Since Tang and VanSlyke first reported efficient electroluminescence from a device based on tris(8-hydroxyquinoline)aluminium(III) (Alq3) as the luminescent layer,1 organic light-emitting diodes (OLEDs), based on these materials, are now at the stage where they are being used as monochrome displays. This results from emission from a ligand centered π, π* excited state, formed in the transition of an electron from a highest occupied molecular orbital (MO) lying mainly on the phenoxide ring to a lowest unoccupied MO predominantly on the nitrogen atom.2 By doping with the appropriate dyes, the emission can be tuned through the visible spectrum,3,4 leading to the possibility of full color OLED displays. The basic processes involved are reasonably well understood,5,6 with electroluminescence involving generation of singlet excitons from electron–hole recombination. From spin statistics, theoretical calculations, and experiment,7 the singlet:triplet excitation ratio is 1:3, limiting the maximum internal OLED efficiency from fluorescent materials to ≤25%. Nevertheless, by doping with heavy atom-containing complexes, such as platinum(II) octaethylporphyrin (PtOEP), it is possible to capture triplet excitons (or charge carriers) to give electrophosphorescence, increasing internal quantum yields dramatically.8 Although of interest for display applications, efficient exploitation requires detailed knowledge of the properties of the lowest triplet state of Alq3, which is not available. We are reporting here what we believe to be the first detailed characterization of this state.

There is relatively little detailed information on Alq3 photophysics. Various values have been reported for the fluorescence quantum yield9,10 and lifetime.3,11 and only indirect information exists on the triplet state.11,12 Attempts to observe phosphorescence have proved unsuccessful,11,12 although some information has been inferred from data on heavy metal quinolates.11 We have shown13 that pulse radiolysis of benzene solutions selectively produces triplet states of conjugated organic polymers by energy transfer from appropriate sensitizers following pulse radiolysis of benzene solutions. The triplet state of Alq3 is characterized in the same way.

Following pulse radiolysis13 of an Ar saturated solution of Alq3 (2.25 × 10^-4 M) and biphenyl (0.01 M) in benzene, the absorption yield of the biphenyl triplet state, 16 a molar absorption coefficient ε^350 M^-1 cm^-1 for the biphenyl triplet state, was determined for the Alq3 triplet state, within the range of values reported for triplets of heavy metal quinolates.11 The triplet state was also studied by laser flash photolysis, exciting an Ar saturated solution of Alq3 (6.7 × 10^-5 M) in benzene with the third harmonic of a Nd:YAG laser (355 nm). A weak band was observed around 350 M, in addition to ground-state depletion at 400 nm. This decayed within ca. 100 μs. Using the benzophenone triplet state in benzene as a standard, gave a quantum yield of triplet state formation, as expected from the above reaction. This quenching by molecular oxygen is expected to involve the Type II energy transfer reaction to produce singlet oxygen. Direct observation of singlet oxygen phosphorescence at 1270 nm following excitation of aerated solutions at 355 nm provided evidence for this. Singlet oxygen luminescence as a function of laser intensity, using 1H-phenalen-1-one as a standard,19 gave a quantum yield of 0.27. Within experimental uncertainty, this is in reasonable agreement with the yield of triplet state formation, as expected from the above reaction. From these two values, we suggest Φ_T = 0.24 with an error of
Figure 2. Phosphorescence spectra observed upon excitation at 393 nm of Alq3 in an ethyl iodide glass.

±25%. This is close to $\phi_T \approx 0.25$ estimated for the meridional isomer at low temperatures. This, coupled with the fluorescence yield, shows the importance of nonradiative decay of singlet excitons in Alq3, with internal conversion being particularly important.

Energy transfer is a valuable method for determining triplet energies. Various sensitizers were used to transfer triplet energy to Alq3 on pulse radiolysis of Ar saturated benzene solutions. Efficient sensitization occurred with 9-fluorenone ($E_{triplet} = 1.97$ eV),22 while none was observed with acridine ($E_{triplet} = 2.10$ eV).22 Some energy transfer occurs, but the rate of decay of the Alq3 triplet state is slower than with the other sensitizers, suggesting equilibrium with the pyrene triplet and, hence, very similar energies. We thus give the triplet energy of Alq3 in benzene as 2.10 ± 0.05 eV. This is close to the value of ca. 2.0 eV estimated by Baldo et al.12 and the value of 2.13 eV reported by Martin et al. from time-dependent density-functional theory calculations. The phosphorescence of Alq3 was studied in an ethyl iodide glass at 77 K.24 The presence of the heavy atom iodine is expected to promote intersystem crossing. A broad band emission was observed, with a maximum at 660 nm (Figure 2), and is assigned to Alq3 phosphorescence. From the spectrum, a triplet energy of 2.17 ± 0.10 eV was estimated, in agreement with the energy transfer value. The lifetime is short and at the limit of our detection system (≤50 μs), which may explain why this emission has previously proved elusive. However, this is consistent with the lifetime determined by pulse radiolysis. Similar phosphorescence is also observed in a benzene glass sensitized by benzophenone (see Supporting Information).

Electrophosphorescence in doped Alq3 systems could arise from Dexter energy transfer.5,25 To test this, triplet–triplet energy transfer from Alq3 to PtOEP was studied. Following pulse radiolysis of Ar saturated benzene solutions of biphenyl (10 mM), Alq3 (20–100 μM), and PtOEP (1–10 μM), the initial absorption of the Alq3 triplet state at 510 nm decayed more rapidly, to be replaced by the PtOEP triplet state absorption at 410 nm. Bleaching of the porphyrin absorption around 540 nm also occurred. These results confirm the triplet energy transfer reaction to the lower energy ($E_T = 1.92$ eV) porphyrin, presumably by the Dexter transfer mechanism

$$^3\text{Alq}_3^* + \text{PtOEP} \rightarrow \text{Alq}_3 + ^3\text{PtOEP}^*$$

A rate constant $k = 3.9 \times 10^9$ M$^{-1}$ s$^{-1}$, within the range typically observed for triplet–triplet energy transfer, was estimated from the grow-in of porphyrin triplet absorption as a function of concentra-

tion. This agrees with some electrophosphorescence in Alq3 devices resulting from Dexter transfer to dopant.8,25 Yet the short lifetime of the Alq3 triplet state and the relatively modest energy transfer rate suggest that, as with conjugated polymer devices containing this dopant,26,27 charge trapping by PtOEP may also be important.

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

References

(15) Pulse radiolysis experiments were carried out using high energy electron pulses from a 12 MeV linear accelerator at Daresbury Laboratories, as described in detail in the Supporting Information.
(20) Using the value of $\phi_T = 0.32$ from ref 10 and the above value gives $\phi_{PEC} = 0.45$.
(24) Phosphorescence measurements were made in glasses at 77 K using a Spec1934D phosphorimeter accessory with a Fluorolog 3-22 instrument.