI) and a model system with *N*-acyl groups in lieu of NDI (OT4-Ac).

vectorial energy transfer from high-energy donor dyes to lower-energy acceptor dyes. We chose OPV3 and OT4 as donor and acceptor chromophores, respectively, once embedded within peptides because the fluorescence from the OPV overlapped reasonably with the absorption of the OT4 [38]. Their size complementarity also did not dramatically perturb the hydrogen bonding networks that are necessary for nanomaterial formation. In coassemblies made up of 1% of the OT4 acceptor dopant, 46% of the OPV matrix fluorescence was quenched (i.e. the reduction in intensity of the vibronic peaks at ca. 425 and 450 nm), and at 9% OT4, complete energy transfer to the OT4 was evident by the persistent emission at ca. 500 nm (figure 5). This key initial finding supported the viability of using peptide-pi conjugated as scaffolds for exciton migration.

We then went a different route with these coassembled materials, hoping to capture both exciton funneling and dissociation events, whereby the exciton could be split in the presence of a suitable excited-state electron acceptor. Although this is a fundamental process in photosynthesis that is attracting increasing interest for excitonic materials [39], we were attracted to this as a mechanism through which to create transient electric fields in biomaterials thus tuning their surface energetics through photonic stimulation. To achieve this process, we covalently attached a naphthalene diimide (NDI) by way of imidation with the terminal amine of a lysine residue included in the backbone of an OT4 peptide [40]. This excited state electron donor–acceptor pair was chosen based on the favorable electron transfer that had been demonstrated previously for this chromophore pair. We prepared a series of NDI-tagged OT4 peptides (e.g. OT4-NDI, figure 6) where the position between the OT4 donor and NDI acceptor was varied, and we also prepared acylated versions of the peptides (e.g. OT4-Ac) in lieu of NDI imidation as control diluent molecules that would support exciton delocalization within nanostructures by virtue of the OT4 inclusion but not undergo intramolecular charge separation.

We probed the solution photophysics of the OT4-NDI dyads as isolated molecules and within self-assembled nanomaterials, and we also diluted the dyads with the *N*-acyl control OT4-Ac peptides. The OT4-NDI dyads were not fluorescent due to the effective excited-state electron transfer, while the OT4-Ac systems showed typical oligothiophene fluorescence in solution. As more OT4-NDI dyad was added to solutions of unassembled OT4-Ac, a progressive and statistical drop in fluorescence intensity was observed, but the relative quantum yield of the OT4 unit stayed relatively constant (figure 7, left panels). In contrast, co-assembly of the two molecules led to much more dramatic quenching (right panels), suggesting that exciton delocalization to the NDI 'trap sites' was operative prior to dissociation and charge separation. We further characterized these charge-separated states with ultrafast transient absorption in collaboration with Arthur Bragg at Johns Hopkins. These studies revealed that the solution lifetimes for the charge sep-

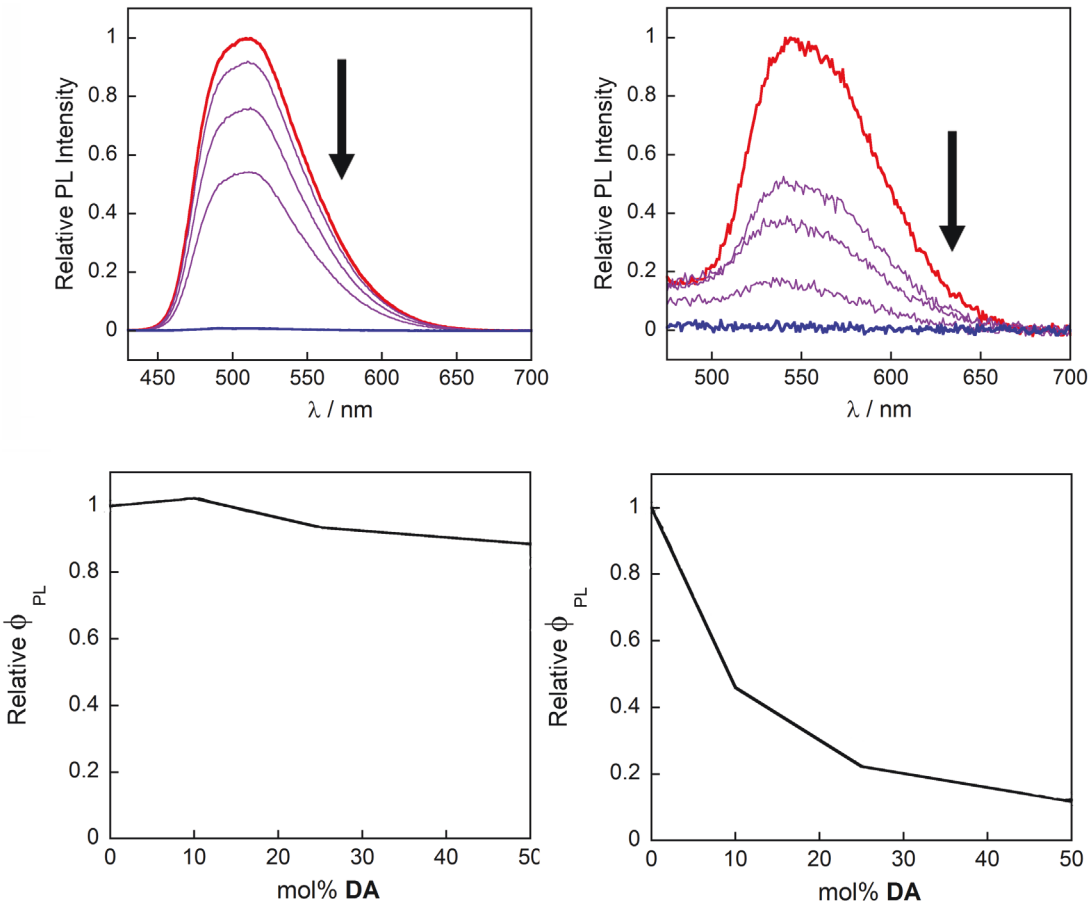

Figure 7. Photoluminescence (top panels) and relative quantum yields of OT4 (bottom panels) in the basic pH molecularly dissolved state (left panels) and in the acidic pH assembled state (right panels). The arrows show the trends as the mol% of OT4-NDI is increased in the majority OT4-Ac matrix. Data taken from [40].

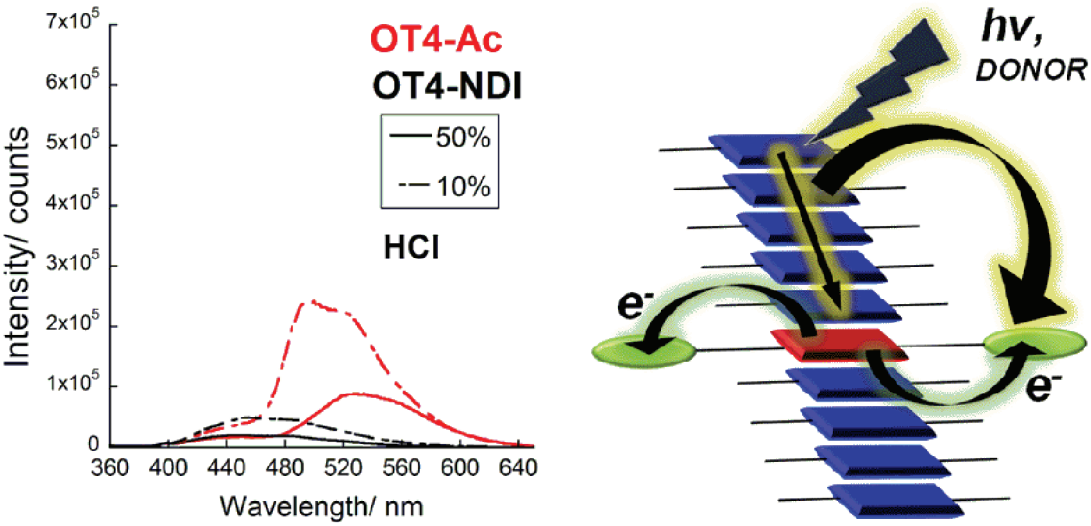

Figure 8. Photoluminescence (left) of OPV3 coassemblies with OT4-Ac (red spectra) and OT4-NDI (black spectra) at 10% (dashed) and 50% (solid) loadings. The image at right shows a depiction of the intimately mixed nanostructure, with OPV3 units in blue, OT4 in red and NDI in green. Data taken from [41].

aration, as evident from the spectral dynamics of the OT4 radical cation and NDI radical anion observed after excitation, were on the order of a few picoseconds. In contrast, the aggregated structures led to charge separated states that persisted for over a nanosecond! Thus, this biomaterial platform can undergo pulsatile photonic stimulation thereby creating transient isotropic electric fields local to the nanomaterial volume.

Most recently, we sought to take this idea one step further, to combine the exciton donor–acceptor

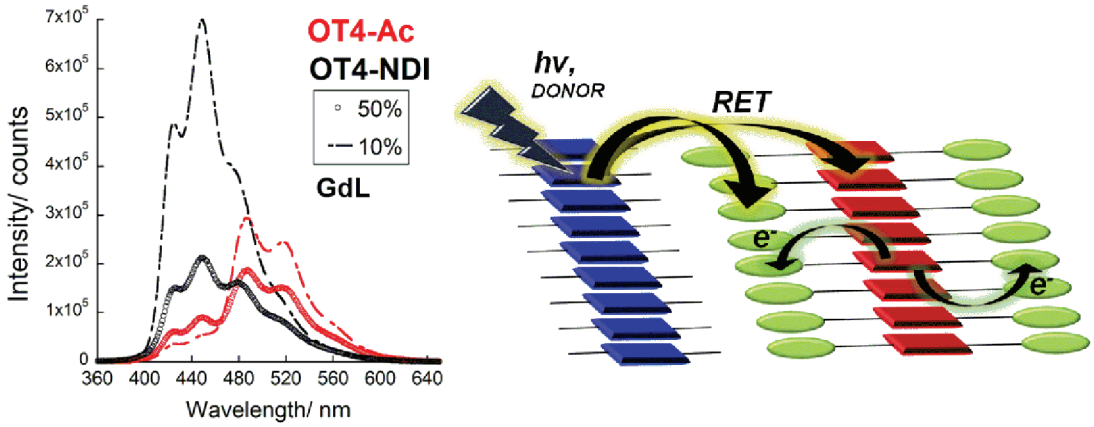

Figure 9. Photoluminescence (left) of OPV3 coassemblies with OT4-Ac (red spectra) and OT4-NDI (black spectra) at 10% (dashed) and 50% (open circle) loadings. The image at right shows a depiction of the self-sorted nanostructures, with OPV3 units in blue, OT4 in red and NDI in green. Data taken from [41].

functionality (figure 5) with the prospects for exciton funneling and separation (figures 6 and 7). Thus, we used an OPV3 peptide to form a majority matrix which was doped varied amounts of the OT4-NDI dyad [41]. Here, the idea was to use OPV3 as the harvesting dye that would transmit excitation to the low energy OT4 unit. At this point, the resonantly excited OT4 could then donate an electron to the NDI acceptor. While the OPV3/OT4 coassemblies revealed OT4 emission upon excitation of the donor chromophore (figure 8, red spectra), the OPV3 coassemblies with the OT4-NDI dyad provided no meaningful OT4 spectral signatures (black spectra), consistent with an effective exciton funneling and subsequent charge separation. Although we have not yet measured the persistence or the strength of the electric field resulting from this charge separation, extensions from our prior studies suggest this multi-chromophore coassembly will be an exciting strategy to direct photonic energy to specific locations within a nanomaterial prior to eliciting new chemistry or use in biomedical contexts.

All of the work above uses dramatic and rapid changes in solution pH to trigger the self-assembly process. Although this leads to kinetically trapped structures, these trapped nanomaterials provide consistent ensemble photophysics as evident in thermal annealing studies and successive pH variations to assemble and disassemble the supramolecular structures. Nevertheless, we were interested in exerting more control over the assembly process. In collaboration with Charles Schroeder (University of Illinois) and William Wilson (Harvard University), we have shown how slowing the rate of acid diffusion into a peptide solution has a marked influence on the nanomaterial morphology, leading to more uniform dimensions [42]. We were also intrigued by a strategy developed by Dave Adams (currently at University of Glasgow) whereby hydrolysis of glucono-d-lactone added in a peptide solution slowly (over 20 h) lowers the solution pH [43]. By proper consideration of peptide side-chain pKa, this slow drop can be used to provide sequential assembly of multiple components in a step-wise manner. Working with his group, we designed the peptide residues expressed on the OPV3 donor and OT4 acceptor to have distinct pKa differences. In doing so, we could achieve self-sorting of the two peptides, rather than intimate co-mixing, as evidenced in part through spectral interrogation and with x-ray diffraction in collaboration with Louise Serpell (University of Sussex). Specifically, the OT4-Ac co-assemblies with OPV3 (red traces, figure 9) show distinct higher-energy vibronic features associated with OPV3 aggregates (absorptions at ca. 425 and 450 nm) along with lower-energy OT4 emission. Similarly, the OT4-NDI co-assemblies (black traces) also show the OPV3 vibronic signatures, but OT4 emission is quenched due to the subsequent excited-state charge transfer. From a photonic perspective, these distinct assembly pathways enable the creation of random blends of disparate energy materials together to direct excitons to low-energy trap sites and segregated structures that might promote donor–acceptor blocks and drive excitations to disparate interfaces (akin to a *p-n* junction). An additional pathway to create more ordered donor–acceptor stacking might arise from the use of oppositely charged peptide sequences in conjunction with pi-electron core variance [44].

Future prospects

Our recent research activities provide a broad foundation of photonic tunability that can be exploited for future materials investigations. The generality of the synthesis methods will allow for continued 'bandgap engineering' whereby energy levels can be tuned for desired luminescence properties or redox potentials. This in conjunction with sequence design will allow for the realization of coassemblies—self-sorted or intimately mixed—with abilities to allow for energy delocalization (e.g. excitonic interactions) or for energy trapping (e.g. by energy offsets or excimeric states). These outcomes can be used to tailor

electrical properties into the peptide nanomaterials in a way that is not available within standard peptide biomaterials. We envision that the versatility of the synthesis chemistry could enable these new photonic functionalities to be merged with several existing nanobiomaterial platforms, such as phages, actin filaments, collagens or filamentous electron transfer conduits. The use of protein-based hydrogels to provide an artificial environment capable of supporting encapsulated cells has received substantial attention in the context of tissue engineering scaffolds that encourage cell proliferation prior to tissue or even organ development. Furthermore, the passive chemical constituents of the scaffold (along with the composition of the aqueous matrix) are also able to guide stem cell differentiation into specific desired cell lineages. We are currently exploring the *in vitro* and *in vivo* impacts of photonically-created electric fields on a variety of cell physiological processes in the context of tissue engineering. The ability to create transient and localized fields in a biomaterial scaffold could hold great promise for a variety of neural and cardiac repair schemes, and we hope to be able to contribute positively to this growing area.

Acknowledgments

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