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# Photoinduced energy- and electron-transfer processes in a *side-to-face* Ru<sup>II</sup>-porphyrin/perylene-bisimide array

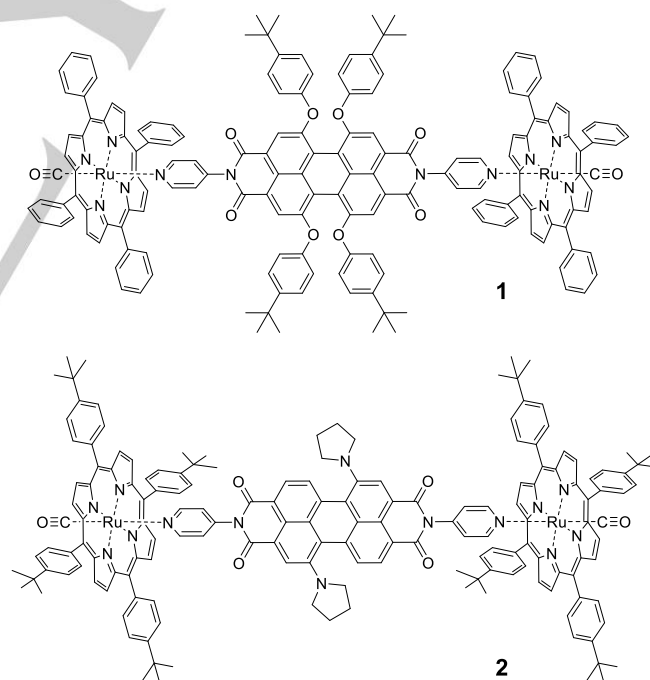
Agnese Amati,<sup>[a]†</sup> Mirco Natali,<sup>\*[b]</sup> Maria Teresa Indelli,<sup>[b]</sup> Elisabetta Iengo,<sup>\*[a]</sup> and Frank Würthner<sup>[c]</sup>

**Abstract:** A *side-to-face* array DPy-gPBI[Ru(4-*t*BuTPP)(CO)]<sub>2</sub>, based on a “green” perylene bisimide chromophore sandwiched between two Ru<sup>II</sup>-porphyrins, has been prepared by self-assembly. Its photophysical properties have been characterized in detail by a combination of steady-state and time-resolved techniques upon selective excitation of the two different components. Different photoinduced processes are observed as a function of the excitation wavelength. Electron transfer quenching is attained upon “red light” excitation of the perylene unit, whilst an energy transfer pathway is followed upon “green light” excitation of the metallo-porphyrin moiety. Regardless of the excitation wavelength efficient population of the triplet excited state of the perylene chromophore is achieved. The photophysical results are discussed within the framework of classical electron transfer theory and compared with those of a previously reported system.

## Introduction

In recent years, we have been particularly interested in the implementation of the “metal-mediated” synthetic strategy which offers the possibility of obtaining multicomponent arrays with the desired photophysical properties by self-assembly of appropriate subunits.<sup>[1-10]</sup> In particular, those featuring facing metallo-porphyrin cores bridged by N-pyridyl ligands have received great attention.<sup>[4-6]</sup> Perylene bisimides (PBIs) are a class of very attractive building blocks for photophysical studies because of their excited state and redox properties that can be easily tuned by chemical design, especially by appropriate choice of the substituents in the “bay” area.<sup>[11]</sup> Thus, a large number of supramolecular systems based on perylene bisimides have been developed in the past decades.<sup>[12-18]</sup> In particular, mixed systems containing covalently linked (metallo-)porphyrins and

PBIs have also been studied, with special emphasis on the occurrence of energy and electron transfer processes between the two types of molecular components.<sup>[19-26]</sup> In the last years, we have employed the self-assembling strategy to construct a few mixed systems containing porphyrins and perylene bisimides as side-to-face molecular components.<sup>[24-27]</sup> The first example of these is made of one “red” perylene bisimide bearing two pyridyl groups at the imide positions axially coordinated to two Ru<sup>II</sup>-porphyrins (DPy-rPBI[Ru(TPP)(CO)]<sub>2</sub>, where DPy-rPBI = *N,N*-di(4-pyridyl)-1,6,7,12-tetra(4-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid bisimide and TPP = 5,10,15,20-tetraphenylporphyrin, **1**, Scheme 1).<sup>[24]</sup> This array presents a peculiar photophysical behavior, extremely dependent on whether the perylene or the Ru<sup>II</sup>-porphyrin components are excited. A small change in the excitation wavelength causes indeed a sharp switch from electron to energy transfer between the two chromophore units.<sup>[24]</sup>



**Scheme 1.** Molecular structure of arrays **1** and **2**.

We have now prepared a new array in which the DPy-rPBI component is replaced by a “green” perylene bisimide, bearing pyrrolidiny substituents at the bay area (DPy-gPBI[Ru(4-*t*BuTPP)(CO)]<sub>2</sub>, where DPy-gPBI = *N,N*-di(4-pyridyl)-1,7-dipyrrolidinyperylene-3,4:9,10-tetracarboxylic acid bisimide and

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Supporting information for this article is given via a link at the end of the document.

4-tBuTPP = 5,10,15,20-tetra(4-*tert*-butylphenyl)porphyrin, **2**, Scheme 1). The “green” perylene bisimide dye differs substantially from both the core-unsubstituted “orange” and the “red” PBI analogues for its featuring absorption near the NIR region and significantly lower oxidation potential.<sup>[28,29]</sup> These differences result from the presence of the pyrrolidinyl substituents in the bay area which donate electrons, thereby increasing the HOMO of the PBI compared to the “orange” and the “red” cases, while maintaining comparable LUMO energies, with the “green” PBI being indeed only slightly more difficult to reduce than its parent dyes.<sup>[11]</sup> As a matter of fact, due to these interesting differences in optical and electrochemical properties, in the presence of essentially identical structural features, all these PBIs have been employed for the construction of a large variety of dye arrays.<sup>[11,25,27,30-32]</sup> Herein, we report a detailed photophysical study of the new *side-to-face* assembly DPy-gPBI[Ru(4-tBuTPP)(CO)]<sub>2</sub> (**2**) aimed at the characterization of the photoinduced processes taking place upon selective excitation of the two different subunits. Interestingly, with respect to the previously investigated array **1**,<sup>[24]</sup> the complementary absorption of the “green” perylene bisimide and the ruthenium porphyrin units throughout the visible spectrum provides a unique way for a fully selective ( $\geq 95\%$ ) excitation of either component.

## Results and Discussion

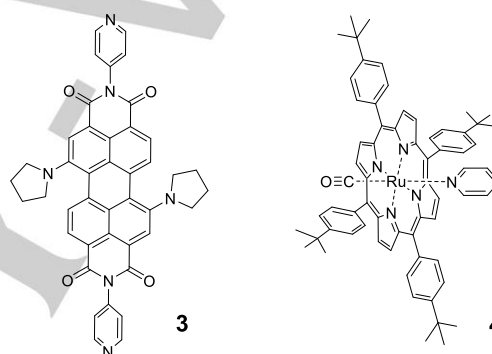
**Synthesis.** DPy-gPBI[Ru(4-tBuTPP)(CO)]<sub>2</sub> (**2**, Scheme 1) was easily prepared in almost quantitative yield by the same method reported earlier for assembly **1** (see Experimental Section).<sup>[24]</sup>

**Stability in solution of **2**.** All the photophysical measurements were carried out in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> solutions. The stability of assembly **2** in these conditions has been checked by a combination of NMR, spectrophotometric, and spectrofluorimetric measurements. These experiments clearly show that at concentrations higher than  $2 \times 10^{-5}$  M compound **2** is completely associated. All photophysical experiments have been thus performed in freshly prepared solutions at concentrations higher than  $2 \times 10^{-5}$  M. The solutions are photochemically stable, as checked spectrophotometrically before and after each experiment.

**Properties of the molecular components.** The “green” perylene DPy-gPBI (**3**, Scheme 2), available as a free species, was used as appropriate model of the corresponding subunit in **2**. [Ru(4-tBuTPP)(CO)(py)] (**4**, Scheme 2) was used as a model compound for the metallo-porphyrin unit. The photophysical and redox behavior of the two model compounds, useful for the subsequent understanding of the photophysical behavior of **2**, can be summarized as follows.

**DPy-gPBI (**3**).** The photophysical and redox properties of this compound have been already reported in the literature.<sup>[25]</sup> Briefly, in CH<sub>2</sub>Cl<sub>2</sub> **3** displays an intense absorption in the red portion of the visible spectrum with a maximum at 713 nm and a shoulder

at 659 nm (Figure 1A, green trace). Upon excitation, a fluorescence is observed ( $\Phi = 0.35$ ) with maximum at 763 nm (Figure 1B, green trace). The singlet excited state has a lifetime of 3.1 ns. Its transient spectrum (Figure S2) can be obtained by ultrafast spectroscopy and consists of an intense bleaching between 650 and 800 nm arising from both ground-state depopulation and stimulated emission. The triplet state can be detected by laser flash photolysis (Figure S3). Its transient spectrum shows two broad positive absorptions, one between 450-600 nm and one above 750 nm, together with the bleaching of the ground state bands in the red region. This species has a lifetime of  $\sim 270$  ms in N<sub>2</sub>-purged CH<sub>2</sub>Cl<sub>2</sub> solution. **3** behaves both as a good electron acceptor and donor. In CH<sub>2</sub>Cl<sub>2</sub> solution it undergoes two reversible electrochemical reduction steps at  $-1.22$  V and  $-1.32$  V vs Fc/Fc<sup>+</sup> and two reversible oxidation steps at  $+0.25$  V and  $+0.38$  V vs Fc/Fc<sup>+</sup>.<sup>[25]</sup>

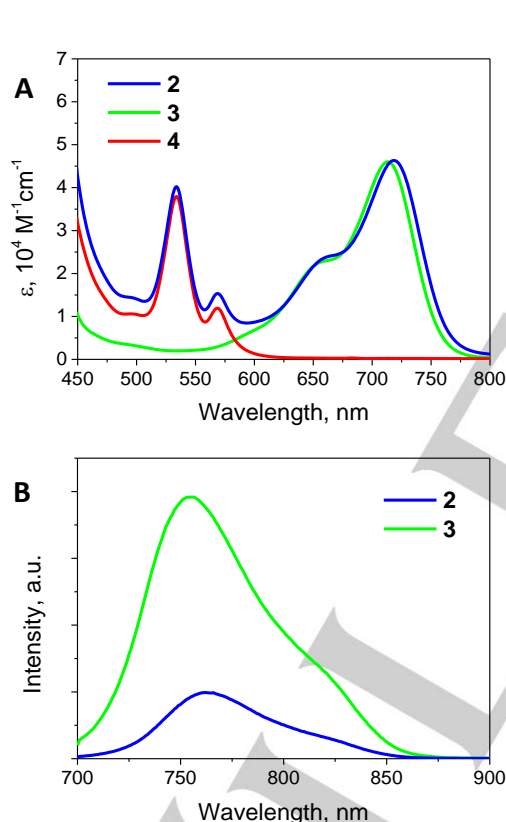


**Scheme 2.** Molecular structure of model compounds **3** and **4**.

**Ru(4-tBuTPP)(CO)(py) (**4**).** The photophysical and redox properties of this model compound have been already reported.<sup>[5,24,34]</sup> Briefly, the absorption spectrum in CH<sub>2</sub>Cl<sub>2</sub> (Figure 1A) shows the Q-bands (maxima at 533 and 568 nm) and Soret band (maximum at ca 400 nm, not shown in Figure 1A) typical of irregular metallo-porphyrins of the hypso type.<sup>[33]</sup> As expected, no fluorescence emission is observed as a consequence of the strong spin-orbit coupling provided by the heavy ruthenium atom, leading to ultrafast ( $< 1$  ps) intersystem crossing.<sup>[24]</sup> At room temperature a weak phosphorescence emission is observed ( $\Phi \sim 10^{-3}$ , maximum at 726 nm). The triplet state can be conveniently monitored by transient spectroscopy and shows a prominent absorption (maximum at 478 nm) with a tail at longer wavelengths with superimposed Q-band bleaching (Figure S4). Its lifetime is  $\sim 30$   $\mu$ s in N<sub>2</sub>-purged solution.<sup>[34]</sup> In CH<sub>2</sub>Cl<sub>2</sub> **4** undergoes two reversible electrochemical oxidation processes at  $+0.35$  V and  $+0.90$  V vs. Fc/Fc<sup>+</sup>.

**Photophysical properties of **2**.** The spectroscopic and photophysical properties of supramolecular array **2** were investigated in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> solutions and compared with those of the model compounds of the individual subunits (**3**, **4**). The absorption spectrum of assembly **2** in CH<sub>2</sub>Cl<sub>2</sub> is reported in

Figure 1A, similar spectral profiles and absorbance are observed in  $\text{CHCl}_3$  solution. The absorption spectrum corresponds appreciably to the sum of those of the separated components. Only a  $\sim 2\text{-}3$  nm shift of the perylene absorption bands is detected which is attributed to an increasing electron-withdrawing character of the pyridine upon metal ion coordination. As typically observed in related supramolecular arrays,<sup>[5-10]</sup> this indicates that negligible electronic interactions between the different molecular units exist at the ground state level. Importantly, as can be observed from the comparison of the absorption spectra in Figure 1, the two molecular components of assembly **2** absorb in different portions of the visible spectrum. Hence, selective excitation of each individual chromophore can be achieved using suitable wavelengths. In particular, selective excitation of the ruthenium porphyrin can be attained using “green light” irradiation at 530 nm, whereas by using “red light” at wavelengths above 650 nm the PBI unit can be selectively excited.

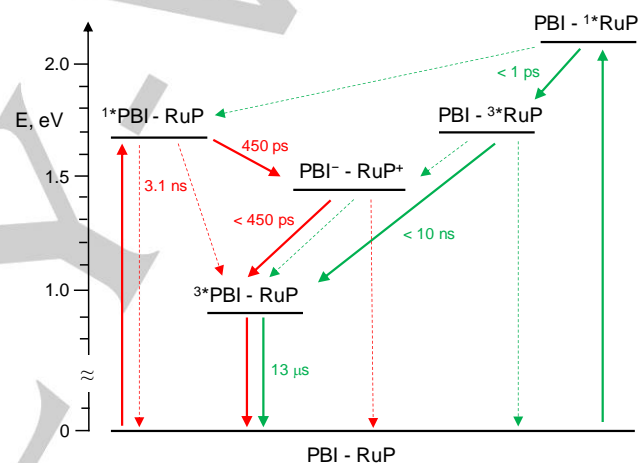
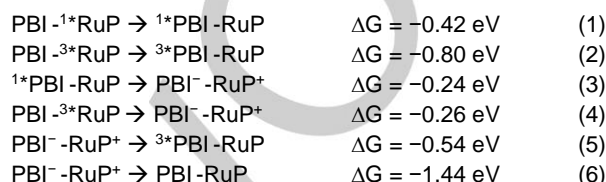


**Figure 1.** (A) Absorption spectra of **2**, **3**, and **4** in  $\text{CH}_2\text{Cl}_2$ ; (B) fluorescence spectra of **2** and **3** (excitation at 680 nm, optically matched solutions).

**Energy levels.** The modular nature of compound **2** allows us to construct the energy-level diagram of Figure 2 from the known spectroscopic and electrochemical properties of the molecular components **3** and **4**. Interestingly, beside the excited state levels of the single molecular units an intercomponent charge transfer state involving oxidation of the ruthenium porphyrin unit and reduction of the perylene bisimide component can be

observed. This state can be potentially accessible upon excitation of both chromophores. Its energy can be estimated from the electrochemical data of the molecular models **3** and **4** (1.44 eV, considering electrostatic work terms).<sup>[35-37]</sup>

A close inspection of the energy level diagram in Figure 2 shows that in array **2**, in addition to the usual unimolecular decay pathways, intercomponent deactivation channels are allowed on thermodynamic standpoint of both energy (eqs 1,2) and electron transfer (eqs 3,4) nature (charge recombination pathways are also shown for sake of completeness, eqs 5,6).



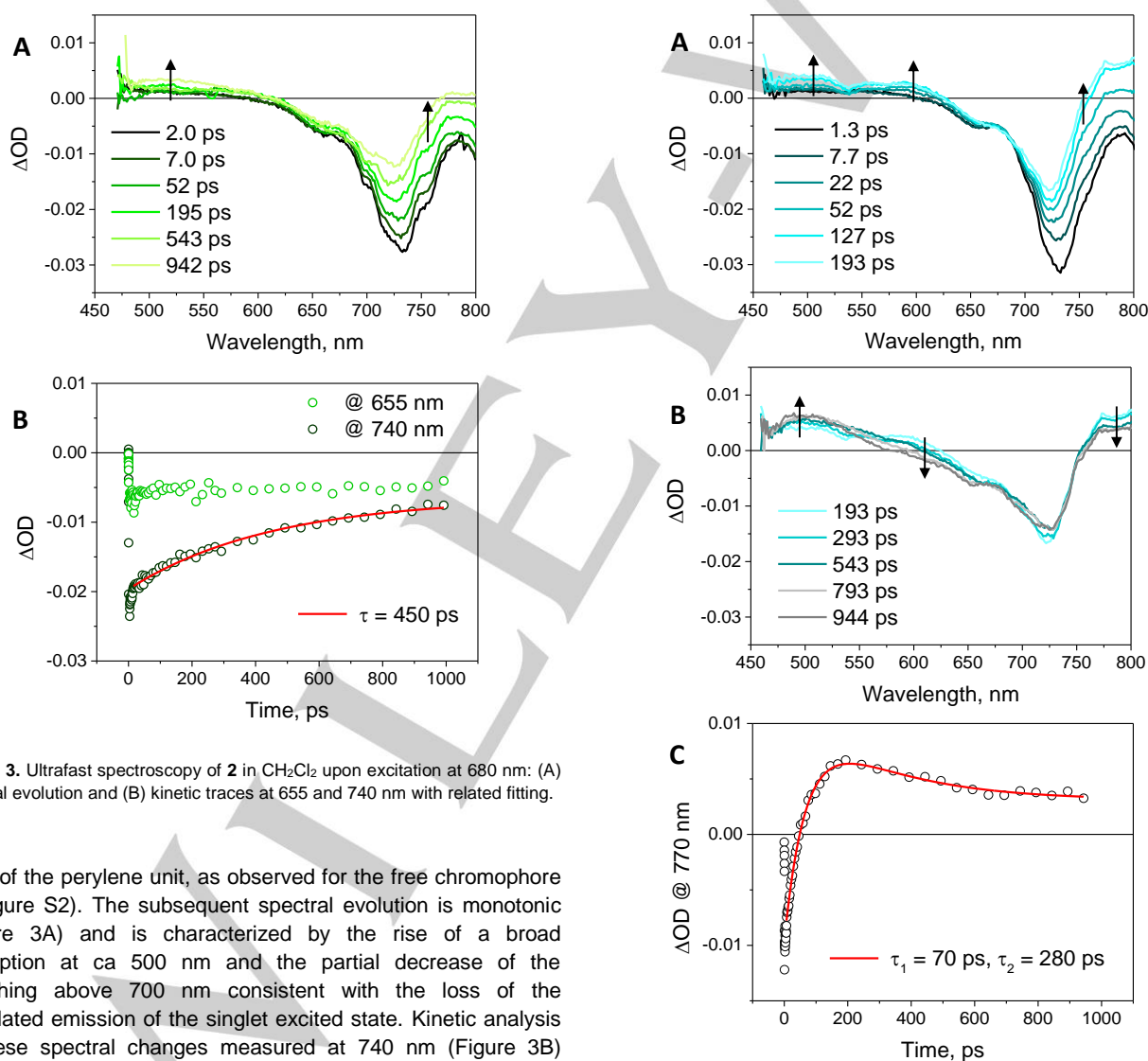
**Figure 2.** Energy level diagram of assembly **2** in  $\text{CH}_2\text{Cl}_2$ . Legend: DPY-gPBI = PBI; Ru(4-tBuTPP)(CO) = RuP; red lines = processes upon selective excitation of PBI; green lines = processes upon selective excitation of RuP. The energy of the singlet excited state of the perylene unit was estimated at the intersection between the normalized absorption and fluorescence spectra, the energy of the triplet was taken from literature data.<sup>[25]</sup> The energy of both the singlet and triplet excited states of the Ru<sup>II</sup>-porphyrin was derived from the literature.<sup>[24]</sup>

A thorough spectroscopic investigation has been thus performed to elucidate the photophysics of the array. The photoinduced processes taking place in **2** are also indicated in the energy level diagram of Figure 2 and are discussed hereafter.

**Excitation at 680 nm.** This wavelength corresponds to selective excitation of the perylene unit. Stationary experiments (Figure 1B) indicate that, in assembly **2**, the characteristic fluorescence of the PBI, although maintaining the same emission pattern, is substantially quenched when compared to that of model **3**. The lifetime of the perylene fluorescence in the array, as measured by TC-SPC experiments, is 0.6 ns in  $\text{CH}_2\text{Cl}_2$ , thus shortened with respect to that of the free perylene unit, confirming that in **2**

the singlet state is quenched. In  $\text{CHCl}_3$  solution, the PBI fluorescence is considerably quenched as well, its lifetime is however below the time-resolution of the TC-SPC apparatus ( $< 0.2$  ns). As to the quenching mechanism, two possibilities may be accounted for: i) photoinduced electron transfer with formation of a charge transfer state of the type  $\text{PBI}^- - \text{RuP}^+$  (eq 3) and ii) enhanced intersystem crossing promoted by the heavy ruthenium atoms. In order to obtain insight into the quenching mechanism, ultrafast spectroscopy experiments have been thus performed. The spectral changes obtained in  $\text{CH}_2\text{Cl}_2$  following 680 nm excitation are shown in Figure 3. As expected on the basis of the selective excitation, the prompt transient spectrum (2 ps in Figure 3A) is the typical spectrum of the singlet excited

trace at 655 nm, Figure 3B) and the formation of the positive absorption at lower wavelengths strongly suggests that the product formed from the singlet state is the triplet state of the perylene unit (see also the comparison with the triplet spectrum measured in model **3**, Figure S3A). As to the triplet excited state formation, two mechanisms might be envisioned according to the energy level diagram of Figure 2: rate-determining photoinduced electron transfer followed by faster and selective charge recombination to the perylene triplet (according to previous hypothesis i) and enhanced intersystem crossing (previous hypothesis ii). In order to discriminate over these possibilities ultrafast spectroscopy of assembly **2** has been investigated in  $\text{CHCl}_3$  as a solvent (Figure 4).



**Figure 3.** Ultrafast spectroscopy of **2** in  $\text{CH}_2\text{Cl}_2$  upon excitation at 680 nm: (A) spectral evolution and (B) kinetic traces at 655 and 740 nm with related fitting.

state of the perylene unit, as observed for the free chromophore **3** (Figure S2). The subsequent spectral evolution is monotonic (Figure 3A) and is characterized by the rise of a broad absorption at ca 500 nm and the partial decrease of the bleaching above 700 nm consistent with the loss of the stimulated emission of the singlet excited state. Kinetic analysis of these spectral changes measured at 740 nm (Figure 3B) yields a time-constant of  $\tau = 450$  ps, in fairly good agreement with the singlet excited state lifetime obtained by emission measurements. Interestingly, the observation of negligible changes at wavelength between 600-680 nm (see the kinetic

**Figure 4.** Ultrafast spectroscopy of **2** in  $\text{CHCl}_3$  upon excitation at 680 nm: (A) spectral evolution between 1.3-193 ps, (B) 193-944 ps, and (C) kinetic trace at 770 nm with related fitting.

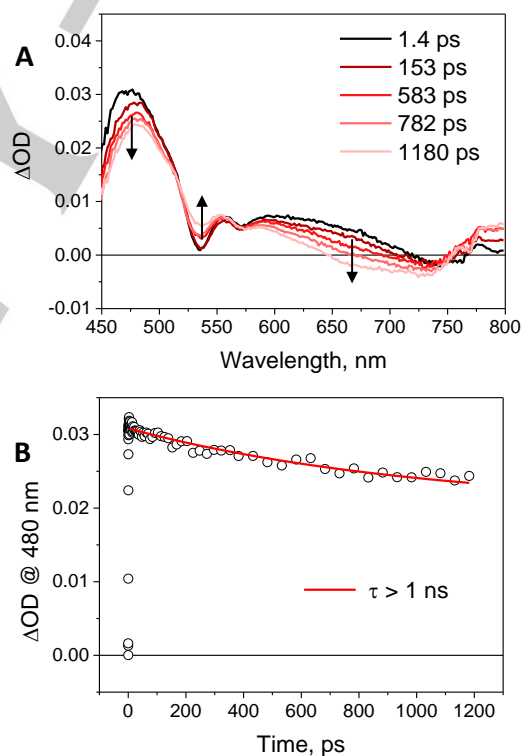


We indeed expect that changing of the solvent polarity may induce an increase of the energy of the  $\text{PBI}^-$ - $\text{RuP}^+$  charge transfer state thus possibly altering the kinetics of the electron transfer processes (hypothesis i). Akin to the  $\text{CH}_2\text{Cl}_2$  case, the prompt signal is still the transient spectrum of the singlet excited state of the perylene unit. The subsequent changes are, however, biphasic in nature. In the early timescale (1-193 ps, Figure 4A) the spectral variations feature the rise of new absorptions between 450-650 nm (maxima at 500 and 600 nm with a relative bleaching at 530 nm) and between 750-800 nm (maximum at 775 nm). These changes are compatible with those expected for both the porphyrin radical cation (absorption between 450-650 nm and 530-nm bleaching)<sup>[6]</sup> and the perylene anion (absorption at 750-800 nm)<sup>[38]</sup> and are thus diagnostic for the formation of the  $\text{PBI}^-$ - $\text{RuP}^+$  charge transfer state according to eq 3. The time-constant of this process is 70 ps (Figure 4C). In the longer timescale (193-944 ps, Figure 4B) the spectral changes involve the decrease of the absorption signals at 600 and 775 nm and the rise of a new absorption with maximum at ca 500 nm characteristic of the triplet excited state of the green perylene (Figure S3A). These spectral variations are thus consistent with the occurrence of a selective charge recombination from the  $\text{PBI}^-$ - $\text{RuP}^+$  charge transfer state to the triplet excited state of the organic dye (eq 5). A time-constant of 280 ps can be obtained for the latter process (Figure 4C).

Overall, the evidences obtained by ultrafast spectroscopy favor the hypothesis that quenching of the perylene fluorescence in **2** is due to the occurrence of a photoinduced electron transfer (hypothesis i above, eq 3). The failure to observe any appreciable signal from the charge transfer state in  $\text{CH}_2\text{Cl}_2$ , on the other hand detected in  $\text{CHCl}_3$ , very likely reflects the respective kinetics of charge separation (eq 3) vs. charge recombination (eq 5) in the different solvents. As to the fate of the triplet excited state of the perylene unit, populated by charge recombination from the  $\text{PBI}^-$ - $\text{RuP}^+$  state, its direct observation is prevented by the absence of a selective 680-nm excitation in our laser flash photolysis apparatus. This transient species is however expected to decay to the ground state in the microsecond timescale (see below).

**Excitation at 530 nm.** At this wavelength, the excitation light is selectively absorbed by the ruthenium-porphyrin unit (95%). The photophysical behavior is identical in both  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . The following discussion will be thus limited to  $\text{CH}_2\text{Cl}_2$  solution, transposition to  $\text{CHCl}_3$  being indeed straightforward. In stationary experiments, negligible perylene fluorescence is observed, as expected based on the very small fraction of direct light absorbed by this unit (5%). On the other hand, no detectable porphyrin-based phosphorescence is observed indicating that the triplet excited state of this unit is quenched in the assembly. Singlet-singlet energy transfer from the  $\text{Ru}^{\text{II}}$ -porphyrin unit to the perylene component (eq 1) can be ruled out as a possible explanation. As a matter of fact, the excitation spectrum of the perylene fluorescence (Figure S5) shows the complete absence of absorption features from the ruthenium-porphyrin and the close correspondence to the absorption spectrum of the perylene unit. As observed in previous

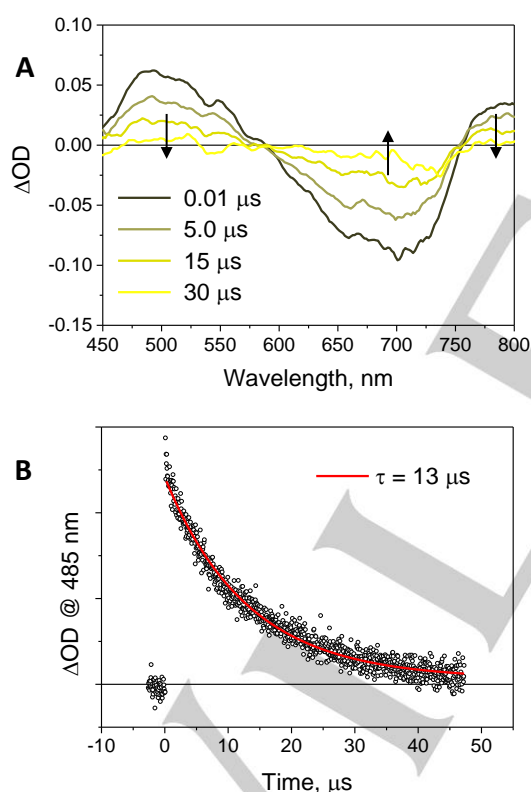
works,<sup>[5,34]</sup> the reason for this behavior is the exceedingly short lifetime of the ruthenium-porphyrin singlet which makes intersystem crossing to the triplet extremely efficient ( $\Phi \sim 1$ ).<sup>[24]</sup> Thus, quenching of the triplet excited state of the metallo-porphyrin may occur through two different mechanisms: i) triplet-triplet energy transfer (eq 2) and ii) photoinduced electron transfer (eq 4). In order to obtain insight into the actual quenching mechanism, ultrafast spectroscopy of **2** upon 530 nm excitation has been performed (Figure 5). It is worth noting that the spectral changes obtained upon excitation at 530 nm are completely different from those observed upon 680-nm excitation (Figure 3 and Figure 5, respectively). The differential spectrum immediately obtained after the laser pulse (time delay, 1.4 ps, Figure 5A) is characteristic of the triplet excited state of the ruthenium-based unit. It is indeed very similar to that exhibited by the model compound **4** (Figure S4) and shows a positive absorption with a maximum at 470 nm, ground-state bleaching of the Q bands in the 550-600 nm region and a broad absorption at longer wavelengths.



**Figure 5.** Ultrafast spectroscopy of **2** in  $\text{CH}_2\text{Cl}_2$  upon excitation at 530 nm: (A) spectral evolution and (B) kinetic trace at 480 nm with related fitting.

The subsequent spectral evolution is monotonic (Figure 5A) and is characterized by a gradual decrease of the absorption at 470 nm together with the recovery of the Q-band bleaching and the formation of a new bleaching in the 650-700 nm region. These spectral changes are consistent with the formation of a perylene-based transient species (most plausibly the  $^3\text{PBI}$ ) from the

triplet excited state of the ruthenium-porphyrin. However, since the transient evolution cannot be fully monitored within the time window of the ultrafast experiment (see also the kinetic trace in Figure 5B), nanosecond laser flash photolysis has been used to obtain more conclusive proofs of the final product. The transient spectra obtained by nanosecond flash photolysis upon excitation at 532 nm are depicted in Figure 6. The prompt spectrum, measured at 10 ns time-delay, displays spectral features which are compatible with those of the triplet excited state of the perylene model **3** (absorptions between 450-600 nm and above 750 nm, ground-state bleaching between 600-750 nm, Figure S2A). This spectrum then undergoes a monotonic decay to the baseline in ca 30  $\mu$ s (Figure 6A). This spectral evolution can be thus assigned to the decay of the perylene triplet to the ground state. A lifetime of 13  $\mu$ s under oxygen-free conditions can be estimated for the triplet excited state of the perylene in **2** (Figure 6B). This value is substantially lower than that measured in model compound **3** (see above) and is due to the acceleration of the intersystem crossing promoted by the heavy atom effect of the Ru<sup>II</sup>-porphyrin units.

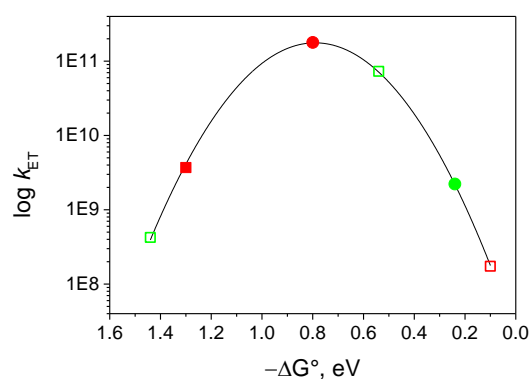


**Figure 6.** Laser flash photolysis of **2** in  $\text{CH}_2\text{Cl}_2$  upon excitation at 532 nm: (A) spectral evolution and (B) kinetic trace at 485 nm with related fitting.

Overall, the experimental evidences from both ultrafast spectroscopy and laser flash photolysis suggest that a triplet-triplet energy transfer process occurs from the excited state of the ruthenium-porphyrin to the triplet of the perylene unit. This

process is very likely to take place within the “blind” time-window of our instrumental setup, namely between 1-10 ns. It should be, however, noticed that, in principle, formation of the triplet state of the PBI moiety may take place through a stepwise mechanism involving photoinduced electron transfer (eq 4) and subsequent charge recombination (eq 5). Although the experimental evidences seem to favor the triplet-triplet energy transfer mechanism, the stepwise pathway cannot be excluded.

**Comparison between 1 and 2.** The photophysical properties in  $\text{CH}_2\text{Cl}_2$  of **2**, based on the “green” DPy-gPBI perylene chromophore, can be compared with those observed in the parent assembly **1**, constituted by the “red” DPy-rPBI analog axially connected to two ruthenium-porphyrins.<sup>[24,39]</sup> For both assemblies the possibility to selectively excite either the metalloporphyrin or the perylene chromophores allows to separately track different deactivation pathways by the suitable choice of the excitation wavelength. Excitation of the PBI in both **1** and **2** is indeed followed by photoinduced electron transfer with formation of a charge transfer state involving oxidation of the ruthenium-porphyrin and reduction of the perylene bisimide. On the other hand, excitation of the porphyrin unit is accompanied by electronic energy transfer at the triplet level with formation of the triplet excited state of the PBI in both assemblies. However, remarkable differences are observed when the kinetics of the photoinduced processes and the fate of the PBI<sup>-</sup>-RuP<sup>+</sup> charge transfer product in compounds **1** and **2** are compared. Photoinduced electron transfer from the singlet excited state of the PBI is indeed faster in the “red” PBI array than in the “green” analog by ca two order of magnitudes ( $k_{\text{ET}} = 1.8 \times 10^{11} \text{ s}^{-1}$  and  $2.2 \times 10^9 \text{ s}^{-1}$  for **1** and **2**, respectively).<sup>[24]</sup> Also, recombination of the charge transfer state in **1** is selective towards the ground state ( $k_{\text{ET}} = 3.7 \times 10^9 \text{ s}^{-1}$ ),<sup>[24]</sup> whereas in **2** selective recombination to the PBI triplet occurs ( $k_{\text{ET}} > 2.2 \times 10^9 \text{ s}^{-1}$ ).



**Figure 7.** Marcus-type correlation of the electron transfer rates in arrays **1** (red symbols) and **2** (green symbols) in  $\text{CH}_2\text{Cl}_2$ . Legend: full symbol, experimentally determined data; empty symbol, extrapolated data; circle, charge separation; square, charge recombination.

This trend in rates and selectivity in charge recombination pathway can be rationalized in terms of classical electron

transfer theory.<sup>[40]</sup> Assuming comparable electronic factors in both charge separation and recombination for both compounds **1** and **2**,<sup>[41]</sup> the experimental rate constants measured can be plotted vs. the driving force of the process and interpolated using a Marcus-type parabola (Figure 7). From this correlation a reorganization energy of  $\lambda \approx 0.8$  eV can be extracted and the rates of the other electron transfer processes extrapolated (namely charge recombination to the <sup>3</sup>\*PBI in **1**, charge recombination to both the <sup>3</sup>\*PBI and ground-state in **2**). According to this treatment, the slower rate observed for the forward electron transfer process (eq 3) in **2** stems from the smaller driving force with respect to the same process in **1** (−0.80 vs. −0.24 eV in **1** and **2**, respectively), with the latter being close to the activationless regime. Furthermore, the selectivity in the charge recombination process in **1** (to the ground state)<sup>[24]</sup> arises from the fact that the spin-forbidden backward electron transfer (eq 5) is highly activated (−0.10 eV only, with an estimated rate of  $k_{ET} = 1.7 \times 10^8$  s<sup>−1</sup> from the correlation in Figure 7), whilst the spin-allowed one (eq 6) is inverted but faster (−1.30 eV, experimental rate of  $k_{ET} = 3.7 \times 10^9$  s<sup>−1</sup>). On the other hand, the selectivity observed in **2** (backward charge transfer to the triplet state) can be attributed to the substantial driving force (−0.54 eV) for the charge recombination to the triplet PBI (eq 5) that places the process near the top of the Marcus parabola (estimated rate of  $k_{ET} = 7.3 \times 10^{10}$  s<sup>−1</sup>, Figure 7), while the corresponding spin-allowed process (eq 6) is expected to be strongly inverted and thus slow (−1.44 eV, estimated rate of  $k_{ET} = 4.2 \times 10^8$  s<sup>−1</sup>).

As to the excitation of the ruthenium-porphyrin unit, in both **1** and **2** a triplet-triplet energy transfer pathway occurs. In both cases the kinetics is not well defined within the available time window of the experimental setup but is presumably similar, with minor differences likely arising from the different energy gap between the two <sup>3</sup>\*PBI/<sup>3</sup>\*RuP triplet states.

## Conclusions

In this work, a new *side-to-face* supramolecular array (**2**) made of a green perylene bisimide and two ruthenium-porphyrins was prepared by self-assembling, which warrants the formation of a single supramolecular species in fairly quantitative yields. The assembly presents remarkable stability in solution thanks to the robustness of the ruthenium-pyridine bonds. The photophysical properties of the system were investigated by a combination of fast and ultrafast emission and absorption techniques. The results show that a change in the excitation wavelength (from 680 to 530 nm) causes a sharp variation in the mechanism of excited state quenching between the two different chromophores. Intramolecular electron transfer occurs upon excitation of the perylene dye with “red light”, while energy transfer at the triplet level takes place upon “green light” excitation of the Ru<sup>II</sup>-porphyrin component. In both cases, efficient population of the triplet excited state of the perylene is observed. Importantly, although the quenching mechanisms are identical to what previously reported for the parent compound based on the red PBI (**1**), the charge transfer kinetics and recombination

pathways upon excitation of the perylene unit are apparently different. This is rationalized in terms of classical electron transfer theory considering that the energy of the PBI–RuP<sup>+</sup> charge transfer product is at higher energy in **2** than in **1**. Overall, similar to what earlier reported for array **1**, the supramolecular strategy exploited opens the possibility to achieve efficient population of the triplet excited states of perylene chromophores, alternatively difficult to promote in the isolated PBI species,<sup>[42,43]</sup> as a consequence of the large singlet-triplet gap.

## Experimental Section

**Materials.** [Ru(4-tBuTPP)(CO)(EtOH)], [Ru(4-tBuTPP)(CO)(py)], and DPy<sub>g</sub>PBI (**3**) (4-tBuTPP = 5,10,15,20-tetra(4-*tert*-butylphenyl)porphyrin and *N,N*-di(4-pyridyl)-1,7-bis(pyrrolidin-1-yl)perylene-3,4:9,10-tetracarboxylic acid bisimide) were available from previous works.<sup>[6,25]</sup> Solvents for spectroscopic and photophysical measurements were of spectroscopic grade and pre-treated, before dissolution of the samples, in the presence of excess Na<sub>2</sub>CO<sub>3</sub> to remove residual acidity. All the other solvents were of reagent grade quality and used as received. CDCl<sub>3</sub>, used in NMR experiments, was treated with K<sub>2</sub>CO<sub>3</sub> prior to use.

**Synthesis of DPy<sub>g</sub>-gPBI[Ru(4-tBuTPP)(CO)]<sub>2</sub> (**2**).<sup>[24]</sup> Addition of **3** (8.8 × 10<sup>−4</sup> mmol) to a chloroform suspension of [Ru(4-tBuTPP)(CO)(EtOH)] (1.77 × 10<sup>−3</sup> mmol) yielded a dark brown solution within minutes. The system was allowed to react overnight at room temperature. The crude product was precipitated from the concentrated solution upon addition of *n*-hexane. The precipitate was collected on a filter, washed with cold methanol and *n*-hexane, and vacuum-dried. Final yield: 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, 25 °C): δ 8.64 (s, 16H, β), 8.13 (dd, *J* = 7.9, 1.9 Hz, 8H, oH'), 8.03 (dd, *J* = 7.9, 1.9 Hz, 8H, oH), 7.96 (s, 2H, Ha), 7.92 (d, *J* = 8.5 Hz, 2H, Hb), 7.71 (dd, *J* = 7.9, 2.0 Hz, 8H, mH'), 7.66 (dd, *J* = 7.9, 2.0 Hz, 8H, mH), 7.30 (d, *J* = 8.4 Hz, 2H, Hc), 5.17 (d, *J* = 7.2 Hz, 4H, py<sub>b</sub>), 3.44 (s, 2H, H4), 2.50 (s, 2H, H<sub>1</sub>), 1.89 (s, 2H, H<sub>3</sub>), 1.78 (s, 2H, H<sub>2</sub>), 1.67 (d, *J* = 7.1 Hz, 4H, py<sub>a</sub>), 1.58 (s, 72H, tBu); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, from HSQC): δ 131.70 (C<sub>β</sub>), 134.15 (C<sub>o</sub>), 134.15 (C<sub>o</sub>), 120.72 (C<sub>a</sub>), 126.74 (C<sub>b</sub>), 123.22 (C<sub>m</sub>), 123.14 (C<sub>m</sub>), 123.56 (C<sub>c</sub>), 121.60 (C<sub>pyb</sub>), 52.40 (C<sub>4</sub>), 52.40 (C<sub>1</sub>), 25.23 (C<sub>3</sub>), 25.23 (C<sub>2</sub>), 145.07 (C<sub>pya</sub>), 32.06 (C<sub>Bu</sub>) (see Figure S1 for labeling scheme); UV-Vis: 533 nm (40,000 M<sup>−1</sup>cm<sup>−1</sup>), 569 nm (15,000 M<sup>−1</sup>cm<sup>−1</sup>), 718 nm (46,000 M<sup>−1</sup>cm<sup>−1</sup>).**

**Apparatus and procedures.** NMR experiments were recorded on a Varian 500 (500 MHz) spectrometer. All spectra were run at room temperature; <sup>1</sup>H and <sup>13</sup>C chemical shifts were referenced to the peak of residual non-deuterated solvents: δ (ppm) = 7.26 and δ (ppm) = 77.16, respectively, for CDCl<sub>3</sub>. UV-vis absorption spectra were recorded on a Jasco V-570 UV/vis/NIR spectrophotometer. Emission spectra were acquired on a Horiba-Jobin Yvon Fluoromax-2 spectrofluorimeter, equipped with a Hamamatsu R3896 tube. Fluorescence lifetimes were measured using a time-correlated single photon counting (TC-SPC) apparatus (PicoQuant PicoHarp 300) equipped with subnanosecond LED sources powered by a PicoQuant PDL 800-B variable (2.5–40 MHz) pulsed power supply. The lifetimes of model compound **3** and array **2** were obtained using a 600 nm excitation source (500–700 ps pulse width) and recorded at an analysis wavelength of 760 nm. The decays were analysed by means of PicoQuant FluoFit Global fluorescence decay analysis software. Nanosecond transient absorption measurements were performed with a custom laser spectrometer comprised of a Continuum Surelite II Nd:YAG laser (FWHM 6–8 ns) with a frequency doubled (532 nm) or triple (355 nm) options, an Applied Photo-physics xenon light source including a mod. 720 150 W lamp



housing, a mod. 620 power-controlled lamp supply and a mod. 03-102 arc lamp pulser. Laser excitation was provided at 90° with respect to the white light probe beam. Light transmitted by the sample was focused onto the entrance slit of a 300 mm focal length Acton SpectraPro 2300i triple grating, flat field, double exit monochromator equipped with a photomultiplier detector (Hamamatsu R3896) and a Princeton Instruments PIMAX II gated intensified CCD camera, using an RB Gen II intensifier, an ST133 controller and a PTG pulser. Signals from the photomultiplier (Hamamatsu R928) were processed by means of a Teledyne LeCroy 604Zi digital oscilloscope (400 MHz, 20 GS/s). Femtosecond time-resolved experiments were performed using a pump-probe setup based on a Spectra-Physics Hurricane Ti:sapphire laser source (fwhm = ca. 130 fs) and an Ultrafast Systems Helios spectrometer. The pump pulses at 530 and 680 nm were generated with a Spectra Physics 800 OPA. The probe pulses were obtained by continuum generation with a sapphire plate (useful spectral range: 450-800 nm). The effective time resolution was ca. 300 fs, the temporal chirp over the white-light 450-750 nm range was ca. 200 fs, and the temporal window of the optical delay stage was ca. 1 ns. The time-resolved spectral data were analysed with the Ultrafast Systems Surface Explorer Pro software.

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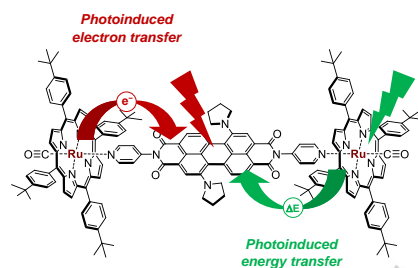
**Keywords:** self-assembly • energy transfer • electron transfer • perylene • ruthenium-porphyrin

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## Entry for the Table of Contents

## FULL PAPER

A novel *side-to-face* array based on a perylene bisimide sandwiched between two Ru<sup>II</sup>-porphyrins, has been prepared and characterized from the photophysical viewpoint showing wavelength-dependent behaviour. Photoinduced electron transfer takes place upon “red light” excitation of the perylene unit, whilst energy transfer occurs upon “green light” excitation of the Ru<sup>II</sup>-porphyrin.



## Supramolecular Photochemistry

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Photoinduced energy- and electron-transfer processes in a *side-to-face* Ru<sup>II</sup>-porphyrin/peryene-bisimide array