

Highly efficient phosphorescent emission from organic electroluminescent devices

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The efficiency of electroluminescent organic light-emitting devices^{1,2} can be improved by the introduction³ of a fluorescent dye. Energy transfer from the host to the dye occurs via excitons, but only the singlet spin states induce fluorescent emission; these represent a small fraction (about 25%) of the total excited-state population (the remainder are triplet states). Phosphorescent dyes, however, offer a means of achieving improved light-emission efficiencies, as emission may result from both singlet and triplet states. Here we report high-efficiency ($\geq 90\%$) energy transfer from both singlet and triplet states, in a host material doped with the phosphorescent dye 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (PtOEP). Our doped electroluminescent devices generate saturated red emission with peak external and internal quantum efficiencies of 4% and 23%, respectively. The luminescent efficiencies attainable with phosphorescent dyes may lead to new applications for organic materials. Moreover, our work establishes the utility of PtOEP as a probe of triplet behaviour and energy transfer in organic solid-state systems.

When the absorption spectrum of the acceptor (dye) overlaps the emission spectrum of the donor (host), efficient energy transfer from the host to the dye can occur via a singlet-allowed, induced-dipole coupling between the molecular species. Hence, for a fluorescent emitter, the maximum external quantum efficiency (photons extracted in the forward direction per electron injected) is^{4,5}:

$$\Phi_{\text{el}} = \chi \Phi_{\text{fl}} \eta_{\text{r}} \eta_{\text{c}}$$

The fraction of charge carrier recombinations in the host resulting in singlet excitons is χ , which from spin statistics is presumed to be $\sim 1/4$, Φ_{fl} is the photoluminescent efficiency of the dye, η_{c} is the fraction of emitted photons that are coupled out of the device, and η_{r} is the fraction of injected charge carriers that form excitons. As both the recombination and fluorescent efficiencies can approach unity for an optimized device, the efficiency is primarily limited by coupling losses and a restriction to singlet excitons imposed by spin conservation in the induced-dipole energy-transfer process.

Although the output coupling of photons can be increased by using shaped substrates⁶, further efficiency improvements require that both singlet and triplet excited states contribute to luminescence. It has been proposed that intersystem crossing in lanthanide complexes may achieve this with an intramolecular energy transfer from a triplet state of the organic ligand to the $4f$ energy state of the ion⁷. However, a more general and efficient solution to the problem is to use phosphorescent emissive materials.

Phosphorescence is the forbidden relaxation of an excited state with spin symmetry different from the ground state; in organic molecules it typically results from a triplet to a singlet

relaxation. Although low-efficiency electroluminescence has been demonstrated⁸ at 100 K using the phosphorescent material benzo-phenone doped into poly(methylmethacrylate), no energy transfer from the host material was found. If a phosphorescent dye participates in energy transfer, then triplet behaviour within the host can be directly examined. This may enable the accurate determination of spin statistics and other triplet properties, as well as resulting in very high electroluminescent efficiency devices.

One relatively well studied red emitting phosphorescent dye is PtOEP. Porphine complexes are known to possess long-lived triplet states useful in oxygen detection⁹. The addition of platinum to the porphine ring reduces the phosphorescence lifetime by increasing spin-orbit coupling; the triplet states gain additional singlet character and vice versa. This also enhances the efficiency of intersystem crossing from the first singlet excited state to the triplet excited state. Transient absorption spectrometry gives a singlet lifetime in PtOEP of ~ 1 ps, and the fluorescence efficiency is extremely weak¹⁰. In contrast, the room-temperature phosphorescence efficiency of PtOEP in a polystyrene matrix is¹¹ 0.5 with an observed lifetime of 91 μs .

Induced dipole (or Förster) energy transfer to the triplet state is disallowed by spin conservation. However, energy transfer may occur by the parallel combination of Förster transfer to the singlet state, along with electron exchange (Dexter energy transfer). Dexter transfer is the 'physical', coherent transfer of an exciton from a donor to an acceptor site¹² at a rate proportional to the orbital overlap of the donor and acceptor molecules. Consequently, it is a short-range process, attenuating exponentially with distance. The transfer rate is proportional to the spectral overlap of the two species because the donor exciton energy must closely match that of the acceptor. Dexter processes allow for the transfer of triplet excitons because only the total spin of the donor-acceptor complex is conserved. Thus it is possible for both singlets and triplets to excite phosphorescence, increasing the theoretical efficiency limit from that for fluorescence by a factor of four or larger.

PtOEP shows¹³ strong absorption at a wavelength of 530 nm, corresponding to the peak emission of the electron transport material, tris-(8-hydroxyquinoline) aluminium (Alq_3); this makes PtOEP a suitable dopant for Alq_3 -based organic light-emitting diodes (LEDs). To study the electroluminescent properties of Alq_3 /PtOEP systems, organic LEDs were produced by high-vacuum (10^{-6} torr) thermal evaporation onto a cleaned glass substrate precoated with conductive, transparent indium tin oxide (ITO). The test structure consists of a 60-Å-thick layer of copper phthalocyanine to aid hole injection from the ITO, a 350-Å-thick layer of the hole transporting material 4,4'-bis[*N*-(1-naphthyl)-*N*-phenyl-amino] biphenyl (α -NPD), a 400-Å-thick layer of Alq_3 doped with varying molar concentrations of PtOEP, and a further 100-Å-thick layer of Alq_3 to prevent quenching of PtOEP excitons at the cathode. Finally, a shadow mask with 1-mm-diameter openings was used to define the cathode consisting of a 1,000-Å-thick layer of 25:1 Mg:Ag, with a 500-Å-thick Ag cap. All measurements were performed in air at room temperature except for the photoluminescence measurements which were performed under nitrogen.

The electroluminescence spectra of the devices with three different concentrations of PtOEP are shown in Fig. 1. No significant emission is found for the previously identified singlet state, expected at ~ 580 nm (ref. 10), but strong emission is observed from the triplet excited state at 650 nm, with weaker emission seen at the vibronic harmonic overtones at 623 nm, 687 nm and 720 nm. At high drive currents, the emission at 650 nm saturates, and increasing emission is seen from other features, especially the broad Alq_3 peak centred at 530 nm. This results in a reversible shift in colour from deep red to orange, corresponding to a shift in the device chromaticity co-ordinates shown in Fig. 1 inset.

Spectral and time-resolved emission measurements were performed with a streak camera on our organic LEDs excited with current pulses. Slow decay of between 10 and 50 μs was observed for

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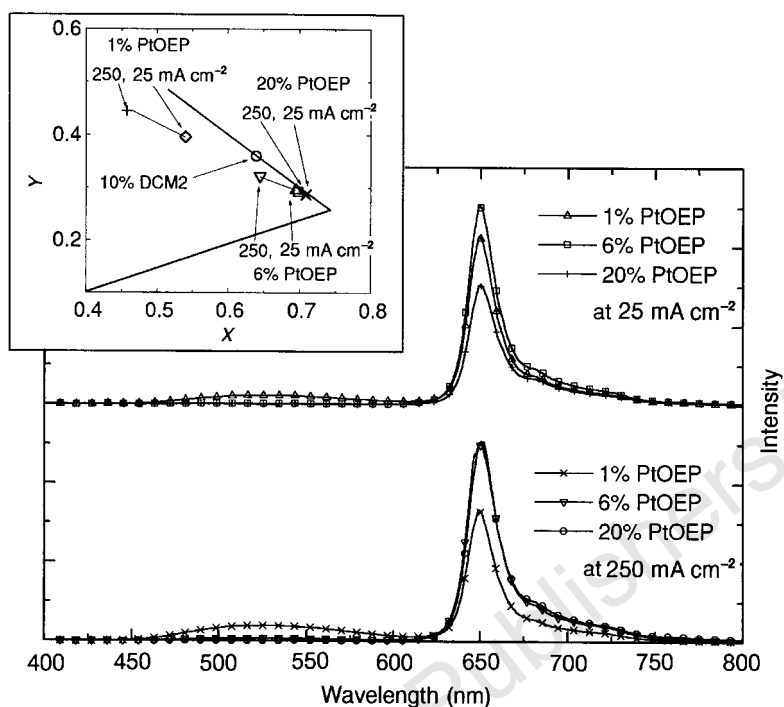


Figure 1 Spectra of the organic LEDs with different molar concentrations of PtOEP at different current densities. Upper traces, 1%, 6% and 20% PtOEP in Alq₃ organic LEDs at 25 mA cm⁻²; lower traces, 1%, 6% and 20% PtOEP in Alq₃ organic LEDs at 250 mA cm⁻². We note the increased Alq₃ emission at 530 nm in the 1% PtOEP organic LED. Insert, Commission Internationale de L'Éclairage (CIE)

chromaticity coordinates for the devices in the main figure at the specified current densities. Only the red corner of the CIE diagram is shown. We note the trend from saturated red to orange with increasing current. The 6% PtOEP in Alq₃ device at 25 mA cm⁻² has a luminance of 100 cd m⁻². The DCM2 result is taken from ref. 15.

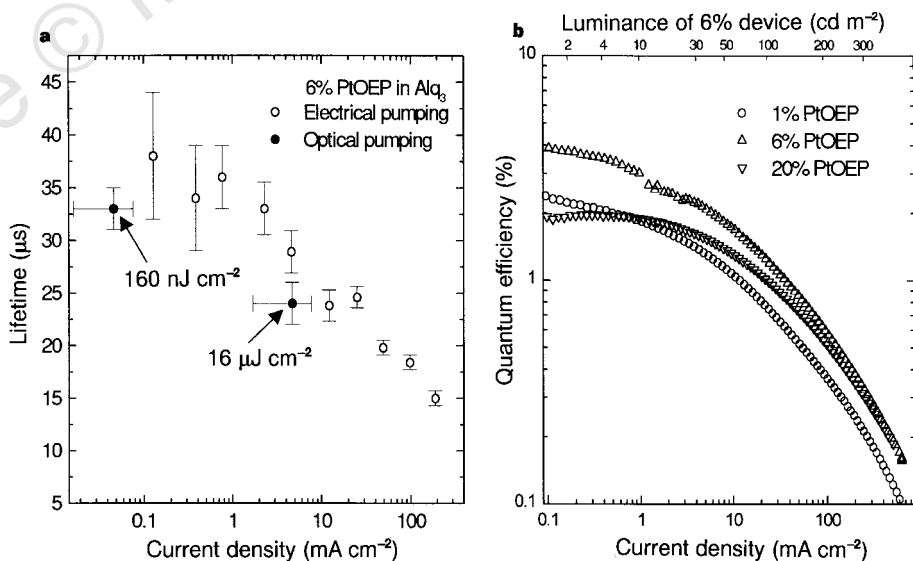


Figure 2 Lifetime and quantum efficiency of PtOEP emission. **a**, Phosphorescent lifetime of the 6% PtOEP in Alq₃ organic LED as function of current density (open circles). To explore the influence of bimolecular processes, PtOEP quenching in the absence of charge carriers was investigated using photoluminescence. This experiment was performed by pumping a 500-Å-thick film of 6% PtOEP in Alq₃ with 500-ps pulses from a nitrogen laser at a wavelength of 337 nm. At a pulse energy density of 16 μJ cm⁻², we measured a PtOEP lifetime of (24 ± 2) μs. This is similar to the lifetime obtained under electrical pumping at current densities of ~5 mA cm⁻². To check if the optical and electrical decay times have a similar origin, we note that the laser output is absorbed principally by Alq₃ with an

absorption coefficient²⁰ of ~3 × 10⁴ cm⁻¹. Hence, ~26% of the nitrogen laser pulse is absorbed, giving an exciton density of 1.4 × 10¹⁸ cm⁻³. Assuming 100% transfer of injected carriers to PtOEP excitons, the current density corresponding to this pumping level is shown above (filled circles). When the pulse energy is decreased to ~160 nJ cm⁻², the lifetime increases to (33 ± 2) μs. The trend in the lifetime of optically pumped samples, which has been previously attributed¹⁴ to bimolecular quenching, is consistent with the trend of the electroluminescent lifetime data, suggesting a common physical origin. **b**, Quantum efficiency of PtOEP emission as a function of doping concentration and current density. The top axis shows the luminance of the 6% PtOEP in Alq₃ device.

the triplet state, confirming the presence of phosphorescence. The luminescent lifetime was also found to decrease with increasing current density, as shown in Fig. 2a for a device with a 6% concentration of PtOEP in Alq₃.

From the spectral data, the fraction of output power in the red (subtracting the Alq₃ emission) can be determined as a function of current to provide the external quantum efficiency (Fig. 2b). As expected¹², the trend in phosphorescent lifetime matches the quantum efficiency results: the shorter lifetimes observed at high current densities corresponds to lower quantum efficiencies. The external quantum efficiency reaches a maximum value of 4% at a PtOEP concentration of 6%. To our knowledge, this is considerably higher than the highest external quantum efficiency obtained to date for red-emitting, fluorescent organic LEDs.

Because PtOEP molecules have a long exciton lifetime, it is possible that saturation is responsible for the decreased quantum efficiency at high currents and low dopant concentrations. This can be examined by comparing the total number of PtOEP sites to the maximum number of photons extracted. For a molar concentration of 1%, the number of PtOEP sites in the ~50-Å-thick recombination zone³ near the α-NPD/PtOEP:Alq₃ interface is ~8 × 10¹² cm⁻². After adjusting for the output coupling efficiency⁶, the internal emitted photon flux saturates at ~3 × 10¹⁶ s⁻¹ cm⁻², yielding a radiative lifetime of ~300 μs, consistent with previous PtOEP phosphorescence efficiency and lifetime measurements¹¹. If sites within the recombination zone saturate, then Alq₃ excitons are less likely to transfer to PtOEP, corresponding to an increase in the probability for radiative recombination in Alq₃. This is supported by the data shown in Fig. 1, which shows increased Alq₃ emission for devices with low concentrations (~1%) of PtOEP.

Saturation of emissive sites is alleviated by increasing the concentration of PtOEP. Yet from Fig. 2b, it is evident that at molar concentrations ≥ 6%, the quantum efficiency again decreases. As high densities of porphyrin complexes often show bimolecular quenching¹⁴, it is likely that the PtOEP/Alq₃ system is also affected by this process. Hence, the decrease in quantum efficiency with increasing current could be partially accounted for by the decreasing

lifetime. As the current increases, the phosphorescent decay becomes bi-exponential, indicating the presence of a quenching process such as bimolecular recombination (see Fig. 2a legend).

The doping concentrations required to maximize quantum efficiency are extremely high compared to devices doped with fluorescent dyes and excited by long-range (~40 Å) Förster transfer. This suggests that the shorter-range Dexter process may be dominant in the Alq₃:PtOEP system. Calculations of the extent of energy transfer from Alq₃ to PtOEP support this hypothesis. Accounting for photons lost via emission through the sides of the device and total internal reflection within the substrate⁶, a maximum external efficiency of 4% corresponds to an internal efficiency of 23%. PtOEP doped in polystyrene has a lifetime of 91 μs and a phosphorescent yield of 50% (ref. 11). Given a maximum exciton lifetime in the PtOEP/Alq₃ devices of 45 μs, we infer a peak phosphorescent yield of ≤ 25%. This implies ≥ 90% energy transfer from Alq₃ to PtOEP, confirming that both triplets and singlet excitons must participate in energy transfer.

Conclusive evidence of Dexter transfer is obtained by examining the non-normalized spectra of the two devices shown in Fig. 3. A 100-Å-thick layer of Alq₃ doped with ~1% DCM2 is placed in the recombination zone of both devices. As DCM2 is fluorescent with efficient energy transfer from Alq₃ (ref. 15), this layer effectively removes singlet excitons from the devices. Remaining singlets eventually recombine in Alq₃, yielding the small shoulder in the spectra at ~530 nm. However, in device 2, an additional layer of ~10% PtOEP in Alq₃ is introduced 200 Å away from the recombination zone. In this device, emission is seen from PtOEP without any change in the intensity of emission from either DCM2 or Alq₃. Hence, PtOEP cannot be an efficient trap, as carriers removed by PtOEP in device 2 would result in a decrease in the DCM2 and Alq₃ emission; an effect clearly not observed. As the DCM2 acts as a filter that removes singlet Alq₃ excitons, the only possible origin of the PtOEP luminescence is Alq₃ triplet states that have diffused through the DCM2 and intervening Alq₃ layers.

Given the observed decrease of quantum efficiency with increasing current, it is important that Alq₃ devices doped with PtOEP achieve a useful luminosity before significant quenching occurs. Unlike some red dyes¹⁶ with peak emission around 650 nm, PtOEP emission is saturated and does not extend significantly into the infrared, thereby maximizing the luminosity. At a molar concentration of 6%, a quantum efficiency of 1.3% and a power efficiency of 0.15 lm W⁻¹ at 100 cd m⁻² is obtained. In comparison with other compounds with saturated red emission, such as the Eu complexes¹⁷⁻¹⁹, PtOEP possesses quantum and power efficiencies that are superior by at least an order of magnitude. Compounds with unsaturated red emission, such as DCM2 and its variants¹⁶, possess comparable quantum efficiencies but emit closer to orange than PtOEP; further red-shifting by increasing the DCM2 concentration causes the quantum efficiency to decrease, along with a considerable increase in infrared emission¹⁵.

Although PtOEP demonstrates the efficiency improvements made possible by the participation of triplet excitons in phosphorescence, the long lifetime of PtOEP (>10 μs) and the short-range nature of Dexter energy transfer cause saturation of emission at low dopant concentrations. It is also observed that bimolecular interactions quench emission at high exciton densities, causing a decrease in quantum efficiency for high currents and doping concentrations. But it is possible that other host materials could be used with PtOEP to increase efficiency even beyond the high values reported here. Given the performance of PtOEP, other phosphorescent dyes emitting in the blue and green regions of the spectrum also present an attractive area of study for display applications. □

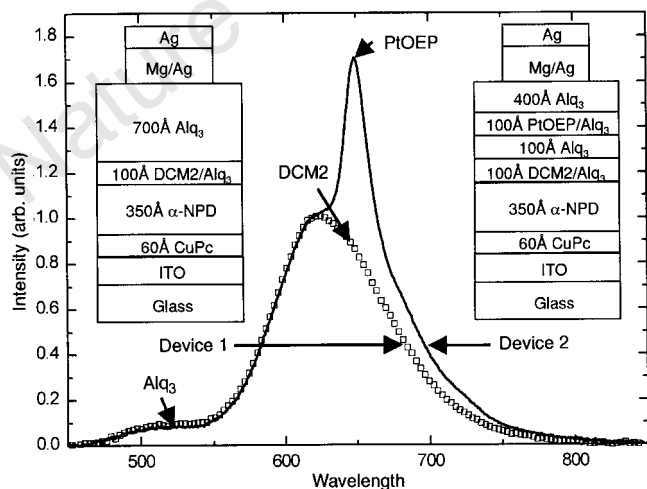


Figure 3 Two electroluminescent devices demonstrating that Alq₃ triplets are transferred to PtOEP. Each device contains a 100-Å-thick layer of ~1% DCM2 in Alq₃ at the recombination zone. This layer acts to remove singlet states. Remaining singlets recombine in Alq₃, yielding the shoulder apparent in the spectra at 530 nm. Device 2 contains an additional layer of ~10% PtOEP in Alq₃ positioned 200 Å away from the Alq₃/α-NPD interface. Strong emission is seen from the PtOEP without a corresponding decrease in emission from DCM2 or Alq₃. The spectra were measured at a current density of 6 mA cm⁻². (DCM2 is [2-methyl-6-[2-(2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizin-9-yl) ethenyl]-4H-pyran-4-ylidene] propane-dinitrile.)

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Synthesis and organization of zeolite-like materials with three-dimensional helical pores

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The increasing demand for enantiomerically pure chemicals has stimulated extensive research into the preparation of heterogeneous chiral catalysts or separation media that combine both shape selectivity and enantioselectivity¹. Helical pores in inorganic materials might be able to perform such functions, but their occurrence is rare¹. Attempts have been reported to synthesize a specific enantiomorph of the chiral zeolite beta², and chiral metal complexes have been used to assemble inorganic precursors into chiral frameworks^{3,4}. Materials with a fully three-dimensional array of helical structural units are particularly rare, because helical structures (such as quartz) are commonly generated by a uni-dimensional symmetry element acting on an achiral structural subunit^{5,6}. Here we report on a family of zeolite-type materials (which we call UCSB-7) that possess two independent sets of three-dimensional crosslinked helical pores, separated by a gyroid periodic minimal surface¹³. We have synthesized the UCSB-7 framework for various compositions (zinc and beryllium arsenates, gallium germanate) using either inorganic cations or amines as structure-directing agents. The helical-ribbon motif that we identify might be exploited more widely for developing useful chiral solid-state structures.

The framework topology of UCSB-7 was determined from gallogermanates synthesized with K⁺ or amines such as NH₂(CH₂)_nNH₂ (n = 2–5). We have grown large crystals of gallogermanate phases with a variety of linear and branched mono-, di- or tri-amines

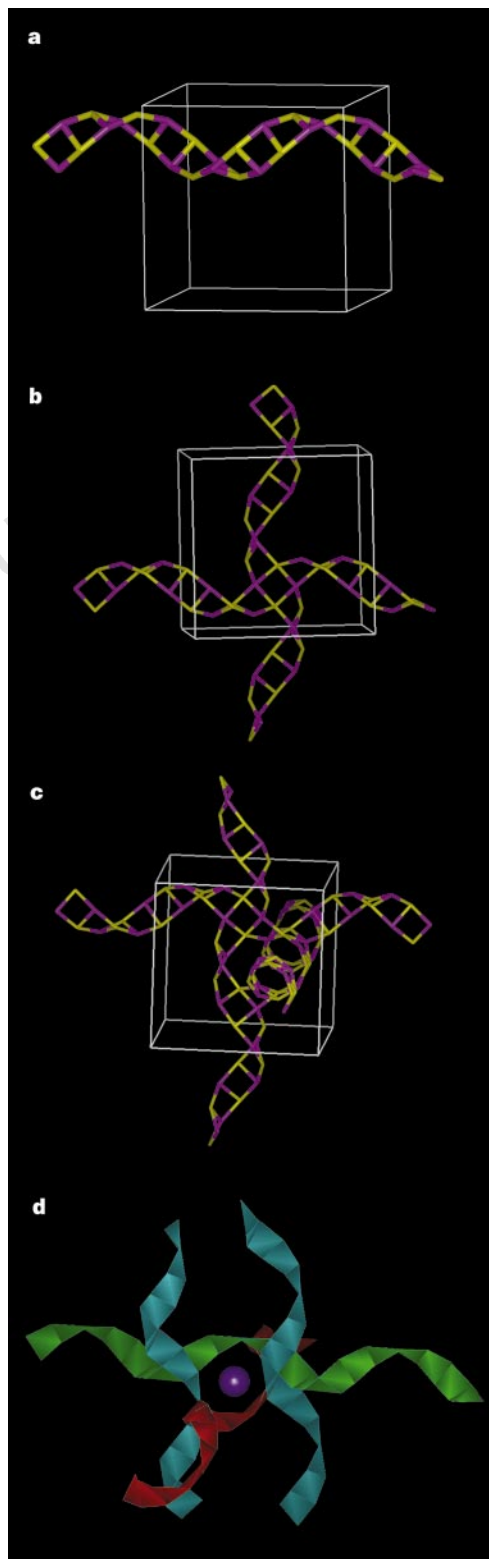


Figure 1 The helical ribbons are crosslinked in three dimensions to give 12-ring pores. From one to three dimensions (a–c): crosslinking of mutually perpendicular inorganic helical chains in UCSB-7K. In all panels the bridging oxygen atoms are omitted. The yellow sites represent Ge⁴⁺ atoms and the purple sites Ga³⁺ atoms. d, The K⁺ ion channel with the 12-ring pore. The purple sphere represents the K⁺ ion.