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Coherent and Incoherent Interactions between Cofacial π-Conjugated Oligomer Dimers in Macrocycle Templates

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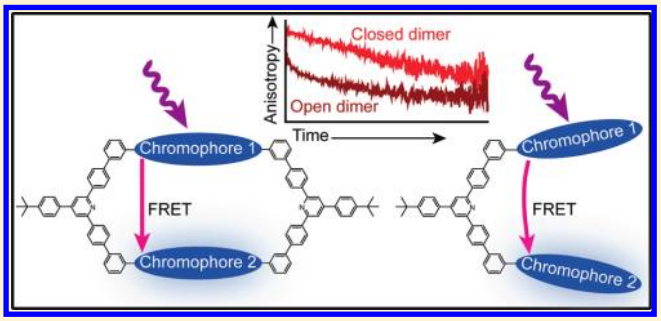
Supporting Information

ABSTRACT: The interactions between two π-conjugated oligomers templated in molecular scaffolds are revealed as a function of separation and orientation, providing models of intermolecular interactions in bulk organic semiconductor materials. For a variety of dimer geometries (acyclic and macrocyclic) of the same model oligomer, no change in fluorescence spectra, fluorescence dynamics, or low-temperature single-molecule emission characteristics is observed. A small red-shift and slowing of fluorescence in the most closely spaced macrocyclic dimer structure is thought to arise both due to an intramolecular solvatochromic shift as well as from weak intramolecular aggregate formation. No corresponding effect is observed in bulk films of the acyclic model oligomer, implying the absence of intermolecular aggregate or excimer formation due to random relative dipole orientations. The largest effect of intramolecular geometry of the model dimer structures is seen in transient fluorescence depolarization, where an open ring geometry leads to rapid depolarization, compared to the corresponding macrocycle, due to the presence of a range of molecular transition dipole moment orientations. Self-assembled monolayers of the molecules on HOPG investigated by scanning-tunneling microscopy further illustrate the conformational variability of the open dimers in contrast to the fixed conformation of the closed dimers.



INTRODUCTION

One of the greatest puzzles in organic electronics relates to the emergence of bulk-like properties from individual molecular building blocks.[1−3] The electronic characteristics of individual molecules are reasonably well understood on a microscopic level,[3−8] and sophisticated empirical models exist to describe the function of bulk materials in devices, such as the creation, migration, and recombination of charges and excitons.[1,9−14] However, few attempts have been made to go beyond the level of an individual molecule to begin to construct the bulk material from the bottom up.[15−21] With present advances in the synthesis of complex organic functional materials by means of structural templating, for example, through rigid macrocyclic scaffolds,[22−24] routes are emerging to precisely control the relative spacing and orientation between individual conjugated segments to assess how cooperative and collective effects emerge on the way from the individual unit to the bulk.[1,25] Interactions between individual units may occur either in the weak or in the strong coupling regime.[4,16,19−21,26] In the former, fluorescence resonance energy transfer (FRET) can arise,[4,26] which, given suitable orientations of the transition dipole moments, can be revealed by means of fluorescence depolarization spectroscopy.[22,23] In the latter regime, a coherent delocalization between excited states arises which modifies both the transition spectrum and lifetime.[16,20,25,27,28] Depending on the relative dipole orientation of the chromophores, oscillator strength may add up or subtract for the lowest-energy transition, leading to a rise or a decrease of radiative rate.[7,21] Such coherent interactions will generally modify the spectra, whereas incoherent interactions will leave the spectra unchanged.[21,26] While there have been several studies on controlled interactions between individual conjugated units *within* a molecule,[4,12,16,25] most commonly in oligoacene derivatives, and attempts have been made to tune interactions between building blocks within the bulk,[13,28] it is much harder to create molecular frameworks in which the coupling of larger units such as the electronically active segments of a conjugated polymer chain can be investigated. Here, we focus on a material system based on oligo(phenylene-ethynylene-butadiynylenes) of defined oligomerization degree, which closely resembles a typical conjugated unit, the chromophore, as is formed in a polymer chain. By tuning the spacing between intramolecularly connected parallel units, and

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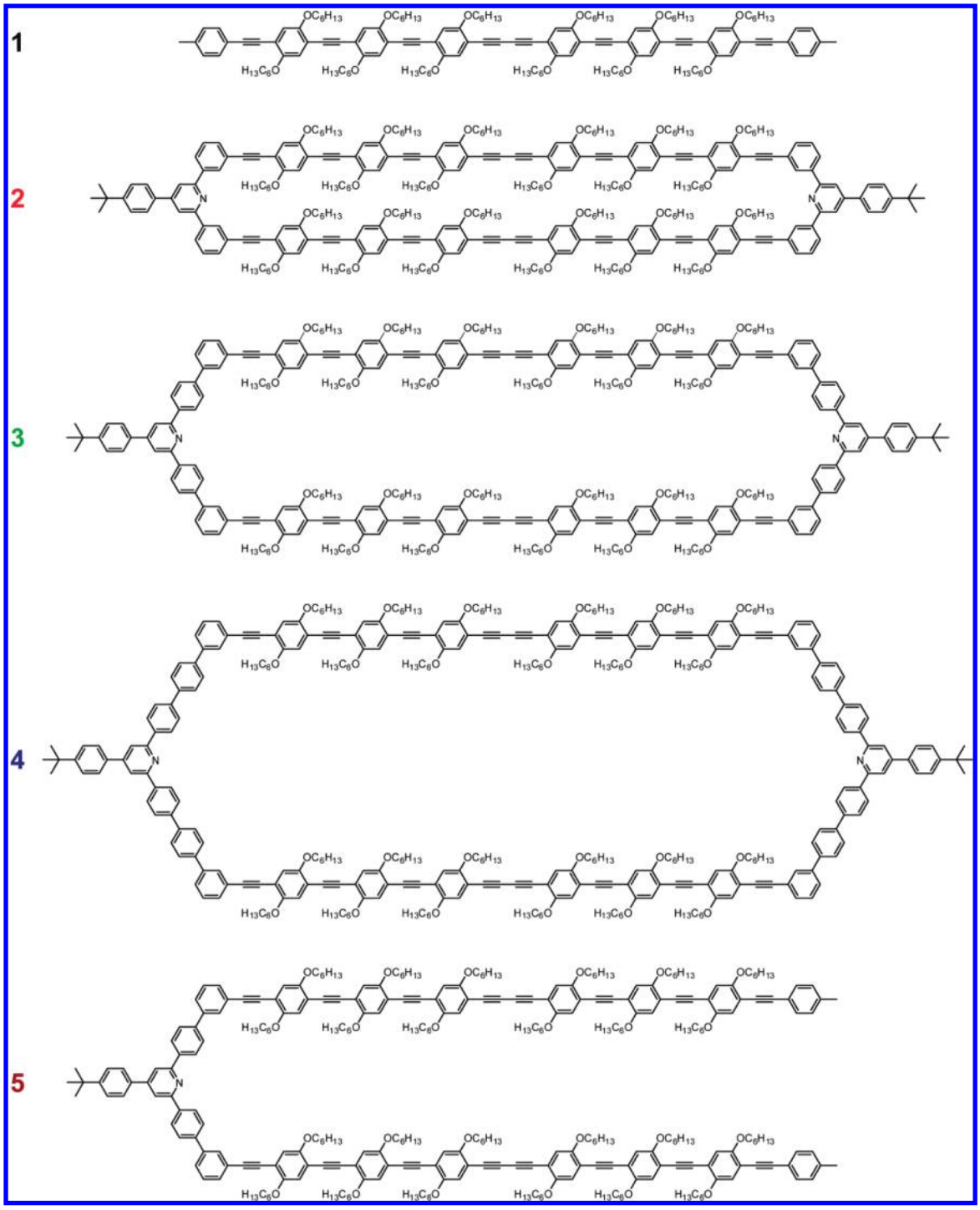

Figure 1. Structures of the phenylene-ethynylene-butadiynylene oligomer **1** and dimers **2**–**5**.

their relative orientation, coherent coupling and incoherent energy transfer can be differentiated.

RESULTS AND DISCUSSION

Figure 1 shows the structures under investigation. The synthesis and a full characterization of the compounds **1**, **2**, **4**, and **5** can be found in the Supporting Information. The synthesis of macrocycle **3** was recently described.[24] All cyclic structures are built up by placing two monodisperse conjugated oligomers in a parallel configuration with a defined distance. The distance of the two chromophores is determined by two rigid aromatic clamps: 0.7 nm (**2**), 1.4 nm (**3**), and 2.1 nm (**4**). To evaluate the effect of the parallel chromophore alignment on the photophysical properties of the compounds, **5** was prepared in which the chromophores are still covalently connected but can adopt different relative orientations (see below). Monomer **1** is investigated as a reference, constituting the basic building block of the cyclic and acyclic model compounds. The basic optical properties of the materials, obtained at room temperature in dilute (10^{-7} molar) chloroform solution, are summarized in Figure 2. On the basis of their parallel arrangement, intramolecular H-aggregate

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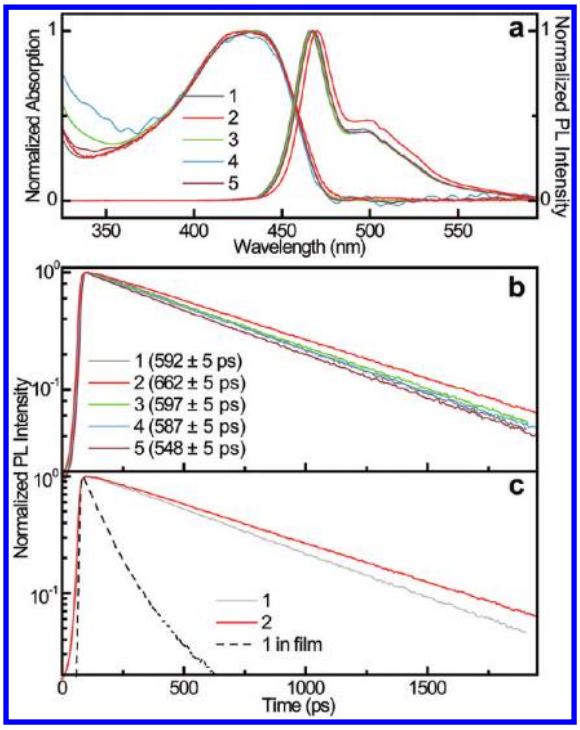

Figure 2. Photophysical characteristics of compounds **1**–**5**. (a) Absorption and fluorescence spectra in dilute chloroform solution. (b) Fluorescence lifetime. (c) Comparison of the film fluorescence decay of **1** to the solution emission decay of **1** and **2**.

formation between the two chromophores on the dimers is an intuitive expectation. Such aggregation should be evident both as a hypsochromic shift in absorption and as a decreased decay rate compared to the monomer, since the lowest-energy transition of the split excited state loses oscillator strength.[17,29] However, the absorption and emission spectra (panel a) are virtually identical for all five compounds, except that a small red-shift is observed in the absorption and emission spectra of the most closely spaced dimer **2**. In the absorption spectrum, the shift of the red-tail by 1.2 nm with respect to the monomer **1** is close to the resolution limit, but in emission, the intramolecular interchromophoric interaction accounts for a bathochromic shift of 4 nm. At the same time, the intensity of the vibronic structure around 500 nm increases with respect to the monomer **1**. The fluorescence decay of the solutions is given in Figure 2b, recorded with a picosecond streak camera under excitation at 430 nm by a frequency-doubled femtosecond laser. Within measurement accuracy, the fluorescence lifetimes of the monomer **1** and the more widely spaced dimers **3** and **4** are identical. The closely spaced dimer **2** displays an increase in fluorescence lifetime of 10% and the open dimer a reduction in lifetime of 7%. The combination of increased lifetime and red-shifted emission in **2** bears signatures of an excimer,[17,28,30−32] a dimer which only exists in the excited state. Since the ground state of such a dimer is repulsive, the transition lifetime is increased with respect to the monomer and the emission spectrum broadens and shifts to the red.[29,33] However, since the spectral changes in the emission are only very weak, it appears more reasonable to describe the closely spaced dimer in the framework of weak H-aggregate formation, as explored in detail by Spano et al.[34−36] and Barford.[37] In this picture, the strength of interchromophoric coupling decreases with increasing conjugation length,[34] explaining why aggregation signatures are so much stronger in molecular crystals than in π-conjugated polymers. The coherent coupling energy for the present dimer structure of separation ~7 Å is estimated to be less than 100 cm^{-1},[35,36] implying a barely discernible blue shift in the absorption spectrum. As a consequence, the 0−0 to 0−1 transition peak ratio in the absorption, which decreases as the coupling strength (as manifested by the exciton bandwidth) increases, remains virtually unchanged upon formation of the dimer.[35] Related weak effects have been extrapolated from investigations of polythiophene films.[35,36] In contrast, the emission is red-shifted and retarded, since it occurs from the lower-energy level of the split exciton dimer. Transitions from this state become (weakly) forbidden for (weak) H-aggregation. Correspondingly, the relative intensity of the 0−1 transition increases slightly, since vibrational coupling can help to mix allowed and forbidden dipole transitions. As discussed below and in the Supporting Information, solvent effects may also shift the emission and absorption spectrum. Since aggregation-induced shifts in absorption and emission can arise in different directions (i.e., a blue shift for absorption, a red shift for emission), solvent shifts may entirely mask any aggregation shift in absorption, while seemingly amplifying shifts in emission.

There has been extensive debate in the literature about the possible emergence of excimers or other aggregate species by intermolecular interactions in conjugated polymers.[10,13,28,34−37] The underlying problem in any spectroscopic approach is that both spectral and lifetime changes in a heterogeneous bulk system may have a range of origins. For example, emissive chemical defects may also be present, whose role can be dramatically amplified by energy transfer in the solid.[38] Given this tentative suggestion of weak H-aggregate formation in **2**, it is tempting to search for aggregate signatures in the bulk film of the monomer **1**, where even closer cofacial packing should be possible than in the dimer **2**. However, the decay of the fluorescence from the film of **1** is significantly *accelerated* with respect to the solution-based measurements of **1** and **2**, as shown in Figure 2c. Thus, the film-based fluorescence decay measurement does not reveal any signatures of possible aggregates in the film of **1** on the level of that seen in the intramolecular aggregate **2**, implying that spontaneous cofacial ordering of the oligomers does not occur in bulk films. Full inspection of the fluorescence spectra and decay characteristics of bulk films created from each molecular system is available in the Supporting Information.

Strong dipolar interactions between adjacent chromophores leading to a splitting of energy levels and an energetic redistribution of oscillator strength are not the only interchromophoric effects which can arise. Many nominally unpolar π-conjugated systems display a substantial solvatochromic response which can be amplified by the presence of polar backbone substituents,[39] such as the alkoxy groups used in the present case. The slight red-shift in the absorption of **2** may therefore arise due to a small modification of the effective solvent shell surrounding the individual chromophore due to the proximity of the two chromophores. This proximity effectively gives rise to a solid-state solvatochromic effect *within* the isolated molecule.[40] We discuss this possibility in detail in the Supporting Information. The formation of aggregates or excimers should not be strongly sensitive to solvent polarity,[32] although the solvent may of course affect the conformation of the chain and thus the effective conjugation length, which in turn can control coupling.[34] To assess the solvatochromic

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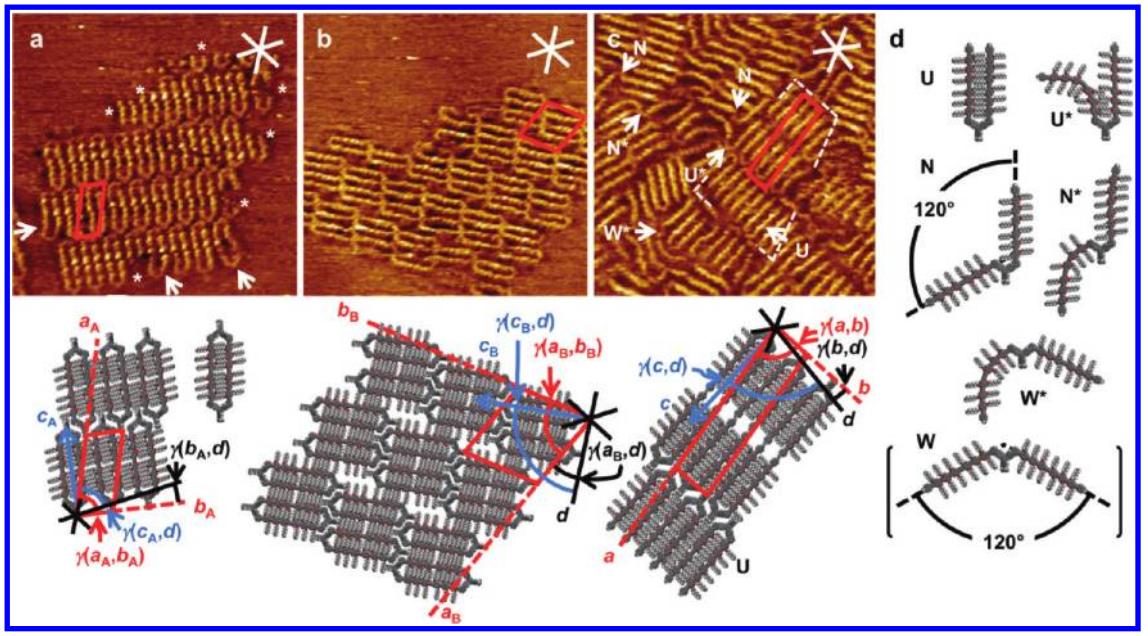

Figure 3. STM images and molecular models of self-assembled adsorbate layers of the closed dimer **3** (panels a, b) and the open dimer **5** (panels c, d) on highly ordered pyrolytic graphite (HOPG). The associated sketches illustrate the observed molecular packing. For the open dimer **5**, different packing is possible due to the variable molecular conformations, as summarized in panel d. U, N, and W indicate distinct planar conformers of **5** after rotation of the rigid rod units around the clamp unit, and U*, N*, and W* illustrate similar conformers where additional bending of the rod units occurs. (a: 35.1 × 35.1 nm^2, V_s = −1.0 V, I_t = 10 pA, unit cell: a_A = 6.3 ± 0.3 nm, b_A = 2.9 ± 0.2 nm, $\gamma(a_A, b_A)$ = 77 ± 2°; b: 41.1 × 41.1 nm^2, V_s = −0.8 V, I_t = 6 pA, unit cell: a_B = 6.5 ± 0.3 nm, b_B = 6.3 ± 0.3 nm, $\gamma(a_B, b_B)$ = 74 ± 2°; c: 37.1 × 37.1 nm^2, V_s = −1.0 V, I_t = 6 pA, unit cell: a = 12.5 ± 0.3 nm, b = 2.9 ± 0.2 nm, $\gamma(a, b)$ = 83 ± 2°. Red, blue, and white (black) lines represent unit cells, directions of the linear rigid rod units, and HOPG main axis directions, respectively. Asterisks in part a indicate partly imaged molecules. See also the Supporting Information).

effect, we performed time-resolved spectroscopy in four solvents with different polarities, and found that the molecules demonstrate obvious solvatochromism. In all cases, **2** shows the most red-shifted spectra and the slowest PL decay compared to the other compounds. We conclude that both aggregation and intramolecular solvatochromism are most likely responsible for the observed distinctive difference of **2** with respect to the other compounds.

The slight acceleration in fluorescence decay of the open dimer **5** may be interpreted as an indication for the occurrence of intramolecular FRET.[12,26] The two chromophores in the dimers have (nearly) identical transition energies and lifetimes. Coupling between the two in the form of FRET should therefore neither modify the emission color nor the fluorescence kinetics substantially. However, the open dimer **5** is by design less rigid than the other dimers so that the chromophores are only accidentally aligned in parallel with respect to each other.[24] This absence of rigidity is readily visualized by directly comparing the molecular self-organization on highly ordered pyrolytic graphite (HOPG) by scanning-tunneling microscopy (STM) for closed (**3**) and open (**5**) dimers. The STM images in Figure 3a and b show that **3** spontaneously orders into regular structures.[24] The cyclic nature of the molecular building blocks can be clearly visualized. The two-dimensional crystal structure is illustrated in the associated molecular models. In contrast, as shown in panel c, the 2D crystalline domains of **5** are of limited lateral dimensions, and separated by amorphous regions. After adsorption from solution (and thus restriction to planar structures), three distinct conformers of **5** with different orientations of the rigid rod units relative to the rotatable clamp unit can be distinguished, which are denoted in the schematic in panel d as N, U, and W (the ideal geometries with rigid oligomer units); and as N*, U*, and W* (which include bending of the rod units). Such a variety of structural conformers is observed in the images in Figure 3c. Further details of this structural analysis are given in the Supporting Information.

To test for the influence of this intramolecular conformational disorder in intramolecular FRET, we measured the depolarization of fluorescence as a function of time. The polarization anisotropy in emission can be defined as $r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$, where the intensities $I_{\parallel}$ and $I_{\perp}$ refer to the fluorescence polarized parallel and orthogonal to the incident laser, respectively. r is expected to decrease with time as the molecule tumbles in solution, starting from an initial value of 0.4 as expected for an isotropic distribution of linear transition dipoles in space.[23,41] Figure 4 exhibits the transient anisotropy for the five model compounds. There is no difference between the rigid dimers **2**, **3**, and **4**, suggesting that these molecules have a similar effective hydrodynamic radius (and therefore the same rotational diffusion coefficient).[22] Fluorescence of the monomer **1** depolarizes more swiftly, since the molecule is smaller and rotates faster in solution. The open dimer **5**, however, displays a rapid drop in anisotropy in the first 200 ps, followed by the same depolarization dynamics as found in the closed rings. See the Supporting Information for a direct comparison of anisotropies of all five compounds, where the anisotropy decay curves are all plotted in the same graph.

Given that the fluorescence spectrum and lifetime of **1**, **3**, and **4** are identical to those of **5**, it is remarkable that such a large difference exists in the fluorescence depolarization kinetics. The depolarization can only be explained by the existence of a range of different conformers of the open dimer, with a large angular distribution of the two chromophores with respect to each other.[5] Although one may expect a significant

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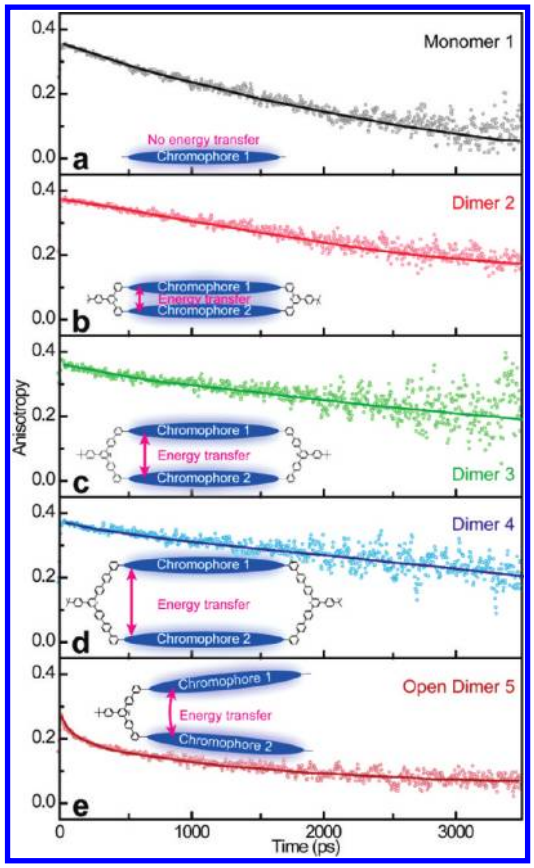

Figure 4. Fluorescence anisotropy decay for the monomer **1** (panel a), closed dimers **2**–**4** (panels b–d), and the open dimer **5** (panel e) in dilute solution.

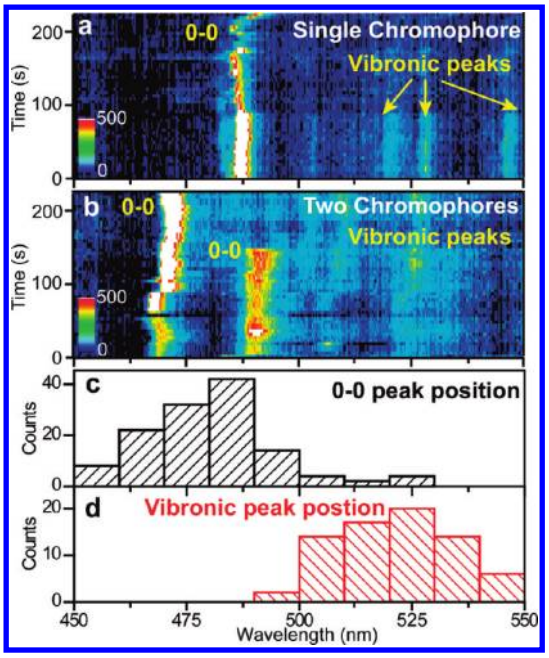

Figure 5. Low-temperature (5 K) single-molecule luminescence spectra as a function of time for a single dimer **5** exhibiting a single dominant peak (a) or two dominant peaks (b). The peaks are attributed to chromophores. Vibrational modes in the fluorescence are also seen, e.g., at 520, 528, and 545 nm in part a. The peak positions of the 0-0 transition and the vibronic progression scatter from molecule to molecule as shown in the histograms in parts (c) and (d), respectively.

degree of freedom to rotate around the phenylene bonds linking the two chromophores in **5**, with both chromophores remaining in the same plane, the results imply the possibility of bending of the molecule in three-dimensional space with the two chromophores twisting out of the molecular plane and opening up like a pair of scissors. The isolated dimer therefore behaves somewhat like a disordered bulk film, with acceptor sites of different orientations available so that FRET can drive depolarization.[22,23,42,43]

In the rigid dimers, the parallel arrangement of the chromophores should imply that coupling by FRET is efficient, even if there is no immediate experimental path to prove this assumption, since the chromophores are nearly isoenergetic (i.e., there is no spectral shift) and no FRET depolarization occurs. An indirect way to test for coupling is to examine the number of chromophores detected in a low-temperature single-molecule experiment. We have previously demonstrated that rigid polyphenylenes are especially prone to the formation of distinct chromophoric units with well-defined spectroscopic signatures.[8] These units can be differentiated by their transition energy, which effectively scatters over the inhomogeneously broadened ensemble spectrum. The number of distinct spectral peaks, i.e., chromophores, scales with the molecular weight of the polymer,[44] so we may expect to see multiple peaks in single-molecule spectra due to the multiple chromophores present in the dimers. Single-molecule fluorescence spectra were measured at 5 K by isolating individual molecules in a Zeonex matrix and recording the emission in a microscope setup as described in earlier work.[45] Figure 5 shows two examples of the temporal evolution of single-molecule emission for **5**, where the intensity is color-coded and plotted as a function of time and wavelength with 5 s resolution. In the upper panel, we display an example where only one single transition is observed. The intensity and wavelength of the single emitter fluctuate over time, due to blinking and spectral diffusion. The bands at longer wavelength, e.g., at 530 and 545 nm in panel a, correspond to the vibronic progression of the electronic transition. The lower panel shows an example where two transitions are seen, one at 470 nm and one at 490 nm. In the course of the experiment, we investigated a number of molecules. The scatter of the peak positions between different single molecules is shown in the histogram: different individual units exhibit different transition energies. Consequently, different units should be detectable within a single bichromophoric molecule. However, virtually all single molecules showed only single chromophore emission line, whereas previous work on single polymer chains often showed multichromophoric emission with multiple peaks in the PL spectrum.[44] For **1**, where single-peak emission is to be expected, 434 molecules showed one 0–0 peak with one molecule showing two. For **2**, **4**, and **5**, the numbers were 195, 0; 59, 1; and 130, 2, respectively. If the chromophores did not couple within the molecule, we would expect to see many more cases of dual-peak emission in the dimers. Since this is not the case, we conclude that energy transfer occurs within the dimer to the lowest-energy unit so that only one emission peak is observed. The conclusion is subject to the assumption that there is no long-range correlation between the two chromophores, i.e., that the scatter in energy between chromophores within a molecule is identical to the scatter between different molecules, as shown in the histogram. The four events of double-line emission recorded out of 818 single-

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molecule spectra may signify a rare situation of FRET blockage, e.g., due to particularly weak dipolar coupling between chromophores with weak vibrational coupling and correspondingly narrow spectral resonances and an absence of spectral overlap between donor and acceptor; or else could arise due to two molecules being present within the diffraction-limited focal spot of the microscope. Interestingly, no difference is seen between compounds **1**, **2**, **4**, and **5** on the single-molecule level in terms of the spectrum, blinking, brightness, and spectral dynamics, implying that efficient incoherent interchromophore coupling to a lowest-energy state also occurs in the most distantly spaced aggregate **4**.

CONCLUSIONS

In summary, we have performed a range of optical and structural studies on open and closed π-conjugated bichromophoric systems as model systems for interchromophoric interactions in organic electronic materials. The spectral properties and emission lifetime are remarkably resilient under structural variations. Introduction of intramolecular disorder by removal of one of the macrocycle clamps reveals interchromophoric intramolecular FRET in terms of an accelerated decay of polarization anisotropy. The occurrence of FRET in the open dimers implies that it must also arise in the closed dimers, even though it can only be inferred indirectly, for example, by the low-temperature single-molecule emission characteristics. Interchromophoric interactions, and especially light-harvesting phenomena, are usually visualized by means of a change in fluorescence spectrum, lifetime, or polarization anisotropy. The systematic approach presented here, by constructing conformationally controlled dimers from individual building blocks, illustrates that interchromophoric interactions may even arise when no immediate observable is available, since neither lifetime, spectrum, nor polarization change in the parallel closed dimers. Realizing the presence of such interactions is crucial for understanding limitations in quantum efficiency of the material, since interchromophoric coupling can promote migration of excitation energy to quenching species. At the same time, large aggregates of parallel chromophores in macrocyclic templates could pose excellent systems for fluorescence quenching-based sensing, with superior interaction cross sections when compared to conventional linear polymers.

ASSOCIATED CONTENT

Supporting Information

Photoluminescence of bulk films, solvatochromism, detailed discussion of fluorescence depolarization, experimental methods, scanning-tunneling microscopy results, and details of synthesis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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