Phosphorescence Quenching by Conjugated Polymers

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Efficient organic light-emitting diodes (OLEDs) have been fabricated with low-molecular weight materials.[1] Hole−electron recombination in these OLEDs leads to the formation of both singlet and triplet excited states (excitons) within the molecular thin film.[2] For most compounds, only the singlet state is emissive, leading to a significant limitation in the OLED efficiency. Incorporation of phosphorescent compounds into the OLED gives a substantial improvement in device efficiency, since both the singlet and triplet excitons are trapped at the phosphor. This approach has led to OLEDs with external quantum efficiencies (photon/electron) of roughly 20% which correspond to internal efficiencies of nearly 100%.[3]

Conjugated polymers have also been used to prepare OLEDs, e.g. poly(phenylenevinylenes),[4a] polyfluorenes,[4b] and poly(*p*-phenylenes).[4c] While these devices can have good power efficiencies (lum/W or W_{opt}/W_{elect}), the polymer-based OLEDs tend to give external quantum efficiencies of less than 5%. Several groups have attempted to increase the quantum efficiencies of conjugated polymer-based OLEDs by incorporating phosphorescent dopants.[5] However, while the efficiencies of conjugated polymer OLEDs are improved by phosphor doping, values are still markedly lower than those of small-molecule-based devices (<5%).[5] In contrast, phosphor-doped OLEDs fabricated with nonconjugated polymers (e.g. poly-(vinylcarbazole), PVK) can have good external quantum efficiencies,[6] with some as high as 8%.[7]

To understand why phosphor-doped OLEDs give low quantum efficiencies with conjugated polymers, we have carried out a luminescent quenching study of phosphorescent emission using a model polyfluorene oligomer as a triplet energy quencher (F_3 shown in Figure 1). The phosphorescent cyclometalated Ir complexes used in this study had a range of emission energies, spanning from blue to red (Figure 2).[8] A fluorene trimer, rather than a polymer, was chosen as a quencher for several reasons. F_3 is estimated to have a triplet energy somewhat higher than that of the polymer, roughly about 540−580 nm.[9] In addition, unlike polyfluorenes, F_3 has negligible absorption in the region where the phosphors absorb strongly (i.e., 435 nm), allowing the direct excitation of the phosphor. Also, on the basis of solution electrochemistry of F_3 and the complexes, the HOMO and LUMO orbitals of each of the phosphors are expected to fall within the HOMO/LUMO gap of F_3.[10] This precludes exciplex formation or excited-state electron transfer as the origin of luminescent quenching. Last, F_3 is more soluble than a polymer and has a discrete molecular weight, making for straightforward Stern−Volmer analysis of the quenching phenomena.

A schematic energy level diagram for F_3 and the Ir phosphors is shown in Figure 1. The singlet state of F_3 is significantly higher in energy than any of the phosphor triplet states, but the F_3 triplet energy is expected to fall somewhere in the middle of the phosphor energy range. Hence, phosphorescence quenching should occur by energy transfer between the excited phosphor and the triplet state of F_3.
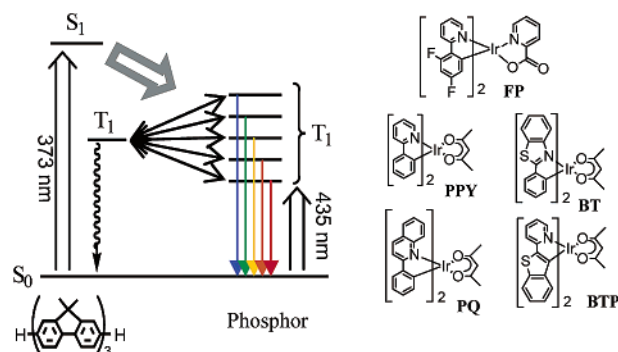

Figure 1. Schematic energy level diagram showing energy transfer between F_3 (left) and the iridium complexes (right).

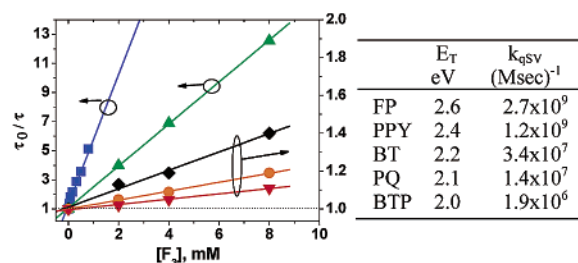|	E_T eV	k_{qSV} (Msec)$^{-1}$
FP	2.6	2.7×10^9
PPY	2.4	1.2×10^9
BT	2.2	3.4×10^7
PQ	2.1	1.4×10^7
BTP	2.0	1.9×10^6

Figure 2. Stern−Volmer plot for quenching of the five phosphors by F_3. (Legend: ■ FP, ▲ PPY, ◆ BT, ● PQ, ▼ BTP). Table: triplet energy[8,10] of phosphors and their Stern−Volmer quenching constants.[11] The estimated errors in the k_{qSV} values are ±10%.

The luminescent lifetimes were recorded in 2-methyltetrahydro-furan as a function of F_3 concentration and plotted using standard Stern−Volmer analysis (i.e., τ_0/τ versus [F_3], Figure 2).[10,11] Quenching rate constants were derived from the slope of linear fits to the data for each complex. The Stern−Volmer quenching rates given in Figure 2 were measured using direct excitation of the complexes with 435 nm light; however, similar rates are obtained when the solutions are excited using 373 nm light and energy is transferred from the F_3 singlet to the triplet levels of the complex, as illustrated by the gray arrow in Figure 1. It can be seen from the data in Figure 2 that quenching of FP and PPY emission by F_3 is an exothermic process, occurring at near diffusion controlled rates, while quenching of the yellow, orange, and red emission (from BT, PQ, and BTP, respectively) is an endothermic process, occurring at rates well below those of FP or PPY. This indicates that the triplet energy of the trimer is less than 2.3 eV, as predicted from Bässler's data.[9]

Upon excitation of Ir phosphor/F_3 mixtures, the Ir complex can either relax directly to the ground state (via radiative or nonradiative pathways) or transfer energy to the F_3 triplet state. Similar behavior in the type of thin films used in phosphorescent OLEDs, where high dopant concentrations (5−10 wt %) are employed, should lead to pseudo-first-order reaction conditions for energy transfer from phosphor to quencher. It is therefore worth noting that emission

from BTP is efficiently quenched by F_3 ($k_{qSV} = 1.9 \times 10^6$ M^{-1} s^{-1}) despite having a lower triplet energy. Using this k_{qSV} value, the half-life for BTP emission quenching in a doped thin film of F_3 (ca. 1 M) is estimated to be 0.4 μs. Since the phosphorescent half-life of an excited BTP molecule is 4 μs (based on a luminescent lifetime of 5.8 μs),[8] near complete phosphorescence quenching is predicted for a BTP-doped F_3 film. Quite the contrary, BTP emission is observed for 5 wt % doped polyfluorene thin films.[5e] This discrepancy comes about because of significant differences between concentrated solid films and the dilute solution mixtures used for our studies. First, the doping levels of phosphors in the solid films are considerably higher than the μM to mM concentrations used in the quenching experiments. The high doping concentrations promote phosphor aggregation;[12] consequently, the reduced intermolecular contact between F_3 molecules and the dopant complexes decreases the phosphorescent quenching rate. Second, energy transfer between the triplets of the phosphor and F_3 is most likely an electron exchange or "Dexter" transfer process. Dexter transfer requires a good intermolecular overlap between the pertinent molecular orbitals of the donor and acceptor.[11] Since molecular motion is inhibited in amorphous solid films, a dopant-F_3 configuration that gives poor Dexter energy transfer cannot readily reorient to a configuration appropriate for efficient energy transfer. Last, in fluid solution, the F_3 and phosphor can physically separate after energy transfer. This physical diffusion enhances quenching by suppressing reverse energy transfer (F_3 to phosphor), especially for those phosphors (e.g., BTP and PQ) where energy transfer to the F_3 triplet state is an endothermic process. In a rigid matrix, such as a doped thin film, physical diffusion cannot occur. In this case, separating excited F_3 and the phosphor involves energy migration from the excited F_3 to an adjacent F_3, a slower process than the competing back energy transfer. These three factors together lead to k_{qSV} values in doped thin films that are lower than those measured in dilute fluid solutions.

The results obtained from our quenching studies highlight an important criterion that needs to be considered when designing polymer-based phosphorescent OLEDs. Energy transfer from either singlet or triplet levels of a conjugated polymer to a phosphorescent dopant certainly looks appealing at the outset. However, one needs also to consider the emission quenching brought about by the low-energy triplet states of the polymer since even endothermic transfer can effectively quench phosphorescence. High-molecular weight polyfluorenes have conjugation lengths that are greater than that of F_3; thus, triplet-state energies are lower for the polymers (2.1 eV) than for the oligomer (2.3 eV).[9] Hence, one can expect that phosphorescence quenching will be more efficient in polyfluorenes than in F_3. With nonconjugated polymers such as PVK, however, phosphorescence quenching is less favorable due to the absence of any low-energy triplet states.[6,7] Although doped OLEDs with moderate efficiencies have been prepared by blending conjugated polymers with red phosphors,[5c−e] it becomes increasingly difficult to use this strategy for devices emitting at higher energy since it requires conjugated host polymers with high triplet-state energies. A solution to this dilemma is either to use nonconjugated polymers, such as PVK, or to design new conjugated polymers with higher triplet energies. Such new polymer systems may then allow fabrication of highly efficient (>10% external) polymer-based phosphorescent OLEDs.

Supporting Information Available: Phosphorescence spectra from the phosphors, synthesis and characterization of F3, electrochemical properties of the compounds, and data for the Stern−Volmer analysis (PDF). This material is available via the Internet at http://pubs.acs.org.

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