Donor–Acceptor Systems

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Polyimide Dendrimers Containing Multiple Electron Donor–Acceptor Units and Their Unique Photophysical Properties**

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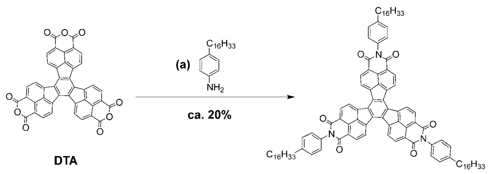
Abstract: *A high-yielding synthesis of a series of polyimide dendrimers, including decacyclene- and perylene-containing dendrimer* ***D6****, in which two types of polyimide dyes are present, is reported. In these constructs, the branching unit is represented by trisphenylamine, and the solubilizing chains by N-9-heptadecanyl-substituted perylene diimides. The photophysical properties of the dendrimers have been studied by absorption, steady-state, and time-resolved emission spectroscopy and pump–probe transient absorption spectroscopy. Photoinduced charge-separated (CS) states are formed on the femtosecond timescale upon visible excitation. In particular, in* ***D6****, two different CS states can be formed, involving different subunits that decays independently with different lifetimes (ca. 10–100 ps).*

Multichromophoric systems are attracting a large amount of interest for their potential role in solar energy production.[1] Therefore, the possibility to synthesize new molecules bearing different light absorbing subunits, such as rylene diimides, represents an appealing possibility to make classes of versatile light-harvesting antenna systems.[2,3] Dendrimers based on perylene diimides are promising materials in the field of photonics, because of their peculiar optical and redox properties.[3] Furthermore, they can form shape-persistent, ordered nanostructures in the bulk state, thereby exhibiting high charge-carrier mobilities.[4]

Modeled after perylene and naphthalene imides, we recently introduced a new class of multivalent molecular materials, namely decacyclene trianhydride (DTA) and triimides (DTIs).[5] DTA is a novel trifunctional building block that establishes a natural candidate for the synthesis of shape-persistent π-conjugated dendrimers.

We report herein the synthesis, characterization, and photophysical properties of a novel polyimide dendrimer with a decacyclene core (**D6**), of related multiimide compounds based on perylene diimides (**D3** and **D5**), and of the building blocks **P1** and **C** (Schemes 1 and 2; the number in **D*n*** identifies the number of perylene diimide dyes in the structure). In the multi-imide dendritic compounds studied herein, the branching units are triphenylamino (TPA) groups, which also play the role of electron donors for accessing photogenerated charge-separated (CS) species. Consequently, this series of compounds introduces a new class of dendrimers, containing both multiple electron donors and multiple dyes with acceptor abilities, in their molecular arrays.



Scheme 1. Synthesis of *N*-(4-hexadecyl)phenyl decacyclene triimide (**C**). Reagents and conditions: a) Hexadecylaniline, quinoline, 180 °C, overnight.

Starting from DTA,[5a] condensation reactions with aromatic amines yield the model compound based on decacyclene studied herein (**C**, Scheme 1). This reaction requires high temperature and the use of $Zn(OAc)_2$ in catalytic amounts, but it is generally low-yielding (ca. 20 %), which is probably due to steric hindrance of the aromatic amines and/

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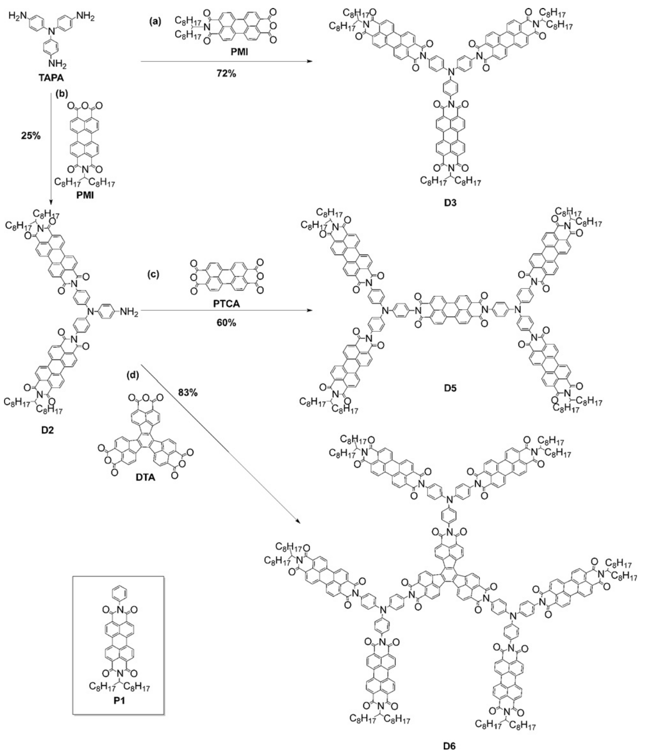

Scheme 2. Synthesis of polyimide dendrimers. Conditions and reagents: a) $Zn(OAc)_2$, imidazole, 180 °C, overnight; b), c), d) $Zn(OAc)_2$, quinoline, 180 °C, overnight. The structural formula of **P1** is also shown on bottom left.

or the low solubility of DTA. To accomplish the synthesis of a π-conjugated dendrimer with a rigid structure, we therefore decided to carry out a convergent growth approach, thereby imparting solubility throughout the dendrimer synthesis. Convergent growths also generate well-defined structures without ill-defined peripheral groups and consequently high purity.

First, asymmetric monoimide perylene anhydride (PMI) was treated three times with the branching unit trisaminophenylamine (TAPA) to yield the model compound **D3** (Scheme 2) in 72 % yield. A careful control of the number of the equivalents (1.78 equiv) used in the reaction easily gave compound **D2** in 25 % yield. These two first reactions were instrumental to prove that TAPA was a good candidate as a branching unit and that controlled reactions affording soluble derivatives are possible following this route. Specifically, compound **D2** was key to perform the synthesis of the second model compound **D5** in 60 % yield, as well as the target dendrimer **D6** in 83 % yield (Scheme 2). The free amino group on TAPA is sufficiently stable to perform all the characterization, but it was always derivatized immediately after purification to avoid possible oxidation of the electron-rich moiety. The purity of compounds **D3, D5**, and **D6** was assessed by high-temperature NMR spectroscopy. Furthermore, solid-state ^{13}C NMR of compound **D6** revealed high purity, which was also confirmed by MALDI mass spectrometry (see the Supporting Information).

All of the dendrimers were isolated as deep-red–purple-colored solutions and powders. They have good solubility in most common organic solvents. Thermogravimetric analysis (TGA) showed high thermal stability for all the dendrimeric compounds (Supporting Information, Figure S13). A 5 % loss of weight is recorded at around 400 °C that is comparable with Kapton-based polymers.[6]

Because of their peculiar structure,[7] we investigated the optoelectronic (see below) and the textural properties of these dendrimers. Nitrogen sorption analysis and X-ray diffraction revealed that these materials are usually non-porous and amorphous (Supporting Information, Figure S14). Indeed, the trigonal nitrogen atoms act as rotational centers that allow for a high degree of disorder in the molecules (Supporting Information, Figure S15, S16).

As for the optoelectronic properties, the visible region of the absorption spectra of the new species is dominated by the typical structured and intense absorption bands of the perylene diimide subunits between 400 and 580 nm, assigned to their lowest-energy spin-allowed π–π* transitions (Figure 1). However, **C** exhibits a broader and less-intense band peaking around 430 nm, which is still assigned to its lowest-energy spin-allowed π–π* transition. The shape of the absorption spectrum of **D3** is identical to that of **P1** (Scheme 2), whereas the molar absorption of **D3** is roughly three times larger than that of **P1** (Table 1), indicating the absence of significant interaction among the perylene diimide dyes of **D3**. The absorption spectra of **D5** and **D6** are slightly

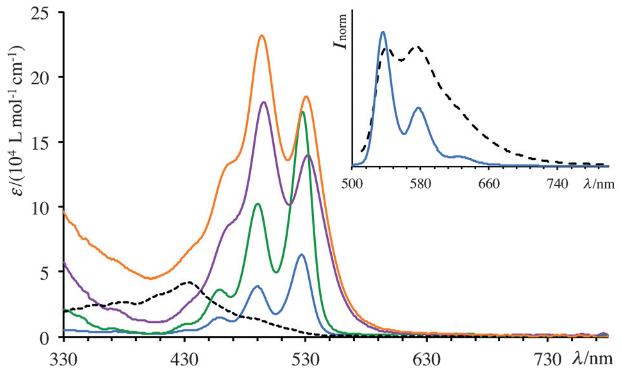

Figure 1. Absorption and (inset) normalized emission spectra of **C** (black, dashed), **P1** (blue), **D3** (green), **D5** (purple), and **D6** (orange) in DCE.

Table 1: Absorption, emission and redox data of the dendrimers and model compounds in 1,2-dichloroethane (DCE) at 298 K.

	Absorption[a]		Redox data[b]		Luminescence		
	λ_{max} [nm]	ε [L mol^{-1} cm^{-1}]	E_{ox} [V]	E_{red} [V]	λ_{max} [nm]	τ [ns]	ϕ
D3	525	17 8000	0.98	−0.76	–	–	–
D5	528	13 6000	0.99	−0.74	–	–	–
D6	527	18 6000	1.02	−0.77	–	–	–
C	429	41 000	–	−0.77	540	6.1	0.07
P1	524	58 000	–	−0.74	534	4.3	0.67

[a] Only data concerning the lowest-energy band are given. [b] The $E_{1/2}$ potentials of first oxidation and reduction processes in the −1.0 V/ +1.2 V potential window versus SCE are reported.

different from the simple addition of the spectra of their individual components, **P1** and **C** (this latter only for **D6**). Rather than ascribing these features to possible interchromophoric interactions in the ground state, we infer that the distinct chemical environment of the central perylene diimide unit of **D5** and the decacyclene core of **D6** may affect the shape and the shift of the spectra. In the absorption spectrum of **D6**, the contribution of the core **C** appears in the region 400–450 nm.

All of the studied species exhibit a reversible process at about −0.75 V vs SCE (Table 1), which is assigned to perylene diimide reduction and/or core reduction in **D6** (perylene and decacyclene imides are reduced at close potentials[5]). Dendrimers **D3**, **D5**, and **D6** are reversibly oxidized at about +1.0 V vs SCE (Table 1); the oxidation processes are assigned to the TPA subunit(s) (Supporting Information, Figures S17 and S18).

P1 exhibits the emission of perylene diimide compounds (see Figure 1, inset),[4] with a lifetime of 4.3 ns and a quantum yield of 0.67, whereas **C** shows a less efficient emission (Table 1).[5a] In both cases, emission is assigned to the S_1 state, which is π–π* in nature. Dendrimers **D3**, **D5**, and **D6** do not show any emission at any excitation wavelength. This finding indicates that in these multicomponent species, additional non-radiative channels are available for S_1 decay of each polyimide subunit. On the basis of redox data, photoinduced reductive electron transfer involving the TPA sites as donors appears feasible. Indeed, by applying the Rehm–Weller equation,[8] and neglecting electrostatic correction, a driving force of about −0.65 eV is found for photoinduced electron transfer from TPA units to the S_1 of the perylene bisimide or decacyclene imide units.

The pump–probe transient absorption (TA) spectrum of **P1** shows a TA band at about 700 nm, typical of perylene diimide S_1 state (Figure 2a).[4] Stimulated emission also appears as an apparent bleach in the 550–640 nm range. Following a small modification occurring within a few ps, which is most likely due to vibrational cooling, such a transient spectrum directly decays to the ground state, as indicated by the isosbestic point at $\Delta A = 0$, with an experimental time constant of 3.8 ns, in agreement with emission lifetime. As expected, **D3** exhibits an initial TA spectrum similar to that one of **P1**, except for the absence of the stimulated emission component (Figure 2b). However, the TA of **D3** increases with time at wavelengths longer than 550 nm, and a peak appears in the near-IR region, at about 960 nm (Figure 2b). These features, not visible in the transient spectrum of **P1**, are present in the absorption spectrum of the electrochemically generated radical anion of **P1** and of **D3**. The electrochemically generated radical cation of **D3**, which is due to TPA oxidation, absorbs in the 550–800 nm region (Figure 2c). Such absorption in the TA of **D3** overlaps with the stronger absorption of the perylene diimide anion at wavelengths longer than 600 nm, in agreement with previous results[9] (for information from the radical anion of **P1**, see the Supporting Information, Figure S20). Despite the overlap of the anion and cation absorption bands in the 600–800 nm, the increase of the TA spectrum of **D3** in the 550–600 nm region suggests the simultaneous formation of TPA cation. Therefore, the spectral evolution of **D3** can be attributed to the formation of the CS state, where the TPA and the perylene diimmide units are the donor and the acceptor, respectively. The CS state formation takes place with a time constant of 1.3 ps and decays to the ground state in 41 ps (Figure 2b; see kinetics at 560 nm in the insets). Such a behavior is qualitatively followed by **D5**, for which photoinduced charge separation and charge recombination occur with time constants of 1 ps and 63 ps, respectively (see transient spectra and decays in the Supporting Information, Figure S19).[10]

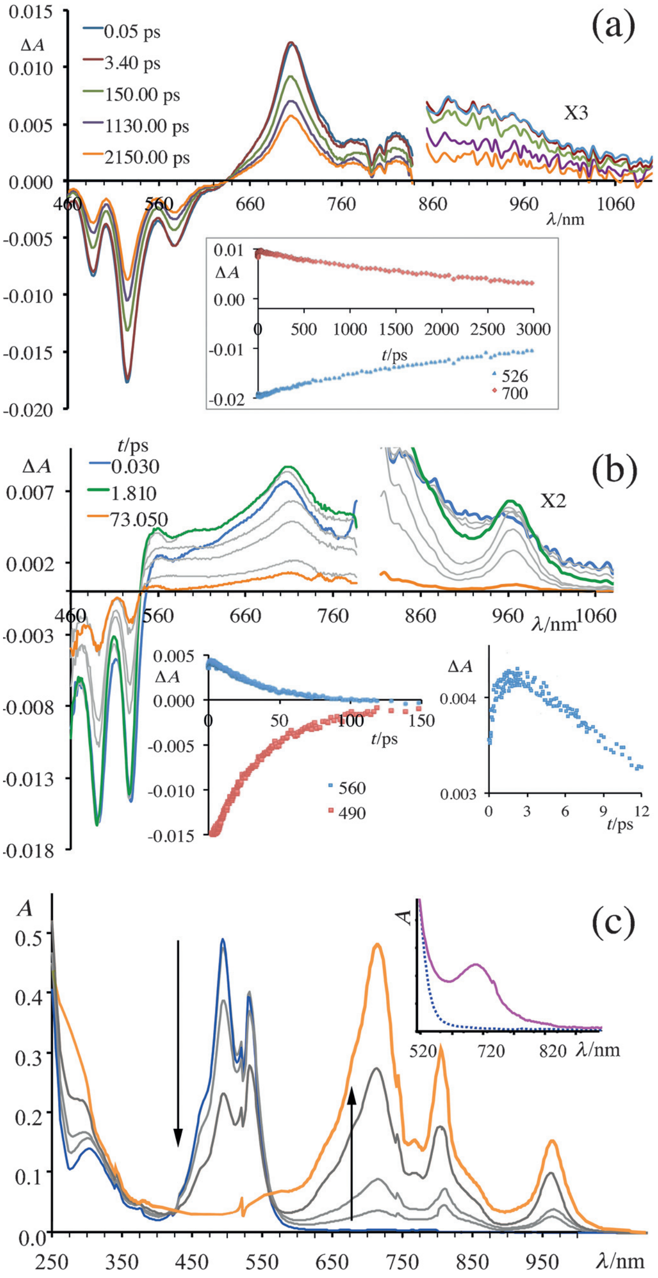

Figure 2. TA spectra of **P1** (a) and **D3** (b) in DCE ($\lambda_{exc} = 400$ nm). In the insets in (a) and (b) show kinetics at different wavelengths. Absorption spectra of the electrochemically reduced (orange) and oxidized (purple in the inset) **D3** are reported in (c); blue lines refer to the neutral **D3**.

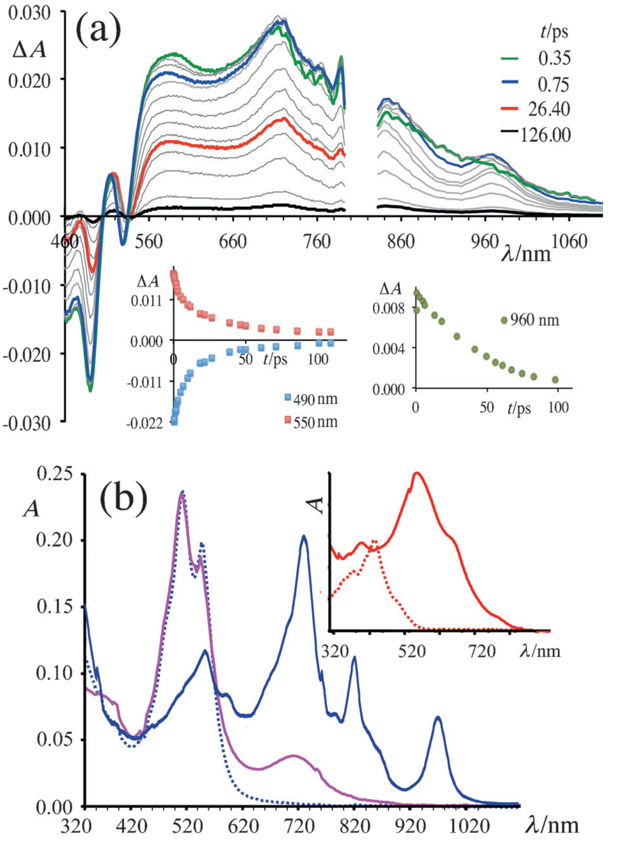

Figure 3. a) TA spectrum and (insets) kinetics of **D6** in DCE ($\lambda_{exc} = 400$ nm). b) Absorption spectra of the electrochemically reduced (blue) and oxidized (purple) **D6**; the reduced **C** spectrum is shown in the inset (red solid line).

The process is more complex for **D6** (Figure 3). Indeed, 400 nm as the excitation wavelength for the pump–probe experiments excites both the decacyclene triimide core and the perylene diimide peripheral dyes (see absorption spectra in Figure 1). The initial transient spectrum, which is expected to be a combination of the singlet states of **C** and **P1**, evolves quite rapidly. This leads to the formation of the signatures of the perylene diimide radical anion at 960 nm,[9] which indicates reductive photoinduced electron transfer involving the S_1 state of a perylene diimide unit, and of a broad absorption in the range 540–800 nm. The experimental time constant, calculated both at 550 and at 960 nm, is about 230 fs (Figure 3a; Supporting Information, Figure S23). Since this value is close to the time limit of our apparatus, the actual time constant for the formation of the CS state involving the perylene diimide subunit(s) is either equal or lower to such value.

A spectroelectrochemical study of **C** (Figure 3b; Supporting Information, Figures S21 and S22) indicates that the radical anion of the decacyclene triimide is characterized by a broad and intense band peaking at about 530 nm, with a shoulder at 620 nm, in the same range where also the perylene diimide anion absorbs. Therefore, the eventual formation of a CS state involving the core as the electron acceptor could be obscured in TA spectroscopy, although some difference in the visible region is expected. In particular, around 530 nm the TA spectrum of the CS state involving the radical anion of perylene diimide should exhibit a strong bleach, while the TA spectrum of the CS state involving the anion of the core would exhibit a strong absorption. This latter consideration, coupled with the difference between TA spectra of **D3** and **D6** around 530 nm (Figures 2 and 3), suggests that radical anions of peripheral and core polyimides are simultaneously present in **D6**. Moreover, the corresponding CS states should be formed within the same timescale (≤ 230 fs).[11,12]

However, whereas the TA spectrum of **D6** cannot give definitive, direct, evidence of the formation of two CS states, its decay yields indirect evidence for the presence of both states. Indeed, the transient spectrum in the visible region, where the radical anions of peripheral and core polyimides absorb differently (see above), undergoes a biphasic decay. The faster decay process, with a time constant of 10 ps, is characterized by shifts in the bleaching maxima in the visible and a slower decay process, with a time constant of 71 ps, ultimately leading to the ground state (Figure 3a). Interestingly, the decay of the TA maximum at 960 nm, where essentially only the reduced **P1**-type subunits absorb, is monoexponential, with a time constant of 72 ps (Figure 3).

From the above results, we can derive the excited-state properties of **D6** (Figure 4): 1) upon 400 nm laser excitation, both decacyclene triimide-based and perylene diimmide-based singlet states are formed; 2) these S_1 states decay to TPA^+–$core^-$ and TPA^+–$P1^-$ CS states, respectively, with time constants of about 230 fs (or faster) in both cases; and 3) the TPA^+–$core^-$ CS state recombines in 10 ps, and the TPA^+–$PD1^-$ CS state recombines in ca. 70 ps. This is further confirmed by TA global analysis, which reveals the lifetimes and spectra of the individual excited-state species (Supporting Information, Figure S25).

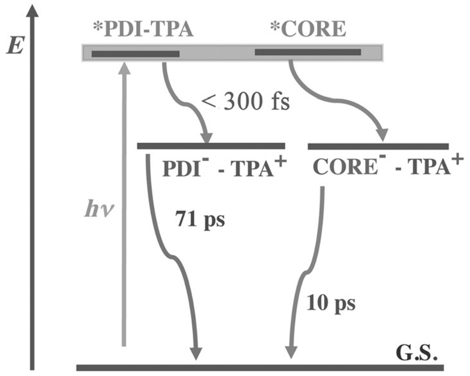

Figure 4. Representation of the excited states and decay channels in **D6**. Similar schemes for **D3** and **D5** are given in the Supporting Information, Figure S24.

The presence of two different CS states within the same dendrimer **D6** can have intriguing consequences for molecular electronics[13] and/or logics.[14] Indeed, these donor–acceptor dendrimers are macromolecular materials with well-defined structures that bear film-forming capabilities similar to polymers and could prove useful in organic photovoltaics for their potential to form ordered nanostructures and to exhibit high charge-carrier mobilities.[12] Furthermore, because of their unique photophysical properties, these systems are functional multimodule molecules, which could be used for information handling in an input-to-output type of configuration, thereby opening new opportunities for Boolean logics.[13] Excitation at wavelength longer than 530 nm (where the core chromophore absorbs negligibly, Figure 1) mainly leads to the formation of the TPA$^+$–P1$^-$ CS state and excitation at about 420 nm mainly leads to the TPA$^+$–core$^-$ level. This observation suggests that the two CS states can be independently addressable. Moreover, suitable modification of the molecular arrays, on the basis of the information gained herein, can be designed to obtain specific excited-state properties. An additional layer of electron acceptor units, easier to reduce than the perylene diimide studied herein and connected via non-redox active branching sites, could be grafted on dendrimers **D3** or **D5**, and would open the way to larger species with long-lived, intra-dendrimer charge-separated states.

In conclusion, we reported the unprecedented synthesis and characterization of a novel class of light- and redox-active polyimide dendrimers based on electron-donor units as branching sites. Compound **D6** is also the first dendrimer containing a decacyclene unit. Interchromophoric coupling among dye subunits is negligible in the ground state but upon excitation very fast photoinduced CS states are formed, where the TPA branching units behave as electron donors. In particular, in **D6**, containing both decacyclene triimide and perylene diimide units, two different CS states can be prepared within 230 fs. Such CS states deactivate independently to the ground state in the 10–100 ps timescale. The results show the very rich excited-state properties of these new shape-persistent dendrimers and pave the way to further developments of polyimides-containing dendrimers based on molecular design.

Keywords: antenna systems · dendrimers · donor–acceptor systems · polycycles · ultrafast spectroscopy

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[10] In principle, the central perylene diimide of **D5** is different from the four peripheral perylene diimides, so two different CS states are possible. However, we only found single processes for CS formation and decay.

[11] The data in Table 1, according to the Rehm–Weller equation, indicate that the two possible CS states of **D6**, involving peripheral and central polyimides, would have very similar energies.

[12] As indicated by emission spectra, the S$_1$ states of **C** and **P1** also have very close energies, so that interchromophoric energy transfer in **D6** is not expected to be very fast and apparently not a competitive decay route with respect to the electron transfer processes, occurring in the fs timescale.

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