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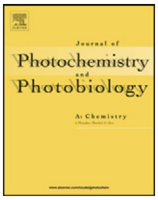

Selective photoinduced single or double electron reduction of perylenebisimides

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ABSTRACT

Selective single and double electron reduction of two soluble perylenebisimides was performed by irradiating these compounds in benzonitrile solutions containing triethylamine 10^{-2} M. Lamp irradiation in the absence of oxygen generates, consecutively, the corresponding radical anion and dianion as persistent species, depending of the irradiation time. These negative PBI species were persistent long enough to be characterized by optical and EPR spectroscopies. Laser flash photolysis determines that the kinetics of PBI reduction follows two first order processes assigned to the presence of two different populations of solvated electrons in the medium. The fastest reduction takes place in tens of microseconds and the slowest occurs with a lifetime longer than hundred microseconds.

1. Introduction

Perylenebisimides (PBIs) [1] have attracted considerable attention due to their remarkable photochemical properties that allow their use as sensors [2], in single photon sources [3], in photoinduced energy/electron transfer systems [4] and as active components in organic field-effect transistors [5], organic light-emitting displays [6], photovoltaic cells [7] and fluorescent biolabels [8], for example.

PBIs can act as electron acceptor molecules giving rise to the corresponding anions [9]. In the present study we report the generation of the corresponding mono- and dianions of two PBIs (see Chart 1) by photolysing them in benzonitrile solutions containing triethylamine.

The structure of the two PBIs under study (compounds **1** and **2**) has in common the presence of four 1,1,3,3-tetramethylbutylphenoxy substituents located at the bay positions of the PBI core leading to a distortion in the perylene skeleton due to the steric congestion present in the bay region. These alkylphenoxy groups have been introduced to increase the solubility of PBIs **1** and **2** in common organic solvents by reducing the strong π–π stacking interactions that are generally present in perylene compounds causing a considerable decrease of their solubility [11]. In addition to an increased solubility, distortion of the perylene ring caused by the steric congestion of the aryloxyl groups should also modify the electronic states and electron acceptor properties of these compound respect to unsubstituted conventional PBIs.

The difference between PBI **1** and **2** is the nature of substituents located at the N atom of the imide groups. Thus, compound **1** contains imidazolium units while in the case of compound **2** there are one 2-ethylhexyl and one 2-hydroxyethyl groups. The rationale behind the selection of these substituents on the imide N atoms is to compare the electron acceptor properties of a PBI having supposedly inert aliphatic substituent (PBI **2**) with that of another PBI containing positively-charged aromatic heterocycles (PBI **1**) that could exert a stronger influence on the molecular properties of PBI. In fact, PBI **1** has been used as precursor to anchor a PBI moiety onto carbon nanotubes through generation of a nitrogen-heterocycle carbene that undergoes dipolar cycloaddition to the nanotube walls, while PBI **2** was utilized to bind PBIs to carbon nanotubes through ester linkages [10]. Therefore, characterization of the photochemical properties of soluble PBI **1** and **2** would allow determining the common behavior of the PBI core as electron acceptor and assessing whether peripheral substituents on the nitrogen atoms exert any influence on the photochemical properties.

2. Results and discussion

Preliminary nanosecond laser flash photolysis studies of PBI **1** and **2** in acetonitrile either at 355 or 532 nm did not allow detecting any transient decaying in the microsecond time scale.

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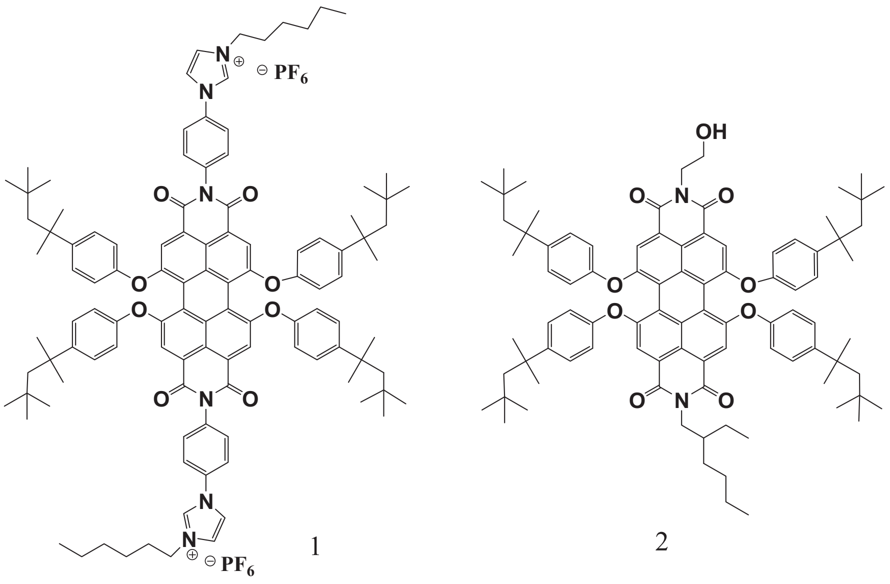

Chart 1. Chemical structure of the two PBIs under investigation.

In order to generate transient anions from PBI **1** and **2** and considering that PBIs can act as electron acceptors, we envisioned an indirect system in which laser excitation of the solvent would lead to charge separation with generation of solvated electrons. These solvated electrons could be trapped by PBIs and, in this way, the corresponding anions would be formed. Considering the solubility of the PBIs under study, the system that we used for that photoinduced generation of electrons was a solution of triethylamine (10^{-2} M) in benzonitrile. PBIs **1** and **2** were highly soluble in acetonitrile and benzonitrile. Benzonitrile was, however, the solvent of choice because it can be photochemically excited by irradiating the phenyl ring chromophore. As the preliminary experiments have shown that the irradiation of PBI **1** and **2** in acetonitrile at 355 nm does not generate any transient, and also taking into account that benzonitrile has still a weak absorption at 355 nm, we selected this wavelength for excitation of the triethylamine/benzonitrile solution.

Fig. 1 shows the transient spectrum recorded upon 355 nm excitation of a 10^{-2} M solution of triethylamine in benzonitrile compared to the transient spectrum recorded under the same conditions but in absence of triethylamine. The differences between these two transient spectra is attributable to the generation of solvated electrons arising from photoinduced electron transfer from triethylamine as electron donor to benzonitrile in its electronic excited state as acceptor as indicated in Eq. (1). $NEt_3^{\bullet+}$ radical cation appearing in Eq. (1) does not exhibit any characteristic absorption band in the visible region. Our proposal is compatible with precedents in the literature showing that triethylamine is a good electron donor in many photoinduced electron transfer processes [12,13]. Attempts to record the optical spectrum of solvated electrons in PhCN by dissolving sodium metal in PhCN were unsuccessful and only a broad continuous band from 350 to 600 nm was recorded. In these experiments using steady-state UV–vis absorption spectroscopy the spectral zone below 350 nm was not accessible due to the absorption of PhCN.

$$\begin{aligned} &\mathrm{PhC{\equiv}N} \xrightarrow{h\nu} \mathrm{PhC{\equiv}N^{*}} \\ &\mathrm{N(Et)_3 + PhC{\equiv}N^{*} \rightarrow N(Et)_3{}^{\bullet+} + PhC{\equiv}N^{\bullet-}} \end{aligned} \tag{1}$$

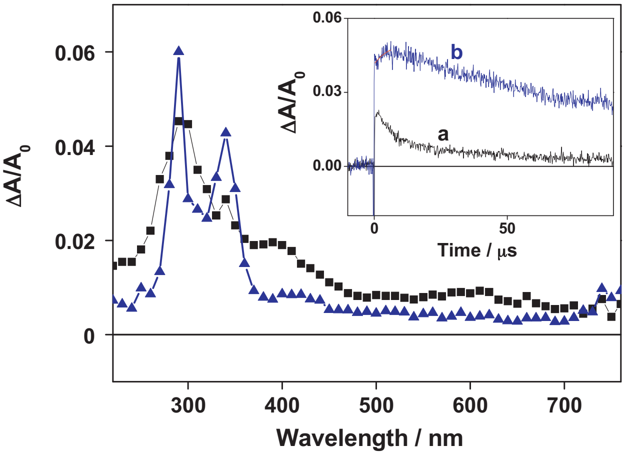

Fig. 1. UV–vis transient absorption spectra of a N_2 purged neat benzonitrile (■) and a N_2 purged benzonitrile solution of triethylamine (10^{-2} M) (▲) recorded 1.2 μs after 355 nm laser excitation. The inset shows the decays of benzonitrile (a) and benzonitrile–triethylamine (b) solutions monitored at 340 nm.

2.1. *Lamp irradiation*

Photochemical generation of electrons in benzonitrile can serve to promote photoinduced reductions of probe molecules. In particular, these electrons could be trapped by PBIs generating the corresponding anions. Alternatively, direct photo excitation of PBIs leading to the generation of the corresponding electronically excited states can lead also to a photoinduced electron transfer from NEt_3 as donor and PBI excited state as acceptor leading to the formation of the PBI anions. These assumptions were confirmed by performing lamp irradiation of benzonitrile solutions of PBIs containing triethylamine in the absence of oxygen and recording the spectral changes by conventional steady-state optical spectroscopy.

Upon lamp irradiation of benzonitrile solutions of PBI **1** and **2** (absorbance at 355 nm 0.03, concentration 4.5 μM) in the presence of triethylamine (10^{-2} M), disappearance of the absorption band corresponding to the neutral PBI concomitantly with the appearance of an absorption beyond 800 nm (the maximum wavelength monitored in our system) was observed. This new absorption spectrum (see Fig. 2) was attributed to the PBI radical anion+ [5e,9b] generated by electron trapping by PBI.

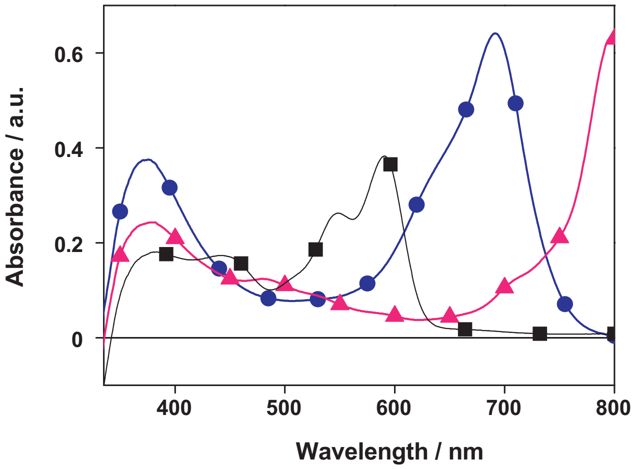

Fig. 2. UV–vis absorption spectra of benzonitrile–triethylamine (10^{-2} M) solution of PBI **1** (absorbance at 355 nm 0.03, 4.5 μM) before (■) and after 10 min (▲) or 20 min (●) irradiation with quasi-monochromatic UV lamp at 350 nm. (For interpretation of the references to color in text, the reader is referred to the web version of the article.)

This assignment of the photochemical products is supported by EPR spectroscopy, where the growth of a signal at 0.6 G with hyperfine coupling 0.658 for N and 0.572 for H was observed (Fig. 3). The experimental EPR spectra agree reasonably well with that calculated for PBI **1** or **2** radical anions (8H, hpc 0.572 Hz, 2N, hpa 0.658 Hz).

Upon continued irradiation of PBIs **1** and **2**, a complete transformation of PBI into $PBI^{\bullet -}$ is achieved. Moreover, if the irradiation is prolonged further, then also $PBI^{\bullet -}$ disappears and a concomitant increase of a new band at about 690 nm with a shoulder in the blue side of the band is observed (see Fig. 2). These changes in the optical spectrum are accompanied by simultaneous disappearance of the signal in EPR spectroscopy indicating that the new species formed has a closed shell configuration. Based on the data reported in the literature obtained by spectroelectrochemistry, we assigned the new species to PBI^{2-} [5e]. The excellent match between the spectra peaking at 690 nm in Fig. 2 with the spectra reported in the literature for the PBI^{2-} dianion provides experimental support to the previous assignments. Eqs. (2) and (3) summarize the species that are generated by consecutive single electron transfer from the medium to PBIs.

$$PhC{\equiv}N^{\bullet -} + PBI \rightarrow PhC{\equiv}N + PBI^{\bullet -} \quad (2)$$

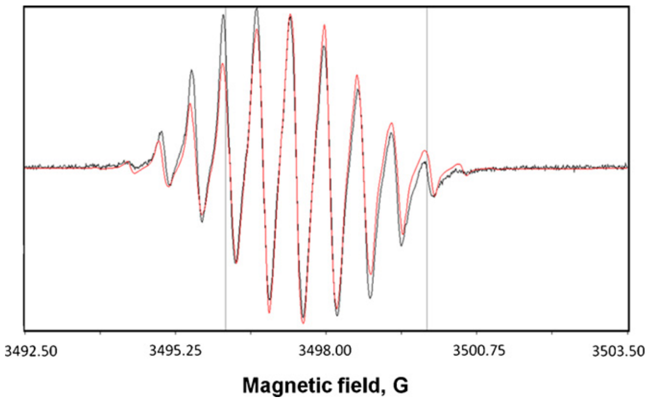

Fig. 3. EPR of a benzonitrile–triethylamine (0.01 M) solution of PBI **1** (absorbance at 355 nm 0.03, 4.5 μM, black line) and the corresponding simulation for PBI **1** radical anion (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

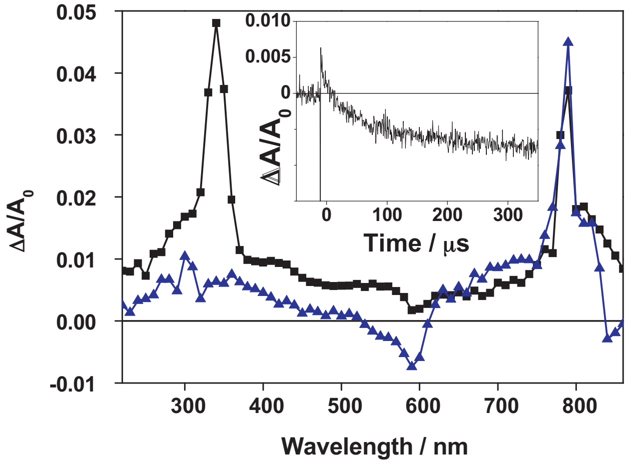

Fig. 4. UV–vis transient absorption spectra of a N_2 purged benzonitrile–triethylamine (0.01 M) solution of PBI **1** (absorbance at 355 nm 0.03, 4.5 μM) recorded at 7 (■) and 319 (▲) μs after a 355 nm laser pulse of 10 mJ. The inset shows the signal monitored at 590 nm.

$$PhC{\equiv}N^{\bullet -} + PBI^{-} \rightarrow PhC{\equiv}N + PBI^{2-} \quad (3)$$

The above experiments were carried out under inert atmosphere in the absence of oxygen. Under these conditions, the photogenerated $PBIs^{\bullet -}$ and PBI^{2-} were persistent for minutes. However, if oxygen is admitted into the solutions, then the changes were fully reversible and both $PBI^{\bullet -}$ and PBI^{2-} return back to the original PBI neutral state. The decay of PBI mono- and dianion back to the parent neutral compound in the presence of oxygen is due to single or double electron transfer from the organic anions to oxygen acting as the terminal electron acceptor according to Eqs. (4) and (5).

$$PBI^{\bullet -} + O_2 \rightarrow PBI + O_2^{\bullet -} \quad (4)$$

$$PBI^{2-} + O_2 \rightarrow PBI^{\bullet -} + O_2^{\bullet -} \quad (5)$$

The photochemical process of $PBI^{\bullet -}$ and PBI^{2-} generation and their quenching by oxygen is fully reversible and no photoproducts are formed in significant amounts to affect it, as it could be repeated four times without observing any fatigue. In agreement with their high chemical stability, PBIs appear to be stable compounds against the attack of $O_2^{\bullet -}$ generated in the medium.

2.2. *Laser flash photolysis*

Using 355 nm laser excitation in benzonitrile containing triethylamine (10^{-2} M) it is possible to photochemically generate electrons in the medium that could be subsequently trapped by PBIs acting as electron acceptors according to Eqs. (1)–(3). The kinetics of the electron capture by PBI can be adequately followed by nanosecond transient spectroscopy. Fig. 4 shows the transient spectra recorded at different delay times after excitation of benzonitrile and triethylamine containing PBI **1**. As it can be seen there, the transient spectra are characterized by a peak at 340 nm due to the solvent (compare to Fig. 1) as well as a bleaching of the signal at 590 nm and a peak beyond 780 nm. The bleaching at 590 nm is related to the disappearance of PBI **1** by accepting electrons and being transformed into $PBI^{\bullet -}$ characterized by the absorption with apparent λ_{max} at 780 nm. The temporal profile of the signal monitored at 590 nm is shown also in Fig. 4 and can be fitted to a two consecutive first order decays with lifetimes of 15.8 and 126.6 μs and relative proportion 30 and 70%, respectively. We suggest that this kinetics reflects the presence in the medium of two main types of electrons, the slowest process corresponding to the trapping of

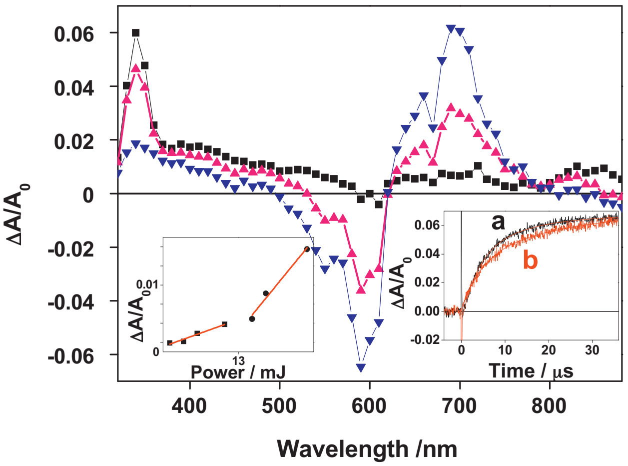

Fig. 5. UV–vis transient absorption spectra of a N_2 purged benzonitrile–triethylamine (0.01 M) solution of PBI **1** (absorbance at 355 nm 0.03, 4.5 μM) recorded at 0.64 (■), 5.15 (▲) and 32.35 (▼) μs after excitation with a 355 nm laser pulse of 15 mJ. The left inset shows the power dependence of the signal monitored at 690 nm and the right inset shows the temporal profile of the signals monitored at 590 (a), multiplied by −1, and 690 (b) nm under N_2 atmosphere.

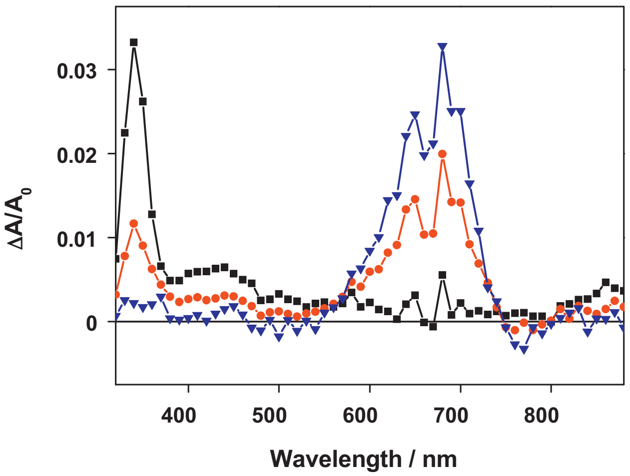

Fig. 6. UV–vis transient absorption spectra of a N_2 purged benzonitrile–triethylamine (0.01 M) solution of $PBI^{\bullet-}$ (absorbance at 355 nm 0.03, 4.5 μM) recorded after 355 nm laser excitation with a pulse of 15 mJ.

the electrons that are located in deeper traps, probably in the nitrile group of benzonitrile. The bleaching of PBI is accompanied by a concomitant increase of the signal due to $PBI^{\bullet-}$ at 780 nm. The location of the latter band in the far red end of our multiplier makes the signal at this long wavelength noisy, rendering kinetic measurements less accurate than when monitoring the signal at 590 nm.

The previous transient spectra and signal kinetics were very similar for PBI **1** and PBI **2** indicating that the electron trapping occurs at the PBI core and that the imide nitrogen substituent is not involved in the process.

We observed that the transient spectrum for the irradiation of PBIs in benzonitrile containing triethylamine varies depending on the laser power. When the laser power increases in the range from 8 to 18 mJ, a gradual decrease of the intensity of the 780 nm band, accompanied by the growth of a new band at 680 nm is observed (see Fig. 5). We attribute these changes to the occurrence of two consecutive electron transfers from the medium to PBI that eventually form the PBI^{2-} dianion. In fact, the intensity of the transient signal monitored at 690 nm does not follow a linear relationship (see left inset in Fig. 5) but can be adequately fitted to two lines having higher slope at higher laser fluencies. This interpretation is in agreement with the observation of a decrease of the peak corresponding to $PBI^{\bullet-}$ as the intensity of the peak due to PBI^{2-} increases. In fact the temporal profiles of PBI ground state bleaching and the growth of the 690 nm band characteristic of the PBI^{2-}, although not exactly coincident, are very similar suggesting that almost all the PBI is rapidly converted into PBI dianion under these conditions. Both PBI **1** and PBI **2** exhibit identical behavior and dependence with the laser power.

The ready transformation of $PBI^{\bullet-}$ into PBI^{2-} was confirmed by an independent experiment in which $PBI^{\bullet-}$ was subjected to photolysis under the same conditions as those of neutral PBI (355 nm laser excitation of benzonitrile containing 10^{-2} M triethylamine).

As we have commented earlier when presenting the results of lamp irradiation, it is possible to obtain a solution of $PBI^{\bullet-}$ starting from PBI by adjusting the irradiation time. We have already mentioned that the persistence of this radical anion under these conditions is sufficiently long to allow studying the photophysical properties of $PBI^{\bullet-}$. In this way, starting from a PBI solution and by means of lamp irradiation, we converted PBI into $PBI^{\bullet-}$ quantitatively as confirmed by optical spectroscopy. At this moment, the solution was exposed to laser flash photolysis to determine the kinetics of the single electron reduction of $PBI^{\bullet-}$. The transient spectra recorded under these conditions are shown in Fig. 6, where the growth of a band from 550 to 730 nm peaking at 650 and 690 nm is clearly observed accompanied by some bleaching at 760 nm due to the photolysis of $PBI^{\bullet-}$. The results presented in Fig. 6 for PBI **1** were very similar to those recorded for PBI **2**.

In addition, lamp irradiation also provides the opportunity to prepare a persistent solution of PBI^{2-}. These solutions were subjected to laser flash photolysis under the same conditions, showing that even in a medium rich on solvated electrons, photolysis of PBI^{2-} gives an instantaneous bleaching of PBI^{2-} and formation of $PBI^{\bullet-}$. This instantaneous bleaching is followed by a slower recovery of the PBI^{2-}. These results can be interpreted considering that photoexcitation of electron rich PBI^{2-} gives rise to an instantaneous electron photoejection that, due to the present of solvated electrons, leads to a recovery of PBI^{2-} from $PBI^{\bullet-}$ (Eqs. (3) and (6)).

$$\mathrm{PBI}^{2-} \xrightarrow{h\nu} \mathrm{PBI}^{\bullet-} + e_{\mathrm{solvated}} \qquad (6)$$

3. Conclusions

Photolysis of a solution of benzonitrile containing triethylamine is a convenient mean to effect the photoinduced reduction of PBIs. The process can take places in two separate steps using conventional lamps or pulsed lasers at low powers or can be performed as an apparent single event at high laser fluencies. The formation of negatively charged PBI species is reversible and the corresponding negative species exhibit high persistence in the absence of oxygen. These conditions have allowed determining the kinetics of electron trapping by PBI that in this medium takes places following two first order kinetics that have been associated to the presence of two types of electrons in this medium, one more reactive and a second more relaxed type of electron. The presence of these two types of electrons would originate two kinetics for the generation of negative PBI species, one of them typically in tens of microseconds and a second one more prevalent occurring at longer time scales on hundreds of microseconds.

4. Experimental

PBIs **1** and **2** where synthesized as reported elsewhere [10]. UV–vis absorption spectra were recorded with a Perkin-Elmer λ35 spectrophotometer.

EPR spectra were recorded in a Bruker EMX-12 spectrometer, operating at X-band, with a modulation frequency of 100 kHz and modulation amplitude of 1.0 G, and irradiating with a UV lamp.

Solutions of PBI (ABS = 0.3 at 355 nm, 4.5 μM) in benzonitrile–triethylamine (0.01 mM) contained on a Suprasil quartz cuvette (0.7 × 0.7) capped with septa were purged with N_2 and irradiated for 10, 20 and 30 min inside a Luzchem multilamp photoreactor with eight 8 W lamps (Hitachi FL8BL-B) emitting mainly at 350 nm.

Laser flash photolysis experiments were carried out in a Luzchem ns laser flash system using the third (355 nm) harmonic of a Q-switched Nd:YAG laser (pulse 10 ns) as the excitation source. The PBIs solution in benzonitrile–triethylamine contained on a Suprasil quartz cuvette ($0.7 \times 0.7\,\mathrm{cm}^2$) capped with septa were purged with a N_2 or O_2 flow at least 15 min before irradiation experiments.

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