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Metal-Free OLED Triplet Emitters by Side-Stepping Kasha's Rule**

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With organic light-emitting diodes (OLEDs) emerging in ever more applications, such as smart phones, televisions, and lighting, it is easy to forget that the present technology is based on a brilliantly simple patch to an inherent problem of fluorescent hydrocarbons: three quarters of the electrically generated energy is dissipated as heat by triplet excitons. Radiative decay from the triplet state via phosphorescence is generally very weak, and has only been resolved in transient spectroscopy at low temperatures in select organic semiconductors.[1] The solution to this problem has been to incorporate metal–organic emitters in OLEDs,[2] which mix spin by enhancing intersystem crossing through spin-orbit coupling: the heavy-atom effect. As this approach relies on the longevity of triplet excitons and the associated diffusion lengths, it is highly effective: in a suitably homogeneous environment even ppm concentrations of covalently bound metal atoms are sufficient to activate electrophosphorescence.[3] The second conceivable approach to harvesting energy from triplets is based on endothermic conversion[4] to a fluorescent singlet by reverse intersystem crossing.[5] This method necessitates control not only over spin–orbit coupling, requiring a heavy atom or a carefully engineered charge-transfer state, but also over the singlet–triplet exchange gap, which can be tuned by excitonic confinement.[6] Although progress has been made recently, conceptually it parallels the former approach: all excitations are converted to either triplets or singlets, thereby losing information on the underlying spin correlations of charge carriers. Evidence is emerging, however, that spin correlations in excitonic electron–hole precursor pairs can be used for exquisitely sensitive measurements of magnetic fields[7] and possibly even for quantum coherence phenomenology,[7b] with analogies to avian radical-pair photomagnetosensory processes.[8] To quantify such spin correlations, it is desirable to develop materials without heavy-atom spin mixing that show both intrinsic fluorescence and phosphorescence.

The third approach to triplet harvesting has not been explored previously: tuning spin–orbit coupling without heavy atoms such that non-radiative internal conversion from the triplet excited state to the singlet ground state is suppressed and phosphorescence is the only remaining relaxation mechanism. Even in low-atomic-order-number compounds such as hydrocarbons, the orbital component of the wavefunction can give rise to substantial magnetic moments, leading to non-negligible spin–orbit energy terms. The effect is well-studied in carbon nanotubes and graphene, where zero-field splitting correlates with nanoscale curvature.[9] For molecular materials, orbital symmetry can induce unusual spin–orbital coupling effects, such as in pyrazine, which shows direct singlet–triplet absorption.[10] Polycyclic aromatic hydrocarbons, such as triphenylenes or annulated compounds like phenazine, are classic metal-free materials that are known to exhibit substantial phosphorescence yields.[6c,11] Although triphenylenes have previously been explored both as emitters and as charge-transporting materials in OLEDs,[12] there are no reports of direct electrophosphorescence, despite renewed interest in room-temperature organic phosphors.[13] Herein, we demonstrate the feasibility of creating a triplet relaxation bottleneck to internal conversion that is so effective that radiative emission can even arise from higher-lying triplets in electroluminescence (EL), bypassing Kasha's rule of internal conversion.

Figure 1 a shows the two materials developed, a thiophene-decorated phenazine **1**; and **1** linked to a triphenylene block in **2**. Details of synthesis and characterization of the materials, and fabrication and performance of the OLEDs, are given in the Supporting Information. To construct OLEDs, we have to prevent concentration quenching, which is particularly strong for long-lived triplets. Therefore a dense film of the compounds cannot be used. The emitters are dispersed in a conducting matrix, poly(9-vinylcarbazole) (PVK). This material has a large optical gap, so that suitable electron- and hole-transporting moieties have to be included: 2-(4-tert-butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) and *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzi-

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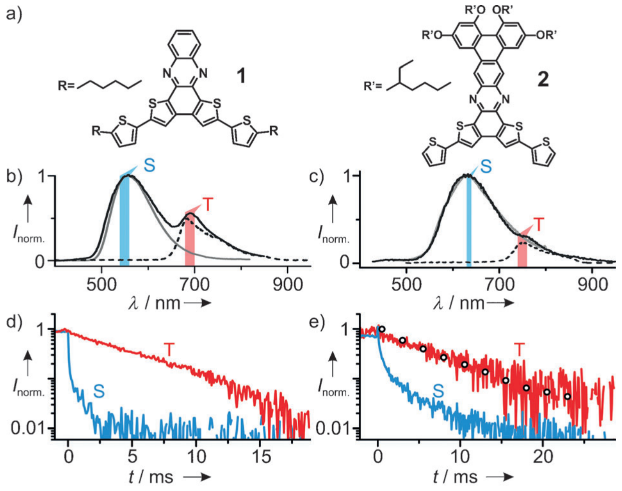

Figure 1. Room-temperature electrophosphorescence from metal-free organic compounds. a) Structures of the materials synthesized. b), c) OLED EL spectra of **1** (left) and **2** (right) compared to solution PL (gray line) and delayed PL from dilute dispersions in polystyrene films (dashed line). The delayed PL is measured in vacuo to prevent triplet quenching. d), e) Time-resolved EL of the triplet (red) and singlet (blue) bands. The phosphorescence decay of **2** under optical excitation is also shown (circles).

dine (TPD), respectively. The emitters **1** and **2** only make up 1% by weight of the active OLED layer, but are easily distinguished spectrally from the other active ingredients in the OLED (see the Supporting Information for spectra of all of the materials used). Room-temperature EL spectra are shown in Figure 1b,c (solid curves), comprising two distinct peaks, at 560 nm and 690 nm for **1**, and at 630 nm and 760 nm for **2**. The solution photoluminescence (PL) spectra are superimposed in gray, which closely match the short-wavelength EL. This feature corresponds to singlet emission, labeled S. Triplet emission under optical excitation only becomes visible when triplet quenching is deactivated, that is, upon dispersion of **1** or **2** in a polystyrene matrix and exclusion of oxygen under vacuum.[11e] The dashed curves in Figure 1b,c describe time-resolved (gated) PL, detected in a 10 ms time window 10 μs after illumination with a 500 ps laser pulse at 355 nm. Under these detection conditions, the prompt, short-lived singlet fluorescence is removed, revealing the long-lived triplet afterglow. This phosphorescence is clearly seen in the EL spectra of **1** and **2**, which are accurately described by a superposition of solution fluorescence and dilute-film gated PL. Such dual EL at room temperature, where both singlet and triplet of a molecule emit under electrical excitation, is very rare (see the Supporting Information for a detailed discussion).[3] In hydrocarbons, only singlets are seen in steady-state EL; electrophosphorescence has only been reported from a couple of materials, at low temperatures, under gated detection.[14] In contrast, in metal–organic complexes, all of the excitation energy is transferred to the triplet manifold. A clue to the underlying mechanism enabling electrophosphorescence here (the high level of triplet protection) is given by the transient luminescence (Figure 1d,e). The spectrally resolved decay of EL intensity in the singlet (blue) and triplet (red) channel, following pulsed electrical excitation of the OLED, are compared. The fluorescence decays within a few tens of microseconds, which is due to recombination of injected charge carriers. In contrast, the phosphorescence displays single-exponential decay with lifetimes of $\tau_1 = 5.5(1)$ ms and $\tau_2 = 7.1(5)$ ms for compounds **1** and **2**, respectively. Identical phosphorescence dynamics could also be detected in the PL of **2** at room temperature (black circles). The phosphorescence lifetime of **1** was determined as 11 ms at 25 K, which is only slightly longer than the room-temperature electrophosphorescence. Temperature, charge injection, or proximal triplets in the OLED apparently do not quench the molecular triplet excitation, implying that the triplet is sheltered from the immediate environment within the molecular structure. A detailed comparison of the results to existing metal–organic OLED triplet emitters, including the significance of triplet-triplet annihilation, is provided in the Supporting Information.

The exceptional degree of intramolecular triplet isolation becomes apparent in low-temperature spectroscopy of **2**. Figure 2a displays the EL spectrum at 4 K (red). Four distinct peaks are seen, at 530 nm, 580 nm, 610 nm, and 760 nm. The peak at 610 nm is assigned to fluorescence from S_1 through comparison with the room-temperature solution PL spectrum (gray), which is slightly shifted owing to temperature. In analogy, the 760 nm peak is identical to room-temperature phosphorescence (see Figure 1c). The narrow peaks to the blue of the singlet also arise from phosphorescence: this triplet lies energetically above the singlet. We compare the steady-state EL spectrum to gated PL, measured at a delay of 50 μs after photoexcitation, indicated by the dashed line. The spectrum is dominated by two narrow-band triplets, which is

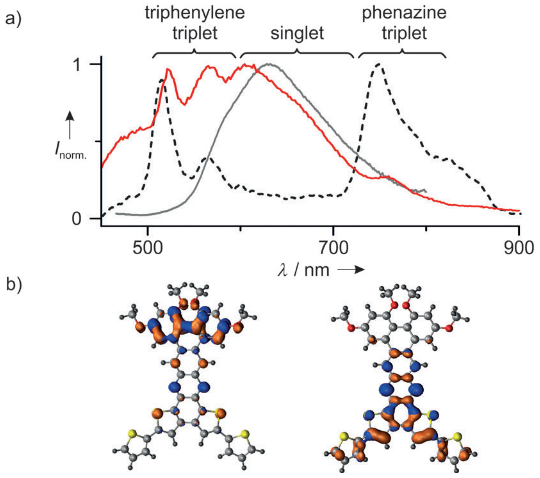

Figure 2. Electrically and optically excited phosphorescence from high-lying triplets of **2** owing to blocking of internal conversion. a) EL spectrum at 4 K (red) compared to room-temperature solution PL (gray) and gated dilute-film PL (25 K, dashed). Two dominant distinct phosphorescence peaks are identified. b) Calculated electronic attachment–detachment density plots of the two triplet transitions. The higher triplet is associated with triphenylene, and the lower triplet with phenazine (see the Supporting Information for computational details).

a signature of dual phosphorescence.[15] The high-energy feature with peaks at 530 nm and 580 nm is identical in position and shape to the low-temperature phosphorescence of triphenylene,[6c] with the 580 nm peak corresponding to a vibronic transition. Quantum chemical modeling provides insight into the energy levels and physical location of the molecular excited states. Only absorption energies were calculated, so that it is most instructive to compare energy differences rather than absolute energies. The comparison between calculated and measured singlet absorption energies shows that the computational methods used give excited-state energies to within 0.2 eV of experiment. The calculations predict one low-energy triplet state T_2 with appreciable oscillator strength (and four less intense transitions from T_1, T_3, T_4), located on the phenazine moiety of **2**; and two possible high-energy triplet states (T_5, T_6), located on the triphenylene, both offset from T_2 by 0.7 eV. This splitting agrees with the measured energy difference between the two phosphorescence peaks in Figure 2 at 530 nm (2.3 eV) and 760 nm (1.6 eV). Further modeling on bare triphenylene, taking into account excited-state structural relaxation, allows computation of the emission energy and indeed predicts a phosphorescence band at 2.3 eV (530 nm), in agreement with experiment (see the Supporting Information). Based on this analysis, we assign the 2.3 eV band to emission from a higher triplet state which is located primarily in the triphenylene region of **2**. The computed attachment–detachment density plots in Figure 2b illustrate how the two phosphorescent states are located on separate regions of **2**. We propose that as temperature increases, vibrations perturb the potential energy surfaces, promoting internal conversion from the "hot" triphenylene triplet to the lower-energy phenazine triplet so that high-energy triplet emission disappears. We stress that while the level assignment is tentative, the quantum chemistry does provide grounds for educated speculation on the origin of blocking of internal conversion (see the Supporting Information). Our observations suggest that materials which exhibit such dual (that is, "hot") phosphorescence[15] may, quite generally, be particularly suited to enabling room-temperature electrophosphorescence.

Long-lived electrophosphorescence may be of limited utility in display applications, where high driving intensities are required which would lead to triplet–triplet annihilation, but can be envisaged for low-level lighting. These organic compounds do not require expensive precious metals in contrast to conventional OLED triplet emitters, and should therefore be beneficial for large-area applications. The compounds also provide a direct window to magnetic-field effects in organic spintronics,[7] and promise to provide insight into radical-pair processes since spin correlations, the ratio between singlet and triplet populations, can be read out non-perturbatively.

Experimental Section

Synthesis and structural and spectral characterization of the compounds employed is described in detail in the Supporting Information. Time-resolved PL spectra were measured on drop-cast films of molecules **1** or **2** dispersed in polystyrene at approximately 1 mM concentration, deposited on a quartz cover-slip. The films were mounted on the copper block of a cold-finger closed-cycle helium cryostat under a vacuum of 10^{-5} mbar. The samples were excited at 355 nm using a pulsed diode laser (0.5 ns, ca. 100 Hz variable repetition rate, ca. 10 nJ pulse energy). The collected PL was dispersed in a spectrometer and recorded using a gated intensified CCD camera triggered by a photodiode picking up the laser pulse.

EL was measured in a cold-finger liquid helium cryostat under pulsed or steady-state driving conditions. OLEDs were fabricated by spin coating on precleaned indium tin oxide glass substrates covered with a hole-injecting layer of poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonate) (PEDOT/PSS). The blend of polymer matrix, phosphorescent molecules, and electron- and hole-transporting molecules was spin-coated on top in a nitrogen glovebox. The top contact was provided by a thermally deposited electrode comprising 0.5 nm CsF and 150 nm aluminum. Devices were encapsulated in the glovebox to prevent electrode degradation owing to atmospheric oxygen and water. Typical operating voltages for devices were between 8–12 V. The phosphorescence intensity decreased with respect to fluorescence upon increasing the driving voltage. Pulsed EL was excited with pulses of 10 ms duration at 10 Hz, and detected using an avalanche photodiode and a multiscaler photon counting setup. Complete device characteristics and an estimation of the quantum yield, as well as a demonstration of the effect of triplet-triplet annihilation, are given in the Supporting Information. Since somewhat different conditions were used for each measurement, the Supporting Information provides a tabular overview over all measurement specifics for each figure.

Quantum chemical modeling was carried out using the Q-Chem 3.2 package. Details on the calculations and their interpretation are provided in the Supporting Information.

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