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Hexa-*peri*-hexabenzocoronene/perylenedicarboxymonoimide and diimide dyads as models to study intramolecular energy transfer

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Abstract—Star-like and butterfly-shaped dyads based on hexa-*peri*-hexabenzocoronene (HBC) as donor and perylenedicarboxymoniimide (PMI) or diimide (PDI) as acceptor were synthesized by Sonogashira coupling reactions and Diels–Alder cycloadditions. Intramolecular energy and electron transfer were investigated by steady-state fluorescence spectroscopy.

Photoinduced energy and electron transfer between photoactive or electroactive donor (D) and acceptor (A) moieties have attracted interest due to potential applications in artificial photosynthesis systems[1] and organic solar cells.[2] Thus many binary covalently and noncovalently linked donor–acceptor systems have been designed and investigated.[3] Donor molecules such as porphyrins, oligo-(poly-) phenylene vinylenes, ferrocene, and others and acceptors such as fullerenes and rylene carboximides have commonly been used in the dyads. Recently, we found that a photodiode based on a simple solution processed blend of a liquid crystalline hexa-*peri*-hexabenzocoronene (HBC) derivative and crystalline perylenecarboxydiimide (PDI) displayed high external quantum efficiency (EQE) and power efficiency.[4] This result prompted us to prepare covalently linked HBC–perylene dicarboximide dyads and study their fundamental energy and electron transfer processes. Herein, the syntheses of two of such model systems, that is, a star-like HBC–perylenecarboxmonoimide (PMI) (**1**) and a butterfly-shaped HBC–PDI molecule **2** (Chart 1), have been achieved and the intramolecular energy/electron transfers have been investigated.

Compound **1** was synthesized in 58% yield by six-fold Diels–Alder cycloadditions between compound **4**[5] and PMI substituted tetraphenylcyclopentadienone **5**[6] in refluxing diphenyl ether (Scheme 1). Compound **2** was synthesized in 91% yield by a four-fold Sonogashira coupling reaction between the tetrakis(4-iodophenyloxy)-substituted PDI **8**[7] and a monoethynylated HBC **7**, which was obtained by a Sonogashira coupling reaction between monobromo-HBC **6**[8] and trimethylsilylacetylene (TMSA) followed by desilylation after treating with tetrabutylammonium fluoride in THF. Compound **2** possesses very poor solubility in common solvents such as toluene, chloroform, THF, and dichloromethane but is easily dissolved in carbon disulfide and dichlorobenzene, indicating its strong tendency to aggregate. All the compounds were characterized by MALDI-TOF mass spectrometry, NMR spectroscopy, and elemental analysis.

The combined UV–vis spectra of compounds **1**,**4**, and model compound **3** (Chart 1) in chloroform ([PMI] = 1.0×10^{-6} M) are shown in Figure 1. Compound **1** displayed the characteristic absorption bands of both HBC (380 nm and 409 nm) and PMI (502 nm and 522 nm) chromophores. The bathochromic shift of the longest wavelength absorption band in molecule **1** with respect to compound **3** is ascribed to the extended conjugation between the PMI and the dendrons. No characteristic charge transfer band was detected in the longer wavelength region. Due to the large overlap of the emission spectra of **4** (centered at about 530 nm) with the absorption spectra of compound **3** (from ca. 400–550 nm), effective intramolecular energy transfer occurred as disclosed in the fluorescence measurements (Fig. 1b). The emission spectra of the compound **1** excited at either 380 nm (absorption maximum of HBC) or 502 nm (absorption maximum of PMI) gave the identical emission band between 520 nm and 750 nm, a typical emission of the PMI moiety. The lack of emission

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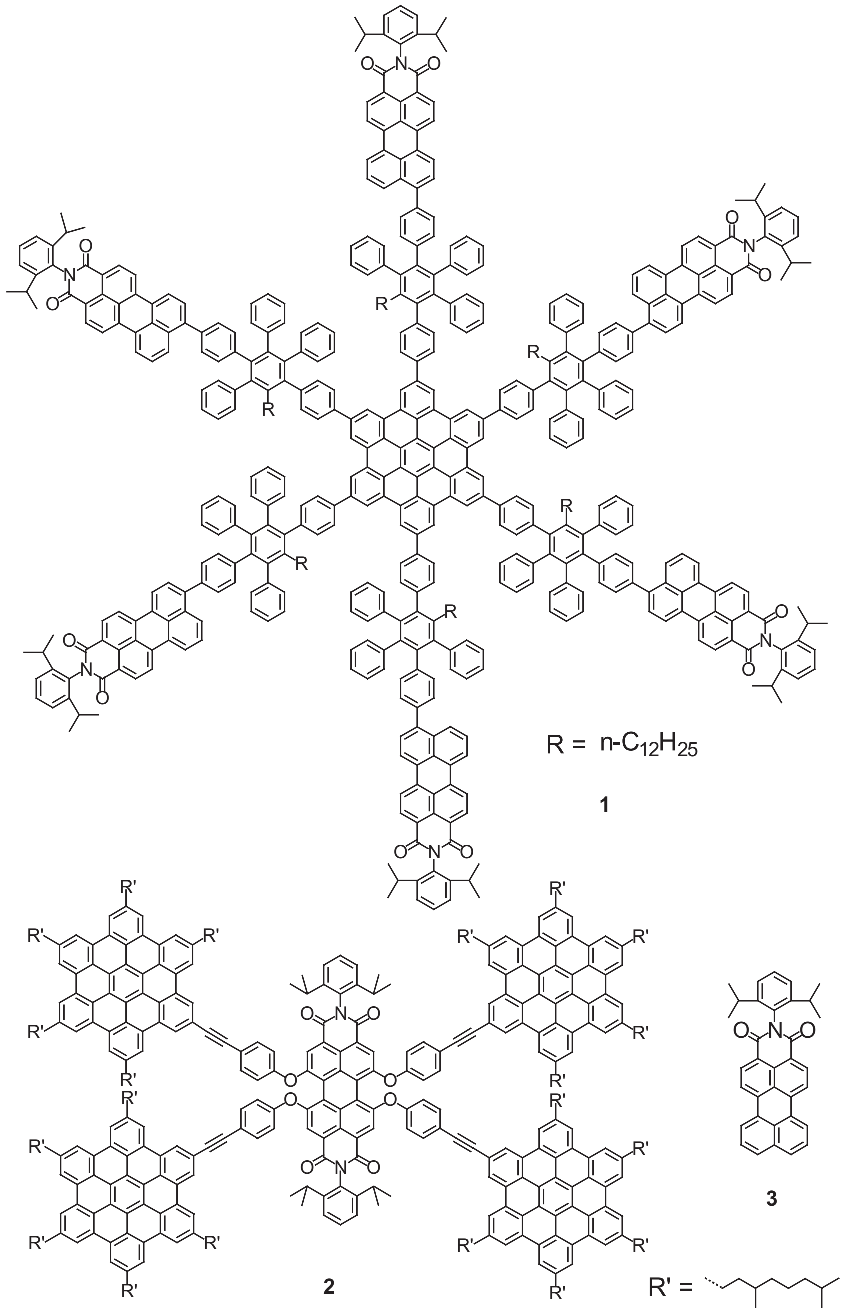
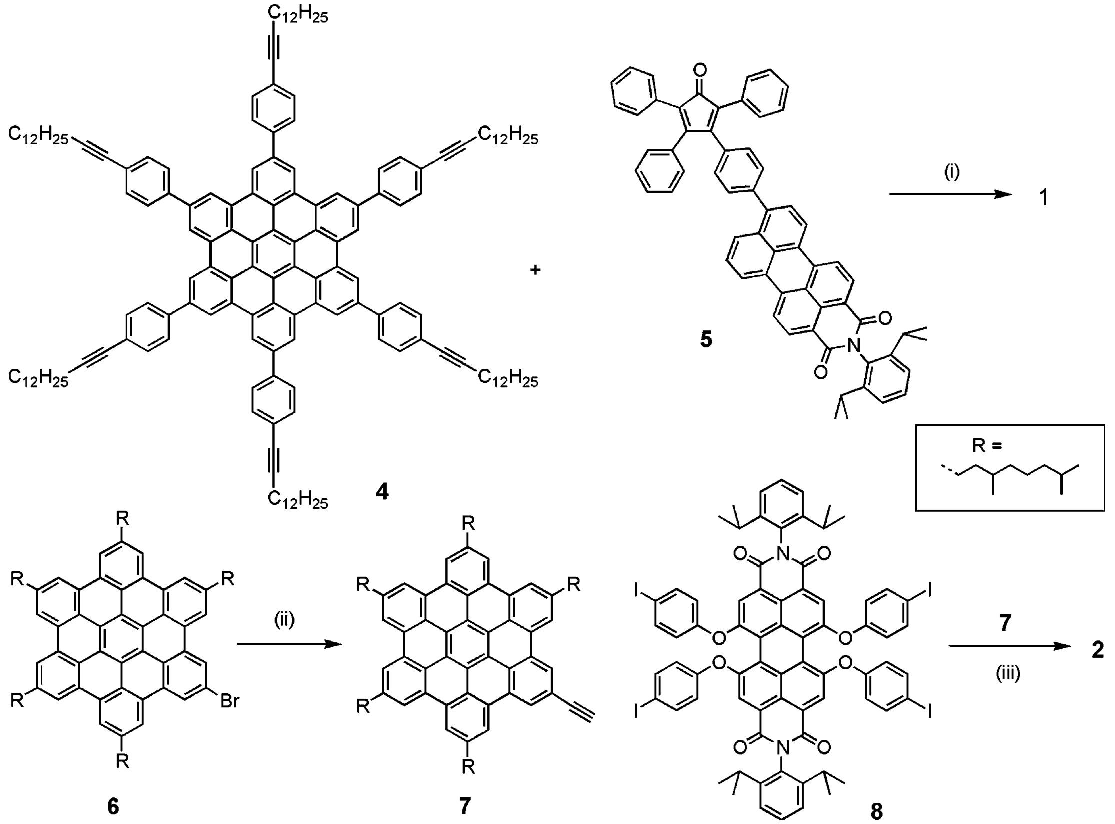


Chart 1.

from the HBC chromophore indicated fast intramolecular energy transfer, after photoexcitation, from the HBC core to the PMI groups at the peripheries. The bathochromic shift of the emission band relative to that of PMI can also be explained by the effect of conjugation. On the other hand, the intensity of the emission maximum decreased 57% compared to that of PMI at the same chromophore concentration, indicating that a possible intramolecular electron transfer process also occurred.

The combined UV–vis absorption and fluorescence spectra of compounds **7** and **8** in 1,2-dichlorobenzene are shown in Figure 2. The fluorescence spectrum of **7** completely overlapped with the absorption band of compound **8**, thus allowing possible efficient energy or electron transfer in the donor–acceptor dyad **2**. As a result, the fluorescence of the PDI moiety in compound **2** was completely quenched when excited at either the absorption maximum of HBC or the PDI chromophores, indicating an efficient intramolecular electron transfer between electron-donor HBC and electron acceptor after photoexcitation (Fig. 2b). On the other hand, the UV–vis absorption spectrum of compound **2** possessed the absorption bands of both HBC and PDI, but no obvious charge transfer band at long wavelength. The more effective charge separation in the HBC–PDI dyad than HBC–PMI dyad clearly shows that PDI is a stronger acceptor. For achieving charge separation in photovoltaics, the HBC–PDI system is



Scheme 1. (i) Diphenyl ether, 250 °C, 58%; (ii) (a) TMSA, $Pd(PPh_3)_4$, CuI, Et_3N, 80 °C, 95%; (b) TBAF, THF, 89%; (iii) $Pd(PPh_3)_4$, CuI, Et_3N, rt, 91%.

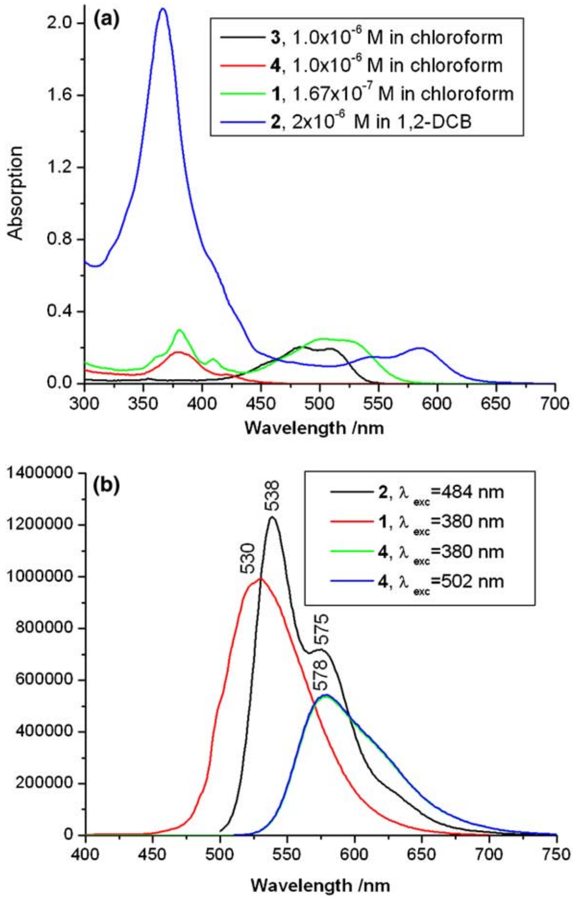


Figure 1. UV–vis and fluorescence spectra of the compounds **1**, **2**, **3** and **4**.

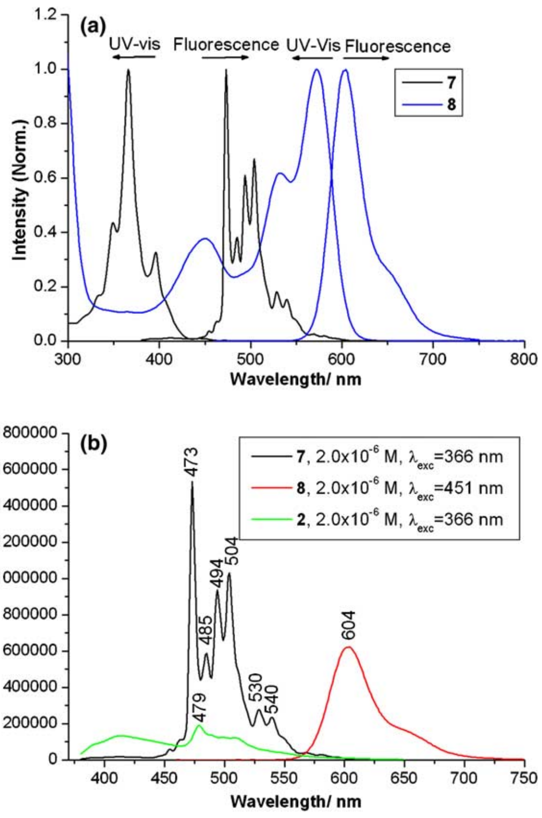


Figure 2. (a) Normalized UV–vis and fluorescence spectra of compounds **7** and **8** in 1,2-dichlorobenzene; (b) combined fluorescence spectra of compounds **2**,**7**, and **8** in 1,2-dichlorobenzene.

thus a better choice. Ongoing time-resolved absorption and fluorescence spectroscopic studies will disclose these electronic processes in detail.

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Supplementary data

Synthetic details for all new compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.12.094.

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