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Variation of the energy gap in fullerene-based dendrons: competitive *versus* sequential energy and electron transfer events

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Artificial molecular models, based on rigid dendrimeric *meta*-substituted phenylenevinylene moieties bearing different electron donating groups and the electron acceptor C_{60}, were probed in an effort to gain control over a sequential *versus* a competitive scenario in energy and electron transfer events.

The design of supramolecular ensembles for use in energy conservation and conversion is a long-standing objective.[1] Understanding the complexity of efficient energy migration and unidirectional electron transfer occurring, for example, in the photosynthetic reaction center[2] offers powerful guidelines for developing artificial devices. A particularly challenging aspect is to explore the role of a sequence *versus* a competition in energy/electron transfer reactions, especially upon altering the energy gaps.

The choice of the connecting spacer in donor–bridge–acceptor (D–B–A) assemblies is fundamental, since it ensures the control over distance, angle and coupling between the donor and acceptor. These parameters govern in large character, rate and efficiency of long distance energy and/or electron transfer processes.[3,4] Dendritic structures provide key criteria such as rigidity and conjugation, which, most importantly, can be chemically fine-tuned.[5] In turn, these unique molecular architectures emerged as versatile building blocks for the preparation of artificial systems.[6]

Previous work has focused mainly on encapsulating flexible dendron units.[7] The flexibility prohibits, however, a detailed comprehension of effects stemming from donor–acceptor separation and/or orientation, which drew our attention to the unique features of a stiff dendritic macromolecule.[8]

Here we report on the synthesis and photophysical studies of D–B–A systems in which four dibutylaniline (**8a**) or dodecyloxynaphthalene (**8b**) electron donors are located at the peripheral positions of well-defined phenylenevinylene-based dendrons and an acceptor fullerene at the focal point of the dendrimer.

Yu and coworkers[9a] and Meier and Lehman[9b] have reported synthetic routes towards formyl-substituted rigid poly(phenylenevinylene) dendrimers starting from different AB_2 type building blocks. A remarkable advantage of the convergent route, presented here is the use of a nitrile group in the readily available AB_2 starting material **1**.[10] This functionality remains unaffected during the Arbuzov and the Wittig–Horner reaction (*i.e.* with aldehydes **3a**,**b**) to yield bisphosphonate **2** and the first-generation dendrons **4a**,**b** with an *all-trans* configuration, respectively.

Subsequent treatment of the nitrile-substituted systems **4a,b** with DIBAL-H in dichloromethane transforms them in good yield to the corresponding formyl-substituted analogues **5a**,**b**. In the next step, a second Wittig–Horner reaction of **5a**,**b** with bisphosphonate **2** affords the nitrile-substituted second-generation dendrons **6a**,**b**. Additional DIBAL-H treatment allowed us to prepare the formyl functionalized dendrons **7a**,**b**. Dyads **8a,b** have been prepared in good yields (30%) by 1,3-dipolar cycloaddition of the respective rigid dendron (**7a**,**b**) to C_{60} in the presence of sarcosine in refluxing toluene (Fig. 1).[11]

The redox properties of the fullerene-containing dendrons **8a,b** were studied by cyclic voltammetry in toluene/acetonitrile (4 : 1 v/v) solutions and revealed several oxidation and reduction steps. In particular, anodic processes with peaks at 0.72 V (**8a**) and 1.30 V (**8b**) refer to the oxidation of the dibutylaniline and dodecyloxynaphthalene moieties, respectively. In the cathodic region three quasireversible reduction waves were recorded (**8a**: −0.65; −1.07, −1.70 V, **8b**: −0.64, −1.03; −1.62 V), which correspond to the stepwise reduction of the fullerene moiety and resemble those observed for a fulleropyrrolidine reference.

Replacement of the poly(arylenevinylene) cores (**8b**) with the analogous dibutylaniline functionalities (**8a**) imposes important consequences on the dendron's physico-chemical properties: red-shifted ground-state maxima in combination with better electron donor character create quite different energy gaps between the dendron's singlet excited state and that of the $C_{60}{}^{\cdot-}$–dendron$^{\cdot+}$ radical pair in **8a** and **8b**.

In general, the strongly fluorescing dendrons **7a** and **6b** with quantum yields as high as 0.47, give rise to an almost entirely quenched emission in dyads **8a** and **8b** (Table 1). For example, in non-polar toluene the dendrimer emission in the visible (400–450 nm) is reduced by more than two orders of magnitude.

From this observation we reach the conclusion that in toluene the dendrimer singlet excited state in **8a**,**b** undergoes a rapid singlet–singlet energy transfer to the energetically lower-lying

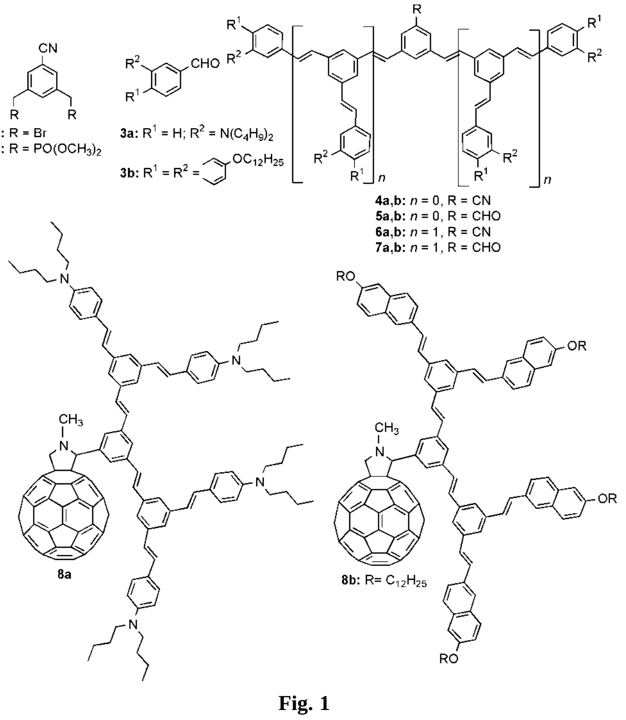

Fig. 1

Table 1 Photophysical properties of dendrons **6b**/**7a** and dyads **8a**/**8b**

	6b	**7a**	**8b**	**8a**
Dendron				
Φ_{FL} (toluene)	0.47^e	0.31^f	3.15×10^{-3e}	2.5×10^{-3f}
Φ_{FL} (THF)			3.07×10^{-3e}	2.2×10^{-3f}
τ_{FL} (toluene)/ns	1.99^e	2.05^f		
$\tau_{singlet}$ (toluene)/ns	1.97	2.01		
$-\Delta G_{ET}{}^{\circ a}$/eV			1.34	1.67
λ^a/eV			1.49	1.42
$-\Delta G_{EnergyT}{}^{\circ}$/eV			1.24	0.99
Fullerene				
$\Phi_{FL}{}^b$ (toluene)			5.4×10^{-4}	3.9×10^{-4}
$\Phi_{FL}{}^b$ (THF)			4.0×10^{-4}	0.6×10^{-4}
$\Phi_{FL}{}^b$ (BzCN)			3.0×10^{-4}	0.4×10^{-4}
$\tau_{FL}{}^b$ (toluene)/ns			1.51	1.48
$\tau_{singlet}{}^c$ (toluene)/ns			1.49	1.40
$\tau_{singlet}{}^c$ (THF)/ns			1.51	0.16
$\tau_{singlet}{}^c$ (BzCN)/ns			1.42	0.09
$\Phi_{triplet}{}^d$ (toluene)			0.60	0.29
$\Phi_{triplet}{}^d$ (THF)			0.43	—[g]
$\Phi_{triplet}{}^d$ (BzCN)			0.30	—[g]
$-\Delta G_{ET}{}^{\circ a}$/eV			0.10	0.68

[a] In benzonitrile; radius: (r_+) dibutylaniline = 3.7 Å; (r_+) naphthalene = 3.5 Å; (r_-) fullerene = 4.4 Å; donor–acceptor separation: (r_{D-A}) **8a** = 16.7 Å; (r_{D-A}) **8b** = 19.1 Å. [b] Measured at the 715 nm maximum, excitation at dendron ground state maximum. [c] Measured at the 880 nm maximum. [d] Measured at the 700 nm maximum. [e] Measured at the 413 nm maximum; excitation at 340 nm. [f] Measured at the 450 nm maximum; excitation at 380 nm. [g] Radical pair.

fullerene singlet (Fig. 2). Evidence that this energy transfer indeed takes place, comes from a set of decisive emission and excitation measurements.

The species evolving from energy transfer, namely, the fullerene singlet excited state (1.76 eV), has been identified *via* the characteristic fluorescence pattern[12] of a fulleropyrrolidine produced in nearly comparable quantum yields. Importantly, the complementary excitation spectrum of the fullerene emission in **8a**,**b** is virtually identical with the ground-state absorption and the excitation spectra of the reference compounds. To further test the above assignment, that is, a rapid singlet–singlet energy transfer, transient absorption spectroscopy was deemed necessary. Despite the unequivocal and nearly quantitative excitation (355 nm) of the dendrimer moieties no spectral evidence for the dendrimer's singlet–singlet absorption (*ca.* 650 nm) was found after the 18 ps laser pulse. Instead the spectral features are identical with the texture of the fullerene singlet excited state. Specifically, a characteristic maximum at 880 nm is a clear attribute of the fullerene singlet–singlet absorption. The rise time of the 880 nm absorption, representing the actual energy transfer event in **8a**,**b**, is, however, masked by the instrument response time and, therefore, prevents a meaningful kinetic analysis of the intramolecular reaction. On a longer time-scale the fate of the fullerene singlet excited state is identical to that known for a fulleropyrrolidine: intersystem crossing, driven by a strong spin-orbit coupling, governs the transformation (*ca.* 6.0 × 10^8 s^{-1}) of the singlet into the triplet excited state. The latter was identified by a long-lived (*ca.* 20 μs) and strongly absorbing triplet–triplet maximum (700 nm).

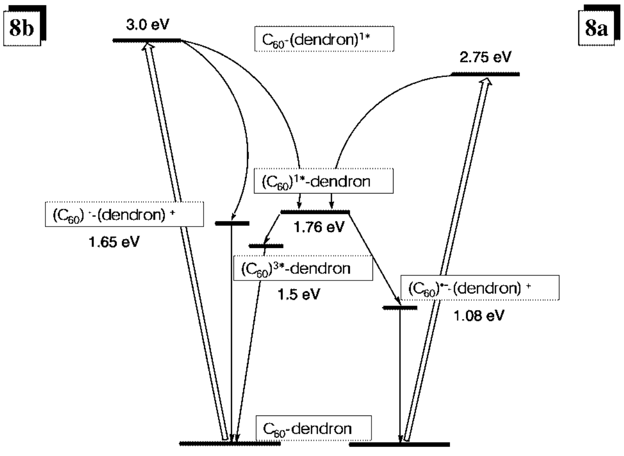

Fig. 2

Upon probing more polar THF and benzonitrile, the fullerene fluorescence in **8b** reveals a gradual decrease of up to 50%, while the dendron emission continued to be almost unchanged relative to that in toluene. This observation is consistent with an assumption that implies an energy transfer scenario, which is in competition with an activated electron transfer. Crucial support for this competitive synopsis evolves from the fullerene singlet lifetimes (Table 1), which are, despite the emission quenching, identical to those of a fulleropyrrolidine in all the solvents investigated.

8a, on the other hand, reveals much stronger reductions of the fullerene emission (up to 94%). Most importantly, much shorter lifetimes of the fullerene singlet excited state, the product of the initial energy transfer, were seen. This suggests, in sharp contrast to **8b**, a sequential energy and electron transfer starting from the initially excited dendron. In its final instance this sequence generates restrictively a radical pair, $C_{60}{}^{\cdot -}$–dendron$^{\cdot +}$.

Formation of the charge-separated state was established for both donor–acceptor systems by means of transient absorption spectroscopy. The fullerene π-radical anion displayed its typical near-IR absorption at 1000 nm, while the one-electron oxidized forms of the donors were evidenced through their absorption in the visible with λ_{max} *ca.* 480 nm (**8a**) and 540 nm (**8b**). It is important to note that for the dibutylaniline-containing dyad **8a** the radical pair, with lifetimes of 350 ns and 725 ns, in THF and benzonitrile, respectively is the sole product, corroborating the sequence of energy and electron transfer. Quite different is the situation for the poly(arylenevinylene) derivative **8b**: both energy transfer and electron transfer products were noted as superimposed spectral features.

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