Phenylene−Ethynylene Macrocycles as Model Systems of Interchromophoric Interactions in π-Conjugated Macromolecules

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Received: January 8, 2008; In Final Form: March 1, 2008

Unraveling the complex photophysics of macromolecular π-conjugated systems requires both the development of suitable model systems to access a particular subset of a material's parameter space and the choice of matching spectroscopic techniques. We address the question of the strength of interchromophoric interactions in macromolecular systems by studying the fluorescence depolarization kinetics of a family of prototypical conjugated macrocycles. Shrinking the size of the molecular system decelerates fluorescence depolarization even though the radius of gyration decreases. Although the smaller macrocycles show faster rotational diffusion, the larger compounds exhibit an additional initial depolarization mechanism, attributed to intramolecular interchromophoric energy transfer. Comparison with fragments of the molecule illustrates that the larger macrocycles can be interpreted as bichromophoric systems, whereas the effectively parallel chromophoric elements of the smaller ring are indistinguishable in terms of polarization. The potential role of strong interchromophoric interaction is discussed. The results illustrate a subtle link between interchromophoric arrangement and ultrafast fluorescence depolarization, phenomena, which are often considered in the context of conjugated polymers: chromophoric alignment can potentially counteract the effect of polarization memory loss through energy transfer.

Few topics in the field of organic electronics have received as much attention in the past as the influence of intersite interactions in bulk materials.[1,2] Clearly, strong intersite couplings can be beneficial in many cases, such as by improving the ability to separate charge carriers in a photovoltaic device or enabling optimal transport of charges from one molecular entity to the next in a field-effect transistor. Alternatively, intersite interactions can potentially lead to a reduction in the overall fluorescence yield, an effect well known as concentration quenching in laser dyes, and even result in the formation of new, intermolecular excited-state species with poor radiative properties.[1] Spectroscopically, intersite interactions are not always trivial to pinpoint. Modifications of an emission spectrum or the fluorescence lifetime, for example, may simply be a signature of changes in intersite energy transfer in the bulk,[3] which may even result in a dramatic amplification of chemical impurity species as in the case of polyfluorenes.[4] In addition, spectroscopy of the bulk phase of a π-conjugated material is often complicated by the fact that both the chain and the film morphology may impact the spectroscopic properties to a level not known a priori.[1] Advances in the understanding of the relevant contributions of different forms of interchromophoric interactions have been made in the past by combining carefully crafted model material systems with appropriate spectroscopic techniques and computational analyses.[5] Both single-molecule[6] and ultrafast spectroscopy[7] have revealed evidence for the occurrence of strong and weak interchromophoric dipole−dipole coupling processes in natural light-harvesting complexes. In the weak coupling limit, an individual chromophore constitutes a distinct entity so that all intersite coupling results in a loss of coherence of the electronic wave function.[8,9] The oscillator strength consequently scales linearly with the number of entities.[10,11] In contrast, under the premise of strong coupling, the excited state becomes coherently delocalized between different chromophoric units, leading to a superlinear increase in oscillator strength with molecular size.[8,10,12−14] Specifically synthesized heterogeneous or homogeneous molecular dyads with variable spacers have also been able to highlight a transition from strong to weak coupling in steady-state spectroscopy combined with quantum chemistry,[10,15−18] as well as in single-molecule spectroscopy.[12−14] Finally, ultrafast fluorescence depolarization in select conjugated systems has revealed signatures

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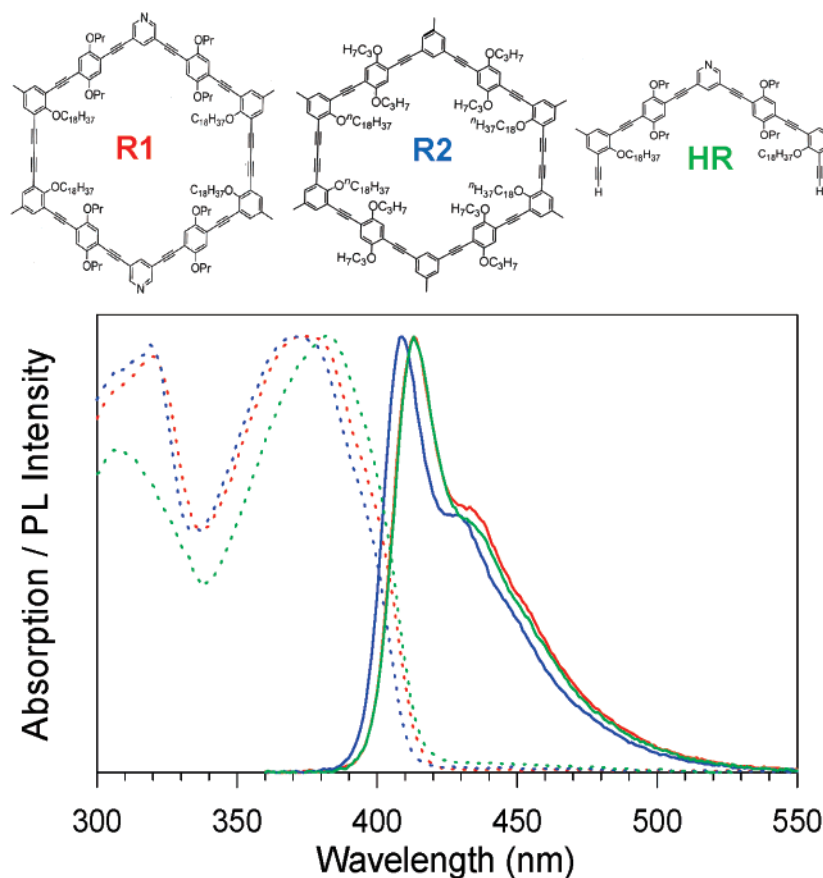* Corresponding author. E-mail: lupton@physics.utah.edu.

Figure 1. Absorption and emission spectra of two macrocycles R1 (red) and R2 (blue) as well as a half ring of R1, labeled HR (green), in toluene solution.

of coherent intersite delocalization.[19−24] Fluorescence depolarization is frequently invoked as a method to study both interchromophoric energy transfer and excited-state relaxation in extended π-conjugated systems such as conjugated polymers.[25−27] As an excitation moves from one chromophore to the next the memory in polarization is lost, providing direct access to relaxation dynamics. However, the interpretation of this process, often referred to as spectral diffusion,[3] assumes the absence of coherent interchromophoric electronic delocalization.

Shape-persistent conjugated macrocycles are structurally fascinating systems[28−35] that have thus far received only limited attention in terms of their optical properties.[24,36−48] In this communication we illustrate how they can be employed to study interchromophoric interactions in multichromophoric macromolecular aggregates such as conjugated polymers. The structurally well-defined model system, phenylene−ethynylene macrocycles, allows us to distinguish between fluorescence depolarization resulting from the conjugated macrocycles rotating out of the plane of polarization used in excitation and interchromophoric energy transfer. The larger rings behave much like π-conjugated polymers, displaying a rapid fluorescence depolarization due to interchromophoric energy transfer,[25−27] followed by a slower rotational diffusion, which is mimicked in the monochromophoric half-rings. The smaller rings, however, display faster rotational diffusion but no rapid depolarization because there is no interchromophoric energy transfer.

We investigated the picosecond fluorescence kinetics of a range of conjugated phenylene−ethynylene macrocycles. Figure 1 summarizes the structures of the macrocycles under investigation along with the absorption and emission spectra of toluene solutions of the compounds (10 μg/L concentration, 375 nm

excitation). Structures R1 and R2 are virtually identical except for pyridine rather than phenylene units linking the two halves of the ring in R1. The half ring structure of R1 is described by compound HR. The absorption and emission spectra of the three materials are very similar. The absorption peaks at 375 and 320 nm (R1), 370 and 320 nm (R2), and 383 and 306 nm (HR), respectively. The emission maxima are observed at 413 nm (R1), 409 nm (R2), and 413 nm (HR). We conclude that, at first glance, little difference exists in the excited-state dynamics because all three compounds display a fluorescence lifetime of 1.0 ns, detected using a Hamamatsu streak camera with 50 ps time resolution under excitation by a 80 MHz repetition rate frequency-doubled Ti:sapphire laser at 375 nm. Apparently, the nitrogen atom in the pyridine unit in the *meta* conjugation does not promote significant electronic delocalization between the two adjacent phenylene−ethynylene units. The absorption and emission of the pyridine containing ring R1 are merely shifted to the red by 4 nm (242 cm^{-1}) with respect to the phenylene-linked ring R2. The optically active segment of the macromolecule, the most highly polarizable chromophore of lowest energy, is therefore approximated accurately, for example, by the half ring structure HR; the emission spectra of R1 and HR are identical. Note that HR contains, strictly speaking, only one chromophore, as is readily seen by noting the longest chain of alternating single and double bonds. Because of symmetry, an excitation may be generated either on the upper or on the lower half of the molecule, defining the lowest energy chromophore. The role of shared *meta*-substituted phenylenes in defining chromophores in conjugated macromolecules has previously been investigated extensively in the context of conjugated dendrimers, where the real-space coupled electronic oscillator picture has clearly illuminated how symmetry breaking occurs
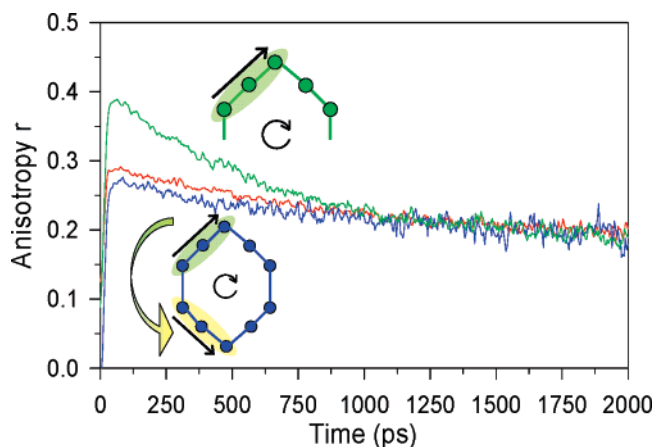
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Figure 2. Fluorescence depolarization of the macrocycles R1 (red) and R2 (blue) and the half ring HR (green). Both rings exhibit a rapid loss of polarization memory on time scales shorter than the measurement resolution (50 ps), leading to an initial polarization anisotropy of below 0.3, in contrast to the case for HR. All three molecules show the identical long-term depolarization trend, attributed to rotational diffusion. The cartoons illustrate that HR contains only one chromophore with a distinct transition dipole orientation, whereas the rings can support two chromophores, giving rise to rapid initial depolarization due to interchromophoric energy transfer.

Figure 3. Absorption and emission of a smaller macrocycle R3 (purple) in comparison to the larger structure R2 (blue).

upon excitation.[22] Importantly, the calculations demonstrate that intramolecular excitation energy transfer cannot occur in a shared phenylene system such as HR.[22]

Although the spectra are not perturbed, the overall fluorescence *kinetics* are modified as the two-half rings are brought together to form the overall ring R1, because now a molecule is constructed with two chromophore units in close proximity. The most straightforward way to study the interaction of these two chromophores is to consider the polarization anisotropy, that is, the change in the polarization of light emitted with respect to the polarization of light absorbed. This polarization anisotropy, r, is readily determined by measuring the polarization of the emission intensity parallel and orthogonal to the polarization plane of the excitation light, yielding $r = (I_{\parallel} - I_{\perp})/(I_{\parallel} + 2I_{\perp})$.[49] For an isotropic arrangement of linear dipoles, a simple geometric consideration predicts $r = 0.4$.[49] However, depolarization of the emitted radiation with time can occur through rotational diffusion of the emitting dipole as well as through energy transfer.[25] Figure 2 illustrates the time-dependent polarization anisotropy of the half-ring HR and the two rings R1 and R2. As expected, the initial half-ring anisotropy is found to be 0.4 and then decreases steadily because of rotational diffusion. Remarkably, both rings display a *smaller* initial anisotropy of 0.3, but from 750 ps onward closely follow the anisotropy decay of the half ring, which decays monotonously and can be described equally well by the temporal functions $r \sim \log(t)$ or $r \sim t^{-0.13}$. Apparently, an additional depolarization mechanism exists in the rings that is not present in the half ring. We attribute this depolarization, which evidently occurs on time scales shorter than the resolution of our measurement of 50 ps, to rapid redistribution of excitation energy via incoherent energy transfer from one chromophore in the macrocycle to the other. The two different depolarization processes of energy transfer and rotational diffusion are indicated in the sketch in Figure 2. We note that the *para*-phenylene-ethynylene unit absorbs over 10 times more light at the wavelength of excitation (375 nm) than the shorter diphenyl-butadiene unit, as discussed previously in the chemical dissection of similar ring structures.[36] We conclude that under the present
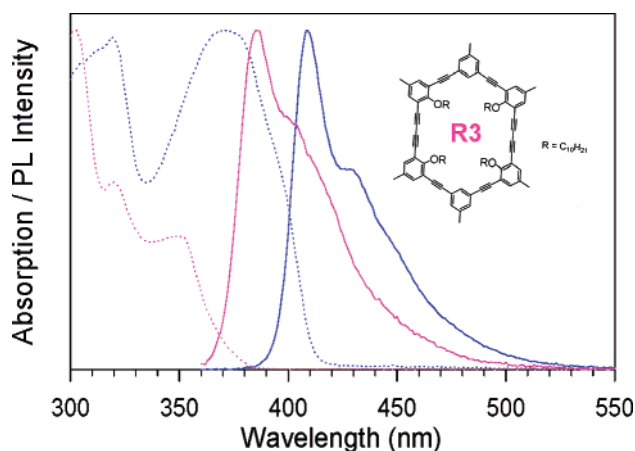
conditions the rings are excited exclusively in the lowest energy chromophore, the *para*-phenylene unit. In addition, it is worth pointing out that for energy transfer between chromophores situated at an angle of approximately 70°, as indicated in the cartoon, one may expect an even lower polarization anisotropy. However, the two lowest energy chromophores on either side of the ring are expected to be near degenerate in energy. Energy transfer from one chromophore to the other is a possible, not a necessary outcome of excitation. The comparatively high initial anisotropy of ∼0.28 therefore suggests that indeed not all individual molecules within the ensemble exhibit deterministic energy transfer.

We conclude that the macrocycles containing 10 phenylene rings can apparently support two distinct chromophore units. The half ring only supports one chromophore and does not display intramolecular energy transfer. With regards to the scaling of optical properties such as the absorption strength with molecular size in large dendrimers[11] and polymers,[50] it is important to establish the size constraints for the formation of multiple chromophores in an individual molecule.[51] Compared to the size of chromophores in *para*-phenylene conjugated polymers, for example, 10 phenylene units appears a fairly small molecular dimension to support two distinct chromophores.[51] We therefore constructed the next smaller conjugated macrocycle by removing one phenylene ring from each segment, leaving a total of 6 phenylene units as shown in structure R3 in Figure 3. The figure compares absorption and emission spectra of R2 and R3 in solution. As expected, reducing the ring size results in a blue shift of the absorption and emission spectra. The emission spectrum of R3 is shifted to the blue by 24 nm (1525 cm^{-1}) and broadened by approximately 25% with respect to that of R2, but remains otherwise similar in shape. The first absorption peak of R3 is shifted to the blue by 19 nm (1460 cm^{-1}) with respect to R2, but the same absorption feature at 320 nm is identified.

Figure 4 compares the fluorescence depolarization dynamics of R3 to those of R2. The initial anisotropy of R3 is found to be 0.4, as expected for isotropic emission from a single linear dipole.[49] Because of the smaller size and radius of gyration of the ring molecule, rotational diffusion is accelerated with respect to the larger ring R2. Despite the structural similarity between R2 and R3, the photophysical kinetics are very different. At first sight, the lack of a rapid depolarization mechanism can be attributed to the fact that the lowest energy conjugated units of the ring on either side, separated by *meta*-substituted phenylenes, are expected to be effectively parallel. Even if incoherent energy
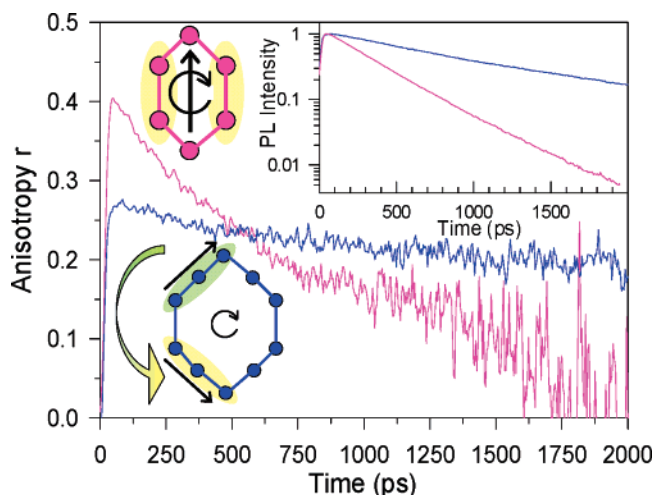
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Figure 4. Fluorescence depolarization of the smaller ring R3 (purple) in comparison to the larger ring R2 (blue). Although the smaller ring exhibits more rapid depolarization on longer time scales because of faster rotational diffusion, on short time scales it exhibits a greater polarization anisotropy than the larger system R2. The sketches summarize the situation: whereas intramolecular energy transfer can occur between the two lowest energy chromophores in R2 with well-defined non-parallel transition dipoles, promoting a rapid loss in polarization memory, the conjugated units in the smaller ring R3 emit in parallel. Interestingly, although the conjugation length and hence the oscillator strength is smaller in R3, an acceleration of the fluorescence decay time is observed (inset), providing an indication of cooperative effects.

transfer occurred between these units, the polarization anisotropy would not be affected.[51] We note that the situation could be more subtle. For chromophoric units in such close proximity, strong coherent interactions could take place, leading to a delocalized electronic state with one single cooperative transition dipole moment.[8,10,12−14,17] Signatures of coherent interchromophoric coupling of dipole aggregates arranged in the head-to-tail configuration are spectral broadening (due to an increase in the torsional modes available to the delocalized excitation[12]) and a loss in vibronic structure; and most importantly an increase in fluorescence radiative rate due to an increase in oscillator strength, which scales superlinearly with molecular size.[10,17] In the present case of R3, the individual transition dipoles are expected to lie parallel, forming a sandwich-type configuration that could lead to the occurrence of an H-type aggregate.[2] In such an aggregate, the lowest energy state is non-emissive and the overall quantum yield in emission is reduced. A signature of such an aggregate occurring could lie in a reduction of the fluorescence lifetime, resulting from an increase in the probability of nonradiative decay.

Generally, shorter conjugated systems also display increased fluorescence lifetimes, as in the case of linear π-conjugated chains such as oligomers, where the fluorescence decay rate and oscillator strength increase with increasing chain length.[51−53] The opposite appears to be true for the macrocycles. The fluorescence decay of *R*3 is compared to that of R2 in the inset of Figure 4. With a fluorescence lifetime of 320 ps, the fluorescence rate of R3 is increased threefold compared to the larger ring R2. We note that the measured fluorescence rate is the sum of radiative and nonradiative rate, and because of the lack of quantitative information on the fluorescence quantum yield we presently cannot pinpoint the origin of the change in kinetics. However, we note that the observed fluorescence decay is surprisingly short-lived for such a small molecule. Strong interchromophoric coupling has previously been associated with

rapid fluorescence depolarization.[19−21,23−24] However, because the chromophoric units are parallel in the present case, even if strong coupling occurred, the net result would still be a *retardation* rather than an acceleration of fluorescence depolarization, even if the fluorescence rate is accelerated by an increase in either radiative (J-aggregate) or nonradiative (H-aggregate) decay.

The geometry of the system is reiterated in the sketch in Figure 4: the dipole orientation *within* the molecule cannot change with time. Future investigations using model systems, dissecting the ring into its individual chromophores, along with quantum chemical studies of the excited-state couplings[51] will provide further insight into the possibility of coherent interchromophoric coupling occurring in the smaller rings. In addition, an accurate determination of the molar extinction coefficient could shed light on strong interchromophoric coupling, which should rise with increasing oscillator strength. Furthermore, shortening the excitation wavelength should allow us to probe non-parallel conjugated segments within the ring, or even higher-lying excited states with transition dipoles orthogonal to the conjugated backbone, which should lead to rapid fluorescence depolarization in R3.

Much of the recent attention paid to depolarization dynamics in conjugated polymers has focused on the ultrafast relaxation and exciton self-trapping processes in the most extended conjugated units of the chain.[8,25−27] Alternatively, delocalization may be beneficial to exciton separation for photovoltaics in suitably constructed heterostructures. In addition, increasing the emissive rate of the primary excitation in a light-emitting diode and thus reducing the sensitivity of detrimental polaron quenching interactions would clearly also be beneficial. Although *intrachromophoric* coherence has been studied in detail previously,[54] it is unlikely that ensemble time-resolved spectroscopy will be able to unambiguously identify signatures of such strong interchromophoric interactions in linear polymer chains because this will be masked by incoherent interchromophoric energy transfer[3] as in the present case of the larger rings. Single-chain fluorescence and excitation spectroscopy, however, in combination with fluorescence lifetime measurements may provide a route to pinpointing and ultimately exploiting sites of strong excitonic interactions in conjugated polymers.

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(50) Note that we excite both R2 and R3 at 375 nm, i.e., the larger ring is excited in the middle of the first absorption band, the smaller ring in the absorption tail. At room temperature, the spectral width of single polyphenylene chromophores has been shown to be comparable to the disorder (see Müller, J. G.; Lemmer, U.; Raschke, G.; Anni, M.; Scherf, U.; Lupton, J. M.; Feldmann, J. *Phys. Rev. Lett.* **2003**, *91*, 267403). We therefore expect to be able to excite all chromophores of one polarization within the molecule with equal probability.

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