Excited-State Lifetime Modulation in Triphenylene-Based Conjugated Polymers

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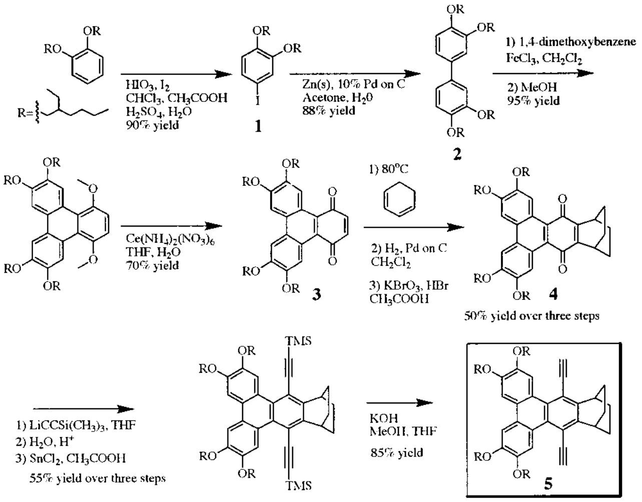
Conjugated polymers are an extraordinary conduit for the transport of electronic excitations[1−4] to segments with the greatest effective conjugation length. To provide the highest amplification in sensory schemes[5] we are interested in enhancing energy migration. Such improvements will allow the excitation a greater diffusion length and a higher probability of encountering a receptor occupied by an analyte. The high efficiency of energy transfer in conjugated systems[5−7] relative to systems with pendant chromophores[8,9] suggests that transport in these systems may be enhanced by the strongly electronic coupled intrachain (Dexter-type) processes in addition to the dipole−dipole (Förster-type) processes that govern weakly interacting chromophores. To determine the relative dominance of these types of processes we have synthesized and studied polymers that by novel design have longer excited-state lifetimes. Increases in lifetime imply a reduction in transition dipole and should therefore decrease the Förster rate, whereas transport by the Dexter mechanism should be enhanced. We report herein that for isolated poly(arylene ethynylenes) in solution that Dexter transport is dominant.

Poly(phenylene ethynylenes) (PPEs) have seen considerable interest due to their rigid geometry and ability to effectively transfer energy over long distances.[10] To modify the lifetimes of these systems we have chosen to incorporate into the polymer backbone triphenylene chromophores with a well-known[11] symmetrically forbidden S_0−S_1 transition. Clearly, the triphenylene wavefunction[12] will be perturbed, and the stringent symmetry responsible for its optical properties will be broken; however, we considered that this strongly aromatic structure should retain some of its individual identity and that poly(triphenylene ethynylenes) (TPPEs) would have extended excited-state lifetimes. In addition to their desired electronic properties triphenylene materials also have a tendency to form π-stacked discotic liquid crystalline phases that facilitate charge and energy transport.[13,14] While our monomer design gives rise to polymers that exhibit desirable thin film photophysical properties, the present study is restricted to solution measurements on isolated polymers.

Scheme 1



The triphenylene monomer is synthesized as depicted in Scheme 1 with an overall yield of 12%. Iodination of 1,2 dialkoxybenzene with periodic acid and iodine[15] affords the 3,4-dialkoxyiodobenzene (**1**), and a subsequent zinc/palladium (0) coupling[16] generates the 3,3′,4,4′-tetraalkoxybiphenyl (**2**) in high yields. The latter reaction offers an alternative to the conventional Ulman coupling which required exclusion of air and high temperature and in our hands led to inferior yields. Iron (III) trichloride and *p*-dimethoxybenzene afford cyclization to the triphenylene. Oxidative demethylation with cerium ammonium nitrate forms the quinone (**3**). A Diels−Alder reaction in neat cyclohexadiene incorportates the bicyclooctane moiety. The isolated double bond is hydrogenated, and oxidation with potassium bromate generates the tetrasubstituted quinone (**6**). Lithiated trimethlysilane acetylide adds to the quinone carbonyls, and subsequent reductive dehydroxalation with tin dichloride reconstitutes the triphenylene ring system. Deprotection with base gives the key diethynyl triphenylene monomer (**5**) which is copolymerized with diiodo-funtionalized monomers using the Sonogashira−Hagihara reaction.[17] The exceptions are polymers **7** and **7a** which are made through an oxidative coupling method.[18] Resulting polymers and some of their physical properties are tabulated (Table 1).

Matched pairs of PPEs and TPPEs were synthesized for comparative photophysical studies (Figure 1). The differences in the molecular weights of the materials as synthesized were in some cases very large; hence, gel permeation chromatography was used to obtain materials with more closely matched molecular weights. The results have high self-consistency, and TPPEs exhibit extended excited-state lifetimes over their PPE analogues as depicted in Figure 2. The TPPEs demonstrate about a 30% lifetime increase without severely compromising quantum yield. The combination of Φ and τ data demonstrate that the enhanced

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Table 1. Physical Properties of Synthesized TPPEs and PPEs

	λ_{max}abs (nm)	λ_{max}em (nm)	M_n[a]	pdi[a]	M_n[b]	τ (ns)[c]	Φ
6	480	505	45000	2.5	102200	0.71	0.27
6a	441	475	20900	2.0	41000	0.52	0.45
7	480	530	10500	1.3	199000	1.27	0.14
7a	430	455	24000	1.8	108000	0.43	0.45
8	490	509	103000	1.9	325000	0.95	0.30
8a	420	459	31400	2.0	253000	0.67	0.39
9	465	518	114000	1.3	256740	0.78	0.20
9a	449	487	22000	3.0	177700	0.44	0.13

[a] As synthesized. [b] After GPC fractionization for spectroscopy. [c] Monoexponential decay.

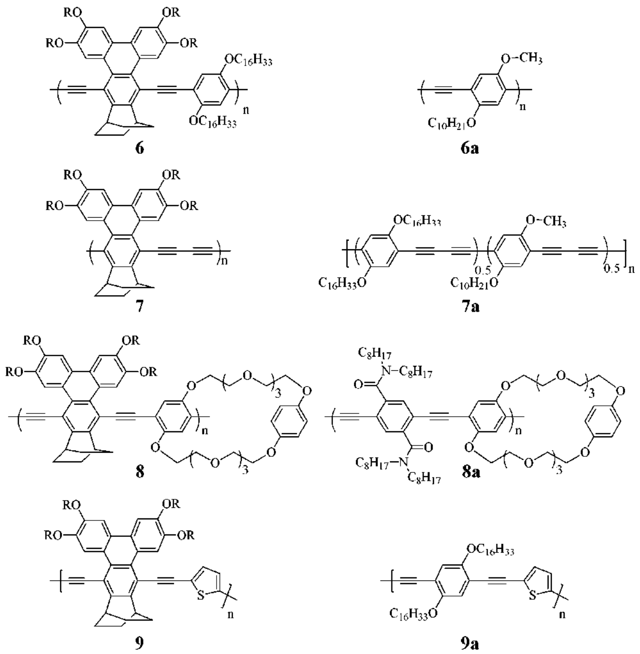

Figure 1. TPPEs and their phenyl analogues. R is a 2-ethylhexyl group, and all other side chains are $n =$ alkyl groups. Polymer **6** and **7a** are regio-random structures, and to maintain solubility at high-molecular weights **7a** was synthesized as a random copolymer.

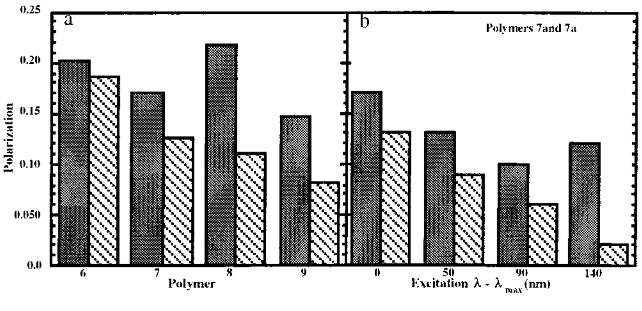

Figure 2. Emission polarization for each polymer. TPPE (stripped bars) and analogous PPE (solid bars): (a) upon excitation at λ_{max}. (b) as a function of excitation wavelength for **7** and **7a**.

lifetimes are principally due to differences in radiative rates and not differences in the nonradiative rates. Supporting our assertion that the triphenylene group is responsible for the lifetime enhancements, we find that **7** displays the largest enhancement and is about 3 times that of **7a**. This material also has the largest fraction of triphenylene chromophore per repeat unit.

The relationship between excited-state lifetime and energy migration can be investigated through fluorescence depolarization measurements. All polymers studied are high-molecular weight materials and can be considered rotationally static over the emission lifetime of the polymer. Therefore, energy migration is the major contributor to the fluorescence depolarization in conjugated polymers, and the exciton loses more of its initial polarization as it diffuses along a disordered polymer chain. The polarization value, P, has been determined from standard equation $P = (I_{vv} - GI_{hv})/(I_{vv} + GI_{hv})$, where I_{vv} and I_{hv} are the intensities of emissions detected parallel and perpendicular to the polarization vector of the incident light and G is an instrumental correction factor.

The full range of allowable excitation energies for each polymer was investigated to separate depolarization due to energy migration from that due to absorption/emission dipole alignment. As excitation energy is increased, both the TPPEs and PPEs display lower P values, consistent with population of higher-energy excitons that readily lower their energy by migration to lower-energy states. Overall, wavelengths the TPPEs consistently reveal lower P values (Figure 2a). The decrease in emission polarization at higher energies may also be the result of exciting triphenylene-localized transitions that have an angular displacement from the emission dipole. In this case, polarization would be expected to decrease more dramatically at certain intervals of wavelengths, not continuously over the range investigated. In TPPEs, a near linear decrease of polarization as a function of excitation wavelength (Figure 2b) is observed supporting energy migration as the major contributor to depolarization. For TPPEs, the lowest attainable P values are a fraction of the P obtained when exciting at $\lambda_{max.}$ In PPEs however, this value is only about half, indicating the radiative rate of emission limits the extent of energy migration. This limitation is overcome in the longer-lived TPPE systems as near 0 P values are obtainable in most of the materials. Studies of polarization as a function of chain length support these conclusions.[19] If the Förster mechanism dominated these systems, then enhanced radiative rates in PPEs would encourage more extensive migration. This is not observed, pointing to the Dexter mechanism as the dominant intramolecular energy-transport process in these materials.

In summary, we have reported a new method for the design of conjugated polymers with longer excited-state lifetimes. The triphenylene-based poly(arylene ethynylenes) display longer excited-state lifetimes when compared to their phenyl analogues. Enhanced fluorescence depolarization is also observed in TPPE systems, indicating that more extensive energy migration has been effected. Longer lifetimes foster both through-bond energy migration and the population inversion necessary to observe stimulated emission. These advances are currently being applied to further amplify sensory responses.

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Supporting Information Available: Experimental details and characterization data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Beyond a critical length the polymers are longer than the diffusion length of the exciton, and P is a minimum value. For the TPPEs the molecular weight needs to be much higher than that of the PPEs to observe the minimum P value.