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Phosphorescent perylene imides†

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Asymmetrically substituted perylene imide derivatives PIa and PIx display phosphorescence in glassy matrices at 77 K. The lifetime is 49.0 ms for PIa and 13.5 ms for PIx. The triplet energy is 1.79 eV for PIa and 1.68 eV for PIx as confirmed by sensitization experiments of the C_{60} triplet.

Perylene bisimides and closely related dyes are attracting increasing interest for their light absorption, high fluorescence, electron transport properties which make them very valuable in colour chemistry,[1] as fluorescence tags[2] and in organic electronics.[3] Due to their high stability and intense spectroscopic signatures these excellent electron acceptors have often been used as components in arrays for light energy conversion both for practical purposes[4] and for mechanistic studies.[5–7]

We recently reported on the photophysical and electrochemical properties of a couple of new asymmetrically substituted perylene imide derivatives, **PIa** and **PIx** (Fig. 1).[8] A remarkable feature of these new PIs is an intrinsic high triplet yield, an unprecedented feature for this class of compounds. Triplet reactivity for PIs has been formerly reported only as a consequence of inter-molecular[9] or intra-molecular sensitization[10–12] or under conditions of induced enhancement of triplet yield in multi-component arrays.[13,14] In the present asymmetrically substituted PIs, in spite of a still high fluorescence quantum yield ($\phi_{fl} = 0.37$ for **PIa** and $\phi_{fl} = 0.58$ for **PIx**), a high triplet yield of the order of $1 - \phi_{fl}$ was observed. For both PIs the triplet–triplet absorption spectrum, with intense bands at around 510–530 nm, was registered and a triplet lifetime in air purged solutions of the order of 10^2 μs was measured at room

Fig. 1 Structures of the asymmetrically substituted perylenes **PIa**, **PIx** and of the parent perylenes **PI0** and **PI**.

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temperature. The reaction rate with oxygen, k_{ox}, was of the order of 2×10^9 M^{-1} s^{-1}. We provided evidence, by measuring the singlet oxygen ($^1\Delta_g$) luminescence at 1268 nm, of the sensitization of singlet oxygen by **PIa** and **PIx** with yields of the order of 0.4–0.6.

These values are those of typical singlet oxygen photosensitizers and suggest that these compounds can be used for this purpose. We also looked for phosphorescence in the glassy matrix of toluene (TL) and, on the basis of the known triplet energy level of the parent symmetric compound **PI**, *ca.* 1.2 eV,[9] we looked for bands in the NIR range. For **PI**, former sensitization experiments allow to derive the energy level of the triplet since the intersystem crossing (isc) yield for this compound is almost zero.[9]

In the NIR range, very weak bands emerging from the fluorescence background of the **PIa** and **PIx** samples, absent in the parent compound **PI0**, could be identified in TL glassy matrixes. These bands were around 900 and 990 nm for **PIa** and in the region 920–990 nm for **PIx**. Similar band values were measured for **PIa** in a 3-methylpentane glass, but the maxima of **PIx** in a dichloromethane–methanol glass were not confirmed (Fig. S1, ESI†). In fact a single broad band at around 950 nm could be detected and this casts doubts on the correctness of the previous assignment.[8] In the present study we intend to address in more detail the phosphorescence issue, to measure a reliable phosphorescence spectrum and derive the triplet excited state energy in order to fully characterize this state for the two compounds.

Absorption at room temperature and luminescence spectra at room temperature and 77 K in TL detected in the UV-Vis region are reported in Fig. 2. The high fluorescence background in the 600–850 nm region does not allow us to detect the comparatively weaker phosphorescence bands.

In order to enhance phosphorescence and be able to locate the phosphorescence emission region, we take advantage of the heavy atom effect on the isc of the compounds. This is expected to greatly enhance isc by increasing spin–orbit coupling and to quench the fluorescence in favour of phosphorescence. The corrected luminescence spectra of the new PIs in glassy solutions (77 K) containing 50% of ethyl iodide (EtI) are measured both with a NIR sensitive spectrofluorimeter and a UV-Vis spectrofluorimeter. They are reported in Fig. 3. The spectra from the two different apparatuses are in excellent agreement and show intense bands respectively at 686, 764 and 862 nm for **PIa** and 737, 830 and 948 nm for **PIx**. One can notice that the bands formerly detected above 900 nm[8] (Fig. S1, ESI†) may represent only the weakest low energy tail of the phosphorescence. Excitation spectra measured on the maxima of the luminescence in the glassy matrix
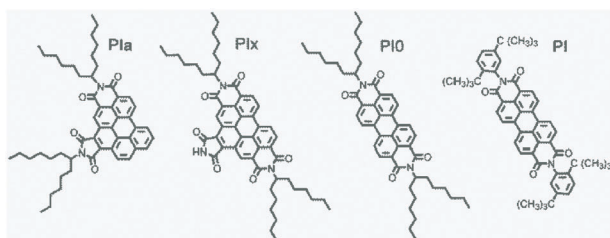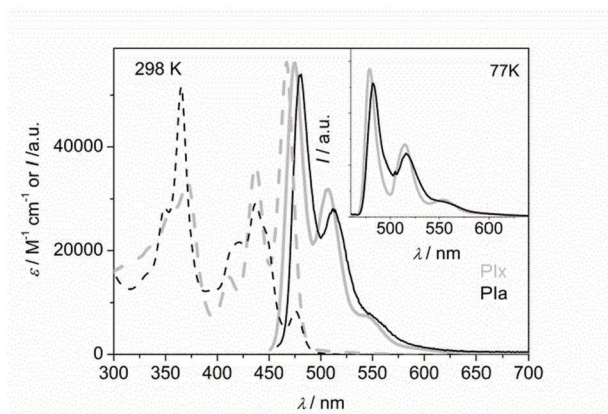
Fig. 2 Absorption spectra of **PIa** and **PIx** (dashed line) and arbitrarily scaled luminescence spectra in the UV-Vis region at 298 K (continuous line) in TL. The luminescence spectra in the UV-Vis region in TL glass at 77 K are shown in the inset.
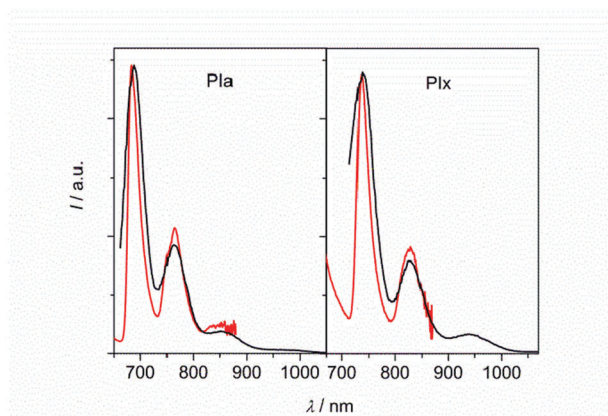

Fig. 3 Corrected luminescence spectra in a DCM–MeOH–EtI (1 : 1 : 2) glass at 77 K measured with a NIR (black line) and a UV-Vis spectro-fluorimeter (red line).

containing 50% EtI, Fig. S2 (ESI†), are in good agreement with the absorption spectra of the solutions, see Fig. 2. This confirms that the observed emissions are indeed produced upon excitation of the PIs and not as a consequence of artefacts or contaminants.

A more direct measure of the phosphorescence in normal, non-heavy atom containing solvents requires a gated detection. This prevents the very strong prompt fluorescence signal from reaching the detector. Gated detection is available only on the UV-Vis spectrofluorimeter, with sensitivity dropping above 850 nm. The uncorrected delayed luminescence of **PIa** and **PIx** in a 1 : 1 mixture of dichloromethane–ethanol (DCM–EtOH) at 77 K is reported in Fig. 4. The spectra show bands at wavelengths of 692 and 762 nm for **PIa** and 734 and 820 nm for **PIx**, in very good agreement with those obtained in the heavy-atom containing solvent. This confirms a genuine phosphorescent nature for the emission. The lifetime measured at 77 K in a DCM–MeOH (1 : 1) matrix is 13.5 ms for **PIx** and 49.0 ms for **PIa**, respectively (Fig. S3, ESI†).

The triplet excited state energy, derived from the phosphorescence band, is 1.79 eV for **PIa** and 1.68 eV for **PIx**. This value is 0.5–0.6 eV higher than that reported for **PI**.[9] The large difference in the triplet excited state is somehow surprising, since
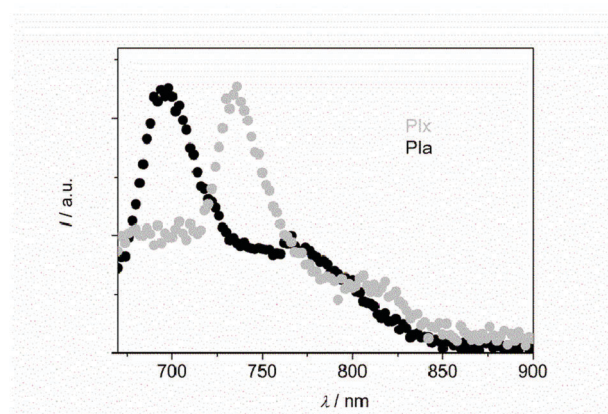

Fig. 4 Delayed luminescence spectra of **PIa** and **PIx** in a DCM–MeOH (1 : 1) glassy solution at 77 K. Both have been registered with a delay of 50 μs after the pulse of the lamp and with a gate open for 20 ms.

the singlet excited state energy level in **PIa** and **PIx** is only 0.3 eV higher than that of model **PI0**. The 77 K fluorescence maximum is in fact at 483 nm (2.56 eV) for **PIa** and at 479 nm (2.58 eV) for **PIx** compared to a 543 nm (2.28 eV) fluorescence maximum for **PI0**.

To confirm the unexpectedly high energy level of the triplet excited state of these PIs, we designed a sensitization experiment with a partner of known, lower triplet energy. In these experiments, the PIs triplet can act as energy donor and sensitize the triplet excited state of the acceptor. PIs display intense T–T absorption bands in TL solutions at room temperature, with maxima at 510 nm (ε *ca.* 7000 M^{-1} cm^{-1}) for **PIa** and at 530 nm (ε *ca.* 14 000 M^{-1} cm^{-1}) for **PIx**.[8] Fullerene (C_{60}) is identified as a convenient energy acceptor since it is a good electron acceptor[15] and therefore thermodynamically unable to undergo electron transfer reactions with the strongly electron deficient PIs.‡ The triplet energy level of the fullerene is 1.57 eV, slightly lower than that found for the two PIs, and its triplet is well characterized by an absorption band at around 750 nm.[16] Furthermore, selective excitation of PIs can be achieved at around 470 nm (Fig. S4, ESI†).

The results of flash photolysis experiments upon selective excitation of **PIx** at 467 nm in a solution containing C_{60} (5×10^{-5} M) are shown in Fig. 5. Fig. S5 (ESI†) shows the results of a similar experiment where **PIa**, excited at 476 nm, is the sensitizer. In both cases the bands of PIs triplets decay at a faster rate than the one measured in oxygen free TL solutions in the absence of C_{60} (τ = 140 μs for **PIx** and τ = 130 μs for **PIa**) whereas the band of C_{60} at 740 nm grows as shown in Fig. 5 and Fig. S5 (ESI†). The lifetime of the decay of the ^{3}PIs band and of the concomitant rise of the sensitized $^3C_{60}$ depends on the concentration of the C_{60} quencher (Fig. 6). The bimolecular energy transfer rate constant is k_{en} = 4.0 × 10^9 M^{-1} s^{-1} for **PIx** and k_{en} = 5.4 × 10^9 M^{-1} s^{-1} for **PIa**. The relative magnitude of the rates for the two PIs reflects the higher driving force of the energy transfer reaction when **PIa** is used as sensitizer (ΔG^0 = −0.22 eV) than when **PIx** is used as sensitizer (ΔG^0 = −0.11 eV). On the other hand, the absolute value of the two rates, lower than the diffusional one (1 × 10^{10} s^{-1}), is typical of exothermic triplet energy transfer reactions. The data from sensitization experiments, showing an efficient sensitization of the triplet of C_{60}, are consistent with the triplet energies for the two PIs derived from phosphorescence experiments.
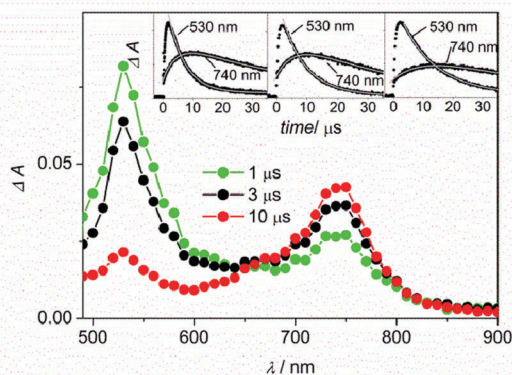
Fig. 5 Transient absorption spectra of **PIx** (2.4×10^{-5} M) in TL in the presence of C_{60} (5×10^{-5} M) at room temperature. Excitation at 467 nm, 0.6 mJ pulse^{-1}. In the inset the time evolutions of the absorbance on the band maxima at C_{60} concentrations of 5×10^{-5} M (left), 3.7×10^{-5} M (centre) and 2.8×10^{-5} M (right) are shown.
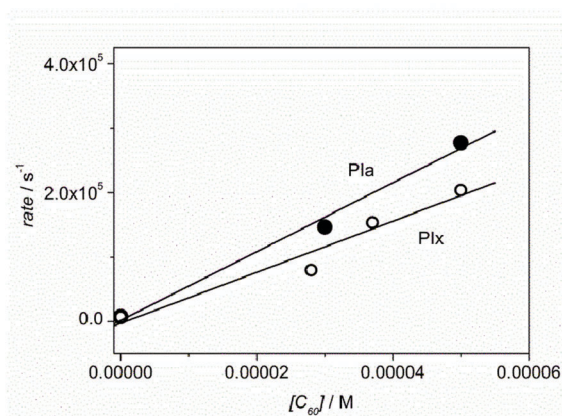

Fig. 6 Pseudo-first order rate constant for the energy transfer process in TL solutions from ^{3}**PIx** and ^{3}**PIa** in the presence of different C_{60} concentrations.

We have here reported for the first time phosphorescent perylene imides. Phosphorescence induced by an external heavy atom effect in EtI glasses has helped to locate the phosphorescence bands which have been confirmed by delayed luminescence experiments in non-heavy atom containing glassy solvents. The triplet energy levels, 1.79 eV for **PIa** and 1.68 eV for **PIx**, remarkably high for perylene imides, have been confirmed by sensitization experiments of $^3C_{60}$. Altogether, the designed experiments confirm the assignment of the bands as unquestionable genuine phosphorescence and open the way to new applications for these dyes.

Notes and references

‡ C_{60} reduces at −0.98 V and oxidizes at +1.26 V vs. Fc/Fc$^+$ in acetonitrile–toluene (1 : 5)[15] which can be converted as ca. −0.55 V and ca. +1.7 V vs. SCE. The first reduction of **PIx** is at −0.58 V and that

of **PIa** at −0.96 V, whereas the oxidation wave is above 1.9 V for **PIx** and at 1.75 V for **PIa**, all vs. SCE.[8] The energy stored in ^{3}PIs ($\leq$1.79 eV) is not sufficient to provide either HOMO–HOMO or LUMO–LUMO electron transfer.

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