Phosphorescent perylene imides†

Barbara Ventura, a Heinz Langhals, b Bernd Böck b and Lucia Flamigni * a

Received 9th February 2012, Accepted 9th March 2012
DOI: 10.1039/c2cc30948c

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. The triplet lifetime is 49.0 ms for PIa and 13.5 ms for PIx. The triplet state for the two compounds.

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 tags2 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 purposes4 and for mechanistic studies5–7.

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-molecular9 or intra-molecular sensitization10–12 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 (ϕfl = 0.37 for PIa and ϕfl = 0.58 for PIx), a high triplet yield of the order of 1.68 eV for PIx as confirmed by sensitization experiments of the C60 triplet.

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 spectrophotometer and a UV-Vis spectrophotometer. 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 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–methyl alcohol glass were not confirmed (Fig. S1, ESI†). In fact a single broad band 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 glass 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 spectrophotometer and a UV-Vis spectrophotometer. 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 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–methyl alcohol glass were not confirmed (Fig. S1, ESI†). In fact a single broad band 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 glassy solutions 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 spectrophotometer and a UV-Vis spectrophotometer. 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 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–methyl alcohol glass were not confirmed (Fig. S1, ESI†). In fact a single broad band 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 glassy solutions 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 spectrophotometer and a UV-Vis spectrophotometer. 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 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–methyl alcohol glass were not confirmed (Fig. S1, ESI†). In fact a single broad band 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 glassy solutions 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 spectrophotometer and a UV-Vis spectrophotometer. 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 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–methyl alcohol glass were not confirmed (Fig. S1, ESI†). In fact a single broad band 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.
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 Pla and Plx 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 Pla and 734 and 820 nm for Plx, in 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) glass is 13.5 ms for Plx and 49.0 ms for Pla, respectively (Fig. S3, ESI†).

The triplet excited state energy, derived from the phosphorescence band, is 1.79 eV for Pla and 1.68 eV for Plx. This value is 0.5–0.6 eV higher than that reported for PI. The large difference in the triplet excited state is somehow surprising, since the singlet excited state energy level in Pla and Plx 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 Pla and at 479 nm (2.58 eV) for Plx 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 Pls triplet can act as energy donor and sensitize the triplet excited state of the acceptor. Pls 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 Pla and at 530 nm (ε ca. 14000 M⁻¹ cm⁻¹) for Plx. Fullerene (C₆₀) is identified as a convenient energy acceptor since it is a good electron acceptor 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. 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 Plx at 467 nm in a solution containing C₆₀ (5 × 10⁻⁵ M) are shown in Fig. 5. The kinetic data (ESI†) shows the results of a similar experiment where Pla, 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 C₆₀ (τ = 140 μs for Plx and τ = 130 μs for Pla) whereas the band of C₆₀ at 740 nm grows as shown in Fig. 5 and Fig. S5 (ESI†). The lifetime of the decay of the PIs band of and the concomitant rise of the sensitized C₆₀ depends on the concentration of the C₆₀ quencher (Fig. 6). The bimolecular energy transfer rate constant is kₜ = 4.0 × 10⁹ M⁻¹ s⁻¹ for Plx and kₜ = 5.4 × 10⁹ M⁻¹ s⁻¹ for Pla. The relative magnitude of the rates for the two PIs reflects the higher driving force of the energy transfer reaction when Pla is used as sensitizer (ΔG° = −0.22 eV) than when Plx is used as sensitizer (ΔG° = −0.11 eV). On the other hand, the absolute value of the two rates, lower than the diffusional one (1 × 10¹⁰ s⁻¹), is typical of exothermic triplet energy transfer reactions. The data from sensitization experiments, showing an efficient sensitization of the triplet of C₆₀, 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 C₆₀ (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 C₆₀ 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 3PIx and 3Pxa in the presence of different C₆₀ 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 PIx, remarkably high for perylene imides, have been confirmed by sensitization experiments of 3C₆₀. 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

† C₆₀ reduces at −0.98 V and oxidizes at +1.26 V vs. Fe⁺/Fe²⁺ in acetonitrile-toluene (1:5) 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 Pfa at −0.96 V, whereas the oxidation wave is above 1.9 V for PIx and at 1.75 V for Pfa, all vs. SCE. The energy stored in Pfa (≤1.79 eV) is not sufficient to provide either HOMO–HOMO or LUMO–LUMO electron transfer.


