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Tuning the Singlet–Triplet Gap in Metal-Free Phosphorescent π-Conjugated Polymers[**]

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Much of the fascination in conjugated polymers stems from the realization of potential device applications,[1] yet the true power of these materials lies in the possibility to synthesize a compound with a particular property from first principles. A defining feature of these carbon-based semiconductors is that spin–orbit coupling is weak, thus making spin states well-defined.[2–3] Electrical injection of charges into an organic light-emitting diode (OLED) leads to triplet and singlet excitations with symmetric or antisymmetric spin wavefunctions. As triplet excitations are typically not dipole-coupled to the molecular ground state, the majority of carrier pairs that recombine in an OLED decay nonradiatively. Incorporation of heavy-atom centers that are mostly in the form of an organometallic luminophore and promote spin–orbit coupling, is employed to promote radiative triplet recombination.[4]

The direct spectroscopic identification of triplet excitations in conjugated polymers became possible by detecting the weak phosphorescence.[5] In this approach, the relative energies of the singlet and triplet excitations are determined by comparing prompt fluorescence to delayed phosphorescence, thus directly revealing the exchange energy. Although small-molecule organometallic complexes display a variety of exchange interaction strengths,[4e,f] it has been proposed that the singlet and triplet excited state are universally split by some 0.7 eV in conjugated polymers.[3c] Here, we present a new series of triphenylene-based metal-free conjugated copolymers with tunable exchange splitting, which is revealed by their distinct fluorescence and phosphorescence signatures. In addition, we show how both singlet and triplet excited states can couple to emissive defects, hence revealing the fundamental mechanism for color purity degradation that is a common problem for poly(*para*-phenylene)s such as polyfluorenes.[6]

Most conjugated hydrocarbons show either weak phosphorescence or no phosphorescence at all.[3] Triphenylenes, and some other polycyclic aromatic hydrocarbons, are an exception: at low temperatures, they exhibit a pronounced afterglow, which is often attributed to the phosphorescence from the triplet state.[7] Although triphenylene-based compounds have recently been investigated as blue singlet emitters in OLEDs,[8] the relevance of the triplet states to OLEDs has not yet been considered.

In the polymers presented herein, the triphenylene **1** is an integral part of the polymer backbone (Figure 1). Incorporation of **1** into the backbone leads to a fully conjugated π system in which the triplet state is localized on the triphenylene unit, yet the singlet state is delocalized over multiple repeat units (Figure 1 a). We synthesized the polymer **2** from **1**,[9] along with four different copolymers **3**–**6** by using transition-metal-catalyzed polycondensation. The prompt and delayed luminescence of the compounds dispersed at a 1 % weight ratio in polystyrene at 25 K is shown in Figure 1 b–g. The prompt luminescence (detected in a 2 ns time window that coincides with the laser pulse) is caused by fluorescence from the singlet state, whereas the delayed emission (detected several hundred microseconds after excitation) can be assigned to phosphorescence from the triplet state.[7] A similar triplet spectrum is observed for all materials (the average peak position is marked by a dashed line), whereas the singlet peak strongly depends on the intricacies of the polymer backbone.[9] The energetic separation between fluorescence and phosphorescence provides an accurate measure of the magnitude of the exchange interaction ($2J$).[3] From **1** to **6**, the singlet emission shifts to the red, while the triplet emission remains unchanged:[9] copolymer **6** has almost degenerate singlet and triplet levels. This degeneracy is unprecedented in conjugated polymers and is particularly surprising given the fact that the triplet level of regular poly(thienylene vinylene) lies at 1170 nm.[3i] Apparently, singlet and triplet excitations can form on different parts of the conjugated system,[10] thus allowing the splitting to be tuned. The series in Figure 1 suggests that it may be possible to design materials in which the regular level ordering is reversed, so that the singlet state lies energetically beneath the triplet state.

The singlet and triplet states of the polymer are not the only spectral signatures seen in **1**–**6**. Poly(*para*-phenylene)s are prone to the formation of oxidative defects that result in broad emission spectra, as has been studied in particular

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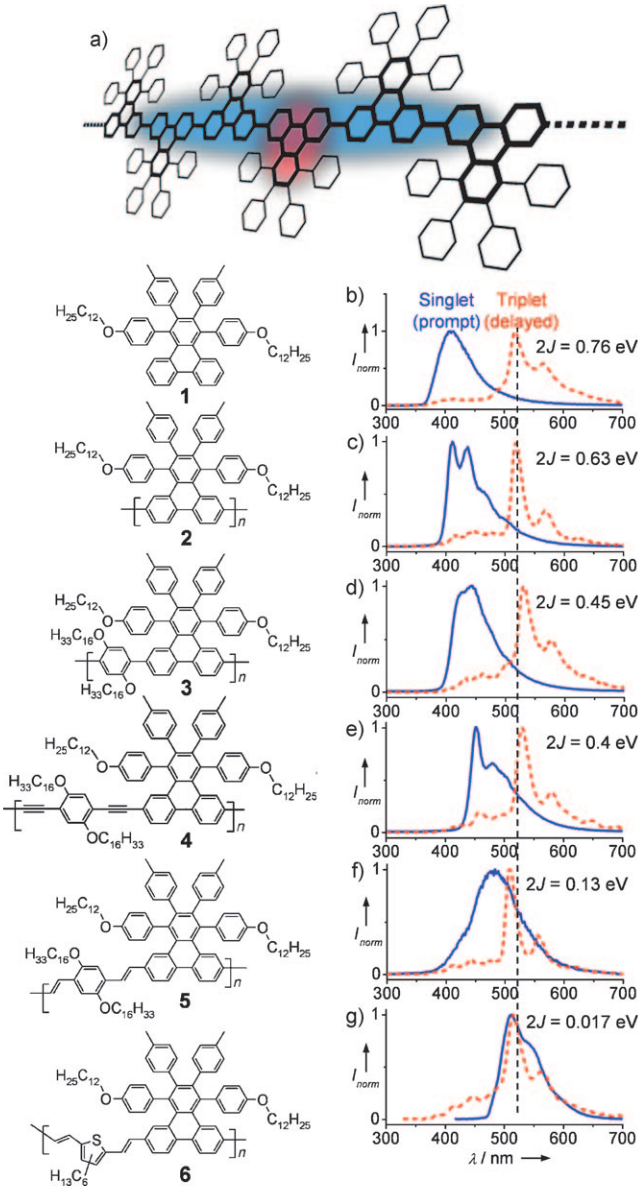

Figure 1. Fluorescence (prompt emission) and phosphorescence (delayed emission) from a triphenylene-based monomer and conjugated copolymers, dispersed in a polystyrene matrix at 25 K. a) Delocalization of singlet excitations (blue) with triplets (red) localized at the triphenylene unit. b)–g) Singlet (solid blue line, integrated 0-2 ns after excitation) and triplet (dashed red line) spectra of the monomer **1** (0.1–1.1 ms delay after excitation), the homopolymer **2** (9–10 ms delay), the *para*-phenylene copolymer **3** (1–2 ms delay), the ethynylene copolymer **4** (1.5–2.5 ms delay), phenylene vinylene copolymer **5** (0.02–1.02 ms delay), and the thienylene vinylene copolymer **6** (0.05–5.05 ms delay). The exchange splitting $2J$ is estimated from the peak separations. The dashed black line indicates the average triplet peak position.

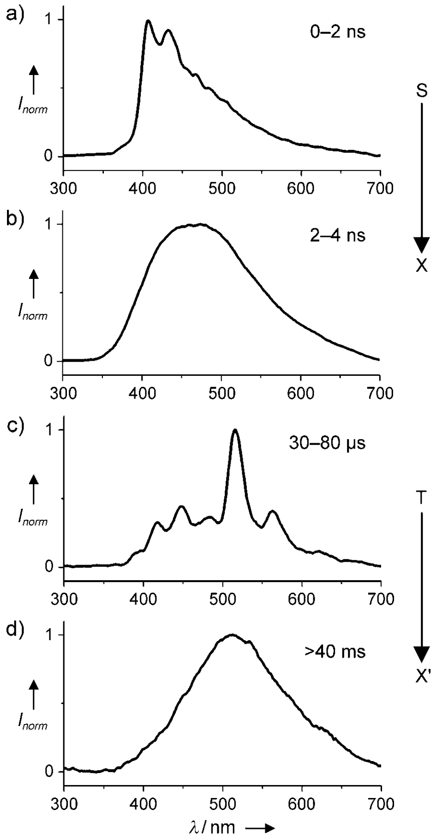

Figure 2. Singlet and triplet excited states that feed the defect states in the triphenylene homopolymer **2** at 25 K. a) Prompt singlet emission gives way to b) a broad defect (X) emission detected in a time window of 2–4 ns after excitation. c) Similarly, long-lived triplet states (detected 30–80 μs after excitation) transfer to the d) defect states (X′). Subsequent emission is seen as an afterglow, which can persist for seconds after excitation.

detail in the case of polyfluorene.[6b] We are now able to elucidate the interplay between triplet excitations and emissive defects as a distinct phosphorescence signature can be induced in the polymer emission. A time-dependent series of normalized emission spectra of **2** is shown in Figure 2. The prompt singlet emission (a) decays within 2 ns, to give a broad, featureless spectrum (b) reminiscent of the fluorenone band in polyfluorene.[6,11] This species is populated by energy transfer: the singlet feeds into a trap (X). Fluorenone-type defect excitations have a charge-transfer character and are less strongly coupled to the ground state than the singlet, hence leading to an increased emission lifetime.[6] Once the species X has decayed, the phosphorescence becomes visible in a time window of 30–80 μs (c) and lasts for several milliseconds (Figure 1). The triplet peak is accompanied by a residual singlet emission around 400 nm that results either from triplet–triplet annihilation[5] or from the delayed recombination of optically-generated carrier pairs.[12b] Subsequently, the defect spectrum reappears at very long detection times: the triplet also feeds into a trap denoted X′, which has an emission spectrum slightly red-shifted relative to that of X (d).

To test for electrophosphorescence, we fabricated OLEDs, in which the majority excitations are triplets. In contrast to polymers that contain trace concentrations of metal centers, which locally promote spin–orbit coupling and thereby enable triplet-diffusion-driven phosphorescence,[12] we have not yet observed any direct emission from the triphenylene triplet, even at low temperatures. Figure 3 shows a comparison of films of the homopolymer **2** under optical

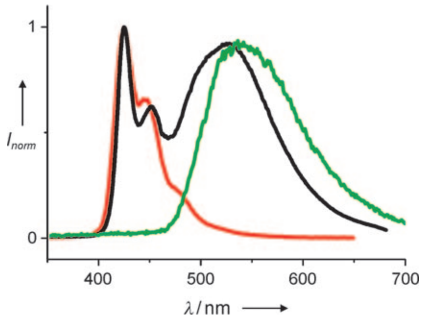

Figure 3. Defect emission and afterglow in triphenylene materials. Comparison of electrical (black) and optical (red) excitation of the homopolymer **2** at room temperature. Electroluminescence is dominated by defect emission, which is similar to the afterglow in the photoluminescence of triphenylene **1** at 25 K, detected at 1 s after excitation (green).

and electrical excitation. In the OLED, an additional broad band appears at 540 nm, which is reminiscent of the keto defect in polyfluorenes and other poly(*para*-phenylene)s [6] and has been observed in other triphenylene-based OLEDs.[8] This band is not visible under steady-state optical excitation. The green curve in Figure 3 shows the afterglow photoluminescence spectrum of **1** (recorded 1 s after excitation), which is remarkably similar in shape and position to the 540 nm defect band seen in OLEDs of **2**, but is clearly distinct from the triplet spectrum shown in Figure 1. The observation of luminescence 1 s after excitation (i.e., X' emission) requires an extremely long-lived state. We thus conclude that triplet states feed directly into defect states, provided that there is an appropriate spatial overlap of the molecular excited-state wavefunctions.

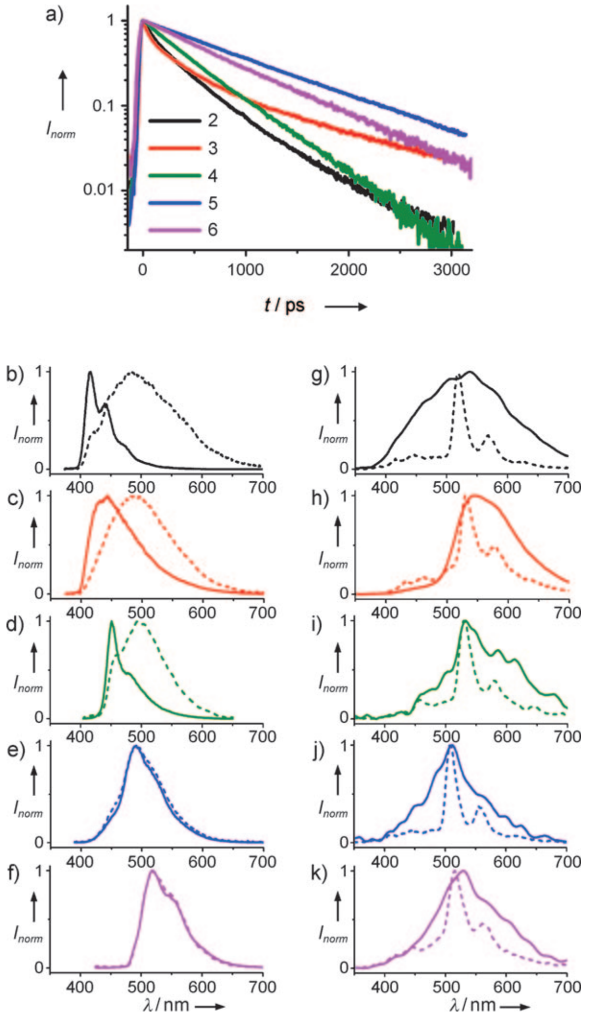

Figure 4. Comparison of singlet and triplet luminescence dynamics of polymers **2**–**6**. a) Room temperature decay of the singlet emission intensity in $CHCl_3$. b)–f) Change of the emission spectra of **2**–**6** within 4 ns of excitation (in $CHCl_3$ at room temperature). Solid lines represent prompt fluorescence (detected in the first 100 ps) and the dashed lines illustrate the delayed spectra (within 3–4 ns after excitation). g)–k) Afterglow spectra at 25 K (in polystyrene films), 1 s after excitation (solid line), compared to the corresponding phosphorescence spectrum (dashed line, from Figure 1).

The compounds presented herein allow a systematic investigation of the energetic prerequisites for singlet or triplet energy transfer to the defect to occur. Generally, the presence of a single excited state decay channel results in exponential luminescence kinetics. However, singlet energy transfer to the species X opens a second decay pathway, thus leading to nonexponential kinetics in the ensemble of molecules. Transient luminescence from solutions of polymers **2**–**6** in $CHCl_3$ are shown in Figure 4a. Whereas the low-J materials **4**–**6** show a single exponential decay, materials **2**–**3** are characterized by nonexponential kinetics. This deviation from exponential decay correlates with the appearance of a secondary emissive species (X) within 3 ns after excitation in polymers **2** and **3** (Figure 4b–f). The species X is much weaker in **4** and cannot be detected in **5**–**6**. We conclude that the polymer singlet state lies above the defect absorption in **2**–**3**, so that energy transfer can occur. The picosecond fluorescence dynamics also relate to the afterglow of the materials recorded 1 s after excitation (Figure 4g–k). Whereas the afterglow is dominated by the defect in **2**–**3**, the narrow triplet features are discernible in **4**–**6**: triplet transfer to the defect is impeded for these materials with smaller J value. Consequently, we found that OLEDs made from **5** showed a much reduced defect emission with a closer correspondence of emission under optical and electrical excitation. We therefore propose that lowering the exchange gap also reduces the tendency of triplet excitations to migrate to emissive defects, which may help in controlling color purity in OLED materials, and could ultimately enable the construction of all-organic phosphorescent OLEDs.

The ability to engineer the singlet–triplet gap in conjugated polymers is likely to be useful for the control of spin excitations in organic devices, such as in spin valves and magnetoresistive magnetic field sensors,[13] because spin manipulation by magnetic or electric fields in organic semiconductors is hindered by the large excitonic exchange interaction.[12b] Our approach shows that this interaction can be reduced to some 20 meV. The tuning of the relative singlet–triplet energies may offer a route to the minimization of triplet gain quenching in laser structures.[14] Such an approach could allow a realistic design of all-injection laser diodes by employing the polymer as a triplet scavenger itself in analogy to nonphotochemical quenching in photosynthesis.[15] Finally, polycyclic aromatic hydrocarbons such as triphenylenes could offer elegant access to the tuning of hyperfine field effects (which control spin-dependent processes[16]), such as by deuteration[13b] or purification of carbon isotopes. This precise engineering of intramolecular exchange interactions is thus likely to further broaden the appeal of conjugated polymers for spintronics applications,[13] and may even be applicable to problems as far afield as quantum information processing.[17]

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[11] We generally observe brighter X and X' emissions in samples exposed to air, thus suggesting that the defects are a result of triphenylene oxidation. Elucidation of the actual chemical structure that is responsible for the defect emission is, however, complicated by the fact that a small number of defects can be populated efficiently by energy transfer,[6] and concentrations are thus likely not very high. We note that some similarity may exist to the well-documented formation of emissive enol groups in anthracene electrochemiluminescence.[6i] A complete understanding of the present traps will presumably require detailed computational modeling.

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