

## Photoinduced Charge Separation in a Donor–Spacer– Acceptor Dyad with *N*-Annulated Perylene Donor and Methylviologen Acceptor

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The first donor-acceptor species in which a strongly emissive N-annulated perylene dye is connected to a methylviologen electron acceptor unit via its macrocyclic nitrogen atom, is prepared by a stepwise, modular procedure. The absorption spectra, redox behavior, spectroelectrochemistry and photophysical properties of this dyad and of its model species are investigated, also by pump-probe fs transient absorption spectroscopy. Photoinduced oxidative electron transfer from the excited state of the dyad, centered on the N-annulated perylene subunit, to the appended methyviologen electron acceptor takes place in a few ps. The charge-separated species recombines in 19 ps. Our results indicate that N-annulated perylene can be connected to functional units by taking advantage of the macrocyclic nitrogen, an option never used until now, without losing their properties, so opening the way to new designing approaches.

The search for new highly luminescent species is a very attractive field for several reasons, including the development of new dyes for 1) fluorescence imaging dealing with the biochemical and medical realms,<sup>[1]</sup> 2) light-emitting dyad systems for illumination,<sup>[2]</sup> and 3) design of new dye-sensitized solar cells (DSCs).<sup>[3,4]</sup> In recent years, a new class of dyes exhibiting quite intense and tunable luminescence has been identified, namely N-annulated perylenes (NAPs).<sup>[5]</sup> Indeed, NAP species exhibit strong visible absorption, efficient photoluminescence, and redox reversibility, all properties that are also largely tunable (e.g. strong absorption up to 700 nm can be obtained), introducing substituents at the peri-position near the amine site.<sup>[6]</sup> Actually, NAPs have recently been exploited as part of multicomponent systems within the field of DSCs, taking advantage of both their absorption properties and reversible oxidation behavior.<sup>[7]</sup> To our knowledge, in all the reported cases

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the NAP dye has been connected to the other subunits of the multicomponent systems (other light absorbers or electron acceptor mediators, in their turn linked to the metal oxide semiconductor electrode) by a substitution at the *peri*-position of the macrocyclic nitrogen. Connection via the nitrogen atom of the *N*-annulated cycle to other photo- and/or redox-active subunits (including metal oxide semiconductor surfaces) has not been explored. In fact, substitution at the nitrogen atom has only been used to improve solubility of NAP species, but not to attach functional (e.g., photo- and/or redox-active) subunits.

Here we report the first example of a donor-bridge-acceptor dyad, **1** (see structural formula in Figure 1) in which the donor is an *N*-annulated perylene, connected to the bridge-acceptor subunits via the nitrogen of the macrocyclic structure, and show its absorption spectra, redox behavior, and photophysical properties, including ultrafast photoinduced charge separation and recombination. Our results indicate that the *N*-annulated perylenes can conveniently be connected via the nitrogen atom to other subunits for photoinduced processes, without losing their properties, thus offering new ways to molecular design of multicomponent systems suitable for light-powered functions. Noteworthy, the *peri*-positions of NAP species are therefore available for further substitution (e.g., to incorporate other functional subunits) or tunability reasons.

The synthetic, modular approach is shown in Figure 1. The *N*-annulated perylene dye obtained via step  $b^{[8]}$  is reacted with  $\alpha, \alpha'$ -dibromo-*p*-xylene (step c) to yield the Br-substituted species in which the NAP chromophore is connected to a phenyl-



**Figure 1.** Structural formulae and modular synthetic pathway and reaction conditions for **1** and **2**: a) 1,4-dioxane/water/HNO<sub>3</sub> (24/9/6), reflux, 1 h; b) P(OEt)<sub>3</sub>, N<sub>2</sub>, reflux, 2 h; c)  $\alpha, \alpha'$ -dibromo-p-xylene (3.8 equiv), KOH (1.5 equiv), KI (0.05 equiv), THF, N<sub>2</sub>, reflux, 48 h; d) methyl-4,4'-bipyridinium hexafluorophosphate (1 equiv), MeCN, N<sub>2</sub>, reflux, 12 h, NH<sub>4</sub>PF<sub>6</sub>; e) bromoben-zyl (3 equiv), KOH (4 equiv), KI (0.12 equiv), THF, N<sub>2</sub>, reflux, 26 h. Full details in the Supporting Information.

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ene unit. This allows the introduction of a spacer to keep the donor and acceptor units separated in the final, designed structure. Similarly, using bromobenzyl instead of  $\alpha$ , $\alpha'$ -dibro-mo-*p*-xylene as a reactant, compound **2** is obtained (step e), which is used as a model for the spectroscopic and photophysical properties of the donor species. Finally, the electron acceptor methylviologen unit (MV<sup>2+</sup>) is connected to the bromo-substituted NAP species (step d), yielding the multicomponent (NAP)–Ph–MV<sup>2+</sup> species **1**.

The absorption spectra of **1** and **2** in acetonitrile (Table 1, Figure 2) are dominated by the typical strong absorption of the NAP compounds, assigned to a spin-allowed  $\pi$ - $\pi$ \* transition. The absorption spectra of **1** and **2** overlap each other in the visible region, indicating that the presence of the MV<sup>2+</sup> electron acceptor does not perturb the ground-state properties of the NAP subunit in **1**. The model species **2** exhibits a quite intense, structured emission (Figure 2, Table 1), both in a acetonitrile liquid solution at room temperature (RT) and in a butyronitrile solid matrix at 77 K. On the basis of the structured spectral shape, lifetime and quantum yield and taking into account the similarities between RT and 77 K spectra and lifetimes, the emission is assigned to fluorescence from the lowest-lying singlet  $\pi$ - $\pi$ \* state; this result is also in agreement with the reported fluorescence of similar NAP species.<sup>[6]</sup> Such

Table 1. Absorption, luminescence and redox data. <sup>[a]</sup>								
	Absorption $\lambda$ [nm] ( $\varepsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ])	Luminesce $\lambda$ [nm] <sup>[b]</sup>	ence, τ [ns]	$\Phi_{\rm em}$	Redox da $E_{1/2(\text{red})}$	ta (V vs SCE) E <sub>1/2(ox)</sub>		
1 2	422 (35450) 421 (36000)	– 435 (432) <sup>[c]</sup>	– 5.0 (5.3) <sup>[c]</sup>	- 0.9	-0.38 -	+ 0.89 + 0.88		

[a] Data in acetonitrile solution at RT, unless otherwise stated; [b] only the highest-energy maximum is reported; [c] in butyronitrile rigid matrix at 77 K.



Figure 2. Absorption of 1 and 2 and emission spectra of 2 in acetonitrile solution (RT) and in butyronitrile rigid matrix (77 K). Full data in Table 1.

an emission is absent in 1, both at RT and 77 K, indicating efficient intramolecular quenching due to the  $\rm MV^{2+}$  subunit, in all the investigated conditions.

The new (NAP)–Ph–MV<sup>2+</sup> donor–bridge–acceptor **1** undergoes a quasi-reversible oxidation process at +0.89 V vs. SCE (Table 1), assigned to oxidation of the NAP subunit (**2** undergoes a roughly identical process), and a reversible reduction process at -0.38 V, typical of MV<sup>2+</sup> units.<sup>[9]</sup> To estimate the driving force for photoinduced oxidative electron transfer involving the excited NAP unit as the donor and the methylviologen electron acceptor,  $\Delta G_{CS}$ , Equations (1) and (2) can be used:<sup>[10]</sup>

$$\Delta G_{\rm CS} = e({}^{*}E_{\rm ox} - E_{\rm red}) \tag{1}$$

$${}^{*}E_{\rm ox} = E_{\rm ox} - (E_{\rm 00}/e)$$
 (2)

In Equations (1) and (2), *e* is the electron charge,  $E_{ox}$  and  $E_{red}$  are the first oxidation and reduction potentials of **1**, respectively, \* $E_{ox}$  is the oxidation potential of the excited state centered in the NAP subunit, and  $E_{00}$  is the excited-state energy of **1**, approximated to the 77 K emission maximum. In Equation (1), the work term is neglected. Application of Equations (1) and (2) yields a value of -1.59 eV for  $\Delta G_{CS}$ , indicating that the photoinduced oxidative electron transfer in **1** is largely allowed by a thermodynamic viewpoint, so justifying the quenching of the NAP-based emission even at 77 K.

To further investigate the excited-state quenching process, pump-probe transient absorption spectroscopy is quite useful; however, identification of expected signatures for radical cations and anions is a prerequisite for pump-probe experiments. Figure 3 shows the absorption spectrum of the electrochemically generated, oxidized form of 1: the radical cation centered on the NAP unit is characterized by a visible absorption in the range 450–800 nm. The radical anion involving the MV<sup>2+</sup> subu-



**Figure 3.** Spectral changes of 1 in acetonitrile obtained by applying a potential of +0.9 V vs. SCE in acetonitrile, so generating the radical cation of the NAP subunit. Initial spectrum is the blue one, the red spectrum is that of the electro-generated radical cation of 1.



nit, obtained by applying a voltage of -0.38 V vs SCE to a solution of 1, is characterized by a less intense absorption band at 480–700 nm and by a broad absorption in the 800–900 nm region (Supporting Information). These pieces of information could be useful to investigate the photoinduced electron transfer by pump-probe transient absorption spectroscopy (see later).

Figure 4 shows the pump-probe transient absorption spectrum (TAS) of 1 in acetonitrile. The initial spectrum, essentially coincident with that of 2 in the same conditions (Supporting Information), and therefore assigned to the S<sub>1</sub> ( ${}^{1}\pi-\pi^{*}$ ) excited state of the NAP unit, shows a bleach centered at about 460 nm, assigned to stimulated emission,<sup>[11]</sup> and a broad transient absorption in the region 460–750 nm. Then, whereas the TAS of 2 decays monotonically to the ground state (Supporting Information), for 1 an absorption peak at 490 nm appears after few picoseconds.

This peak is attributed to the formation of the radical cation of the NAP unit, as it derives from a spectral combination due to the formation of the radical cation band in the range 400-750 nm, evidenced by the spectroelectrochemistry in Figure 3, and the red tail of the bleaching of the ground-state absorption. Simultaneously, also the bleach due the stimulated emission at about 460 nm is fully recovered. To definitely assign the fast quenching process to photoinduced electron transfer leading to the charge-separated state of 1, which can be represented as a (NAP<sup>+</sup>)-Ph-MV<sup>+</sup> species, formation of the reduced form of the acceptor MV<sup>2+</sup> subunit would be also useful. However, spectroscopic identification of the reduced form of the MV<sup>2+</sup> subunit is a difficult task. In fact, the 480–700 nm region, where the radical species MV<sup>+</sup> absorbs (Supporting Information), is obscured by the more intense absorption of the NAP cation (Figure 3). The 800-900 nm region is experimentally problematic due to laser pulse. The UV region, sometimes used to identify the reduced methylviologen,<sup>[12]</sup> is not accessible to our pump-probe equipment for technical reasons. Although identification of MV<sup>+</sup> is therefore not feasible in our case, we attribute the guenching process to photoinduced electron transfer, since this process is the only one reasonable by a thermodynamic viewpoint and identification of the radical cation NAP strongly supports our hypothesis.<sup>[13]</sup>

From the kinetic traces in Figure 4, the time constant for the formation of the charge-separated (NAP<sup>+</sup>)–Ph–MV<sup>+</sup> species, from the excited state of the NAP subunit is 5 ps (see also Figure 5). The charge-separated state decays to the ground state with a time constant of 19 ps (Figure 4), assigned to back electron transfer (i.e., charge recombination). According to Equations (1) and (2), and as illustrated in Figure 5, driving force for the charge recombination,  $\Delta G_{CR}$ , is 1.29 eV. Comparison between forward and backward electron transfer rate constants in **1**, however, would require other pieces of information, like reorganization energy, that are not available at the moment and are outside the scope of this paper, so this aspect will not be discussed here.

Noteworthy, the kinetics of charge separation and recombination for **1** are similar to those recorded in a somewhat related dyad made of a boron-dipyrromethene (bodipy) fluoro-



**Figure 4.** TAS of 1 in acetonitrile and its decay kinetics. Middle: complete 3D TAS matrix representation; top: sketch evidencing the spectral evolution; bottom: decay kinetics (early times in the inset).  $\lambda_{\text{exc.}}$ : 400 nm.

phore and a methylviologen unit.<sup>[14]</sup> For such a species, photoinduced charge separation was obtained with a time constant of 7.1 ps, and charge recombination had a lifetime of 59 ps. This comparison further confirms that the NAP subunit has excited-state properties that can compete with those of the most popular bodipy dyes.

In conclusion, the macrocyclic nitrogen atom of an *N*-annulated perylene species has been used to link such a dye, via



Figure 5. State diagram and decays of 1.

a phenylene spacer, to an electron acceptor subunit, namely a methylviologen moiety. This has allowed the preparation of a donor-spacer-acceptor species by a design approach never explored so far, as in all reported cases N-annulated perylene dyes have been connected to other photo and/or redox-active units exclusively by substitution at the peri-position of the macrocyclic nitrogen. The spectroscopic, redox, and photophysical results indicate that in the so-formed, novel donorspacer-acceptor dyad the N-annulated perylene subunit maintains its remarkable photophysical and redox properties, allowing to efficiently generate, by photoinduced oxidative electron transfer, a charge-separated species with a time constant of 5 ps, which recombines in about 20 ps. Such results open further perspectives to the molecular design of multicomponent systems containing the quite interesting, new N-annulated perylene chromophores and suitable for light-powered functions.

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**Keywords:** charge-separated state · femtosecond pumpprobe spectroscopy · luminescence · *N*-annulated perylene · photoinduced electron transfer

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