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Energy Transfer in Calixarene-Based Cofacial-Positioned Perylene Bisimide Arrays

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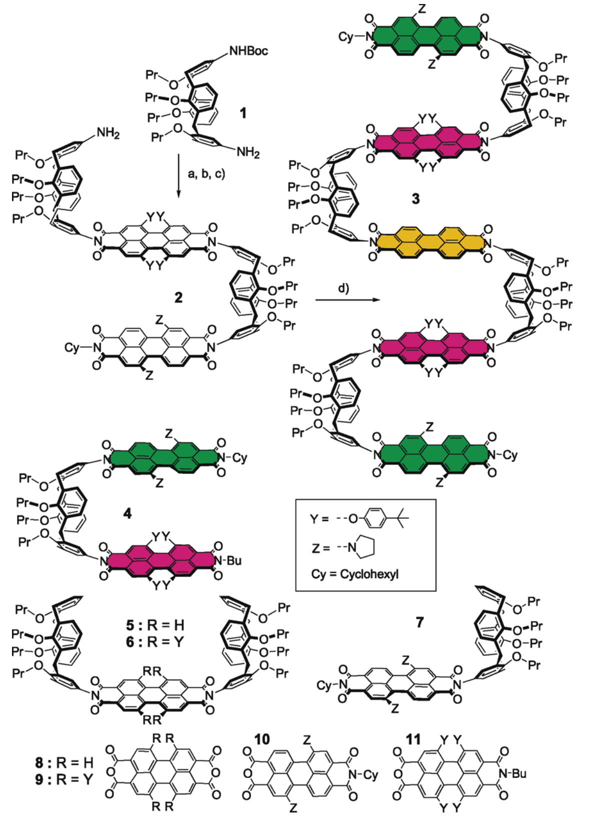
The high efficiency of natural photosynthesis is an outcome of proper organization of a multitude of chromophores in space that exhibit distinct absorption, emission, and redox properties.[1] Inspired by these biofunctional systems, many organic chemists aim at artificial structures containing multiple chromophores that provide sequential energy transfer, but the realization of high efficiency and directionality remains a challenging task. On one hand, this is due to the synthetic challenge to position dyes at predefined spatial positions, and, on the other hand, competing processes such as photoinduced electron transfer may take place between photoexcited dyes located in close proximity.[2] To date, the majority of covalent multichromophoric architectures showing efficient directional energy transfer are based either on dendrimers[3,4] (in general, with energy transfer from peripheral dyes to the core dye) or linear arrays of chromophores that are mostly linked by rigid π-conjugated spacers.[5,6] Despite the existence of interesting examples from nature (e.g., DNA) and from supramolecular chemistry (e.g., $\pi-\pi$-stacked dye aggregates),[7] there are only a few reports on covalent dye cascades where the chromophores are cofacially positioned (i.e., on top of each other).[8]

Here we report the first examples of calix[4]arene-based light harvesting arrays containing up to five perylene bisimide dyes (Scheme 1).[9] For the synthesis of array **3**, mono-Boc protected calix[4]arene **1** was reacted with the violet perylene bisanhydride (PBA) **9** in refluxing toluene/Et_3N. Deprotection and partial imidization with the green perylene monoimide (PMI) **10** in quinoline (catalyst $Zn(OAc)_2$, 150 °C) yielded the NH_2-functionalized precursor **2**, which was further reacted with the orange PBA **8** (quinoline/$Zn(OAc)_2$, 165 °C) to afford the desired array **3** containing five perylene bisimide chromophores in 18% yield. The bichromophoric calix[4]arene **4** was obtained from compound **1** by successively employing PMIs **11** and **10**. Compounds **2**−**7** were purified by column chromatography (SiO_2); compounds **3** and **4** were additionally purified by preparative TLC (SiO_2) and HPLC (SiO_2, normal phase).

Compounds **3** and **4** and the reference compounds **5**−**7** were studied by UV/vis absorption and steady state and time-resolved fluorescence spectroscopy in CH_2Cl_2. Their photophysical data are summarized in Table 1. For arrays **3** and **4**, no additional absorption or emission bands emerged, which indicates insignificant ground-state interaction between the chromophores. The UV/vis spectrum of **3** in Figure 1 shows the characteristic maxima of all three perylene bisimide (PBI) chromophores: the spectrum is composed of absorption bands of one orange PBI (maxima at 526 and 490 nm), two violet PBIs (at 579 nm), and two green PBIs (at 701 nm). Thus, the absorption properties of array **3** are determined by the individual patterns of the parent chromophoric units.

Scheme 1. Synthetic Routes and Chemical Structures of PBI−Calix[4]arene Arrays Studied[a]



[a] Reagents and conditions: (a) **9**, Et_3N, toluene, reflux, yield 10%; (b) CF_3COOH, CH_2Cl_2, rt; (c) **10**, $Zn(OAc)_2$, quinoline, 150 °C, yield 17% over two steps; (d) **8**, $Zn(OAc)_2$, quinoline, 165 °C, yield 18%.

Table 1. Photophysical Properties of Compounds **3**−**7** in CH_2Cl_2 [a]

	UV/vis abs		fluorescence emission					
	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	λ_{max} (nm)	Φ_{fl}	τ^b (ns)	τ^c (ns)	τ^d (ns)	τ^e (ns)
3	701	71100	739[f]	0.17[h]	5.2	1.2	5.3	4.9
4	701	44600	738[g]	0.18[i]		0.8	5.4	5.0
5	526	97200	532	<0.001				
6	579	54000	610	0.71		5.1		
7	701	47300	742	0.19				5.2

[a] All spectra were recorded at room temperature. [b] $\lambda_{ex} = 490$ nm, $\lambda_{det} = 825$ nm. [c] $\lambda_{ex} = 560$ nm, $\lambda_{det} = 610$ nm. [d] $\lambda_{ex} = 560$, $\lambda_{det} = 825$ nm. [e] $\lambda_{ex} = 680$, $\lambda_{det} = 825$ nm. [f] $\lambda_{ex} = 490$ nm. [g] $\lambda_{ex} = 560$ nm. [h] $\lambda_{ex} = 450$ nm. [i] $\lambda_{ex} = 560$ nm.

Upon photoexcitation of compound **3** at $\lambda_{ex} = 490$ nm (almost exclusive absorption of the inner orange dye unit), fluorescence emission of the outer green PBI chromophore at 744 nm is observed. Spectra in Figure 1 also show very weak concomitant fluorescence emission from the violet PBI unit at 610 nm. Quantum yields of

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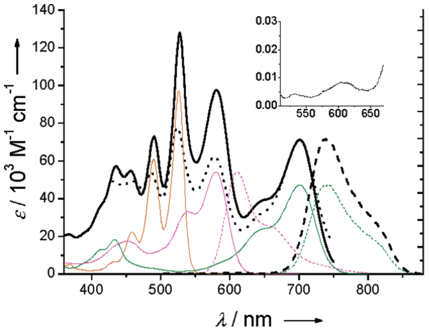

Figure 1. Optical spectra of compounds **3**, **5**−**7**, all in CH_2Cl_2. UV/vis absorption of **3** (black, solid), fluorescence emission of **3** (black, dashed; $\lambda_{ex} = 490$ nm), fluorescence excitation of **3** (black, dotted; $\lambda_{det} = 850$ nm), UV/vis absorption of **5** (orange, solid), UV/vis absorption of **6** (violet, solid), fluorescence emission of **6** (violet, dashed), UV/vis absorption of **7** (green, solid), and fluorescence emission of **7** (green, dashed). Inset: magnified fluorescence emission spectrum of **3**.

arrays **3** and **4** were measured for three different excitation wavelengths ($\lambda_{ex} = 450$, 560, and 615 nm); for **3**, values of 0.17, 0.14, and 0.15, and for **4**, values of 0.19, 0.18, and 0.21, respectively, were determined. Thus, the quantum yield of both arrays are independent of excitation wavelength. Furthermore, these values are very similar to that of the green reference compound **7** ($\Phi_{fl} = 0.19$). In the fluorescence excitation spectra of compounds **3** and **4** ($\lambda_{det} = 850$ nm) all absorption bands of the parent chromophores are observed, and thus all perylene units contribute to the emission from the S_1 state of the green PBI. Obviously, the fluorescence emission properties of both compounds are determined by the lowest energy S_1 state of the green PBI. Furthermore, a significant decrease in the fluorescence lifetime of the violet PBI chromophore for compounds **3** and **4** ($\tau = 1.2$ and 0.8 ns, respectively) is observed compared to reference compound **6** ($\tau = 5.1$ ns).[10] This indicates efficient energy transfer.

The significant emission of compound **3** upon excitation of the orange dye at $\lambda_{ex} = 490$ nm is particularly impressive because reference compound **5** is almost nonfluorescent due to photoinduced electron transfer (PET) between the electron-poor PBI unit and the electron-rich calix[4]arene substituents.[11] Thus, the energy transfer processes to adjacent chromophore units in compound **3** have to be significantly faster than the fluorescence quenching by PET processes from the neighboring calix[4]arene unit. The optical spectra and photophysical data of **4** suggest equally efficient energy transfer (see Table 1 and Figures S3 and S5 in Supporting Information).

Assuming a Förster-type resonance energy transfer (FRET), the transfer rate depends on the following factors: the extent of spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor, the quantum yield of the donor, the relative orientation of the donor and acceptor transition dipoles, and the distance between the donor and acceptor molecules.[12] The Förster distance R_0 (distance at which the energy transfer efficiency is 50%) can be calculated according to the simplified equation $R_0 = 0.211[\kappa^2 n^{-4} \phi_D J(\lambda)]^{1/6}$, where κ^2 is the orientation factor, n the refractive index of the medium, ϕ_D the fluorescence quantum yield of the donor in the absence of an acceptor, and $J(\lambda)$ the overlap integral of the donor emission and the acceptor absorption spectra. Employing this equation, we exemplarily calculated R_0 for compound **4** as 62.7 Å, with $\kappa^2 = 1$ (assuming parallel orientation of chromophores[13]), n (CH_2Cl_2) $= 1.4240$, $\phi_D = 0.71$, and $J(\lambda) = 3.98 \times 10^{15}$ M^{-1} cm^{-1} nm^4. The rate of energy transfer from a donor to an acceptor is given by $k_T = [1/\tau_{DA} - 1/\tau_D]$. With a τ_{DA} (decay of the donor in the presence of the acceptor) value of 0.8 ns for compound **4** (see Table 1), k_T is calculated as 1.05×10^9 s^{-1} for this compound. Thus, the efficiency of the energy transfer E can be calculated according to the equation $E = [1 - \tau_{DA}/\tau_D]$ as $E = 0.85$.

In summary, we presented perylene bisimide arrays containing up to five chromophores ordered in a cofacial arrangement by calix[4]arene spacer units. In our system composed of orange, violet, and green perylene bisimide chromophores, remarkably efficient energy transfer processes could be observed even from originally nonfluorescent dye units. This demonstrates the potential of cofacially oriented chromophores for the construction of light harvesting arrays, which we will further elaborate toward regulation of energy and electron flow.

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Supporting Information Available: Experimental details and spectral data of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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