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Core-Extended Perylene Tetracarboxdiimides: The Homologous Series of Coronene Tetracarboxdiimides

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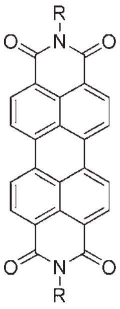
ABSTRACT



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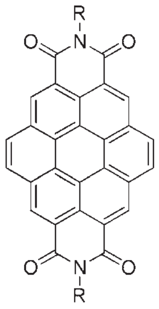

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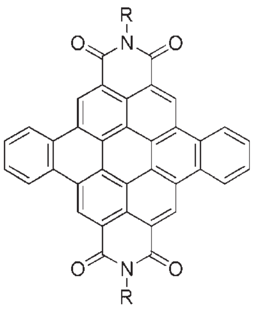

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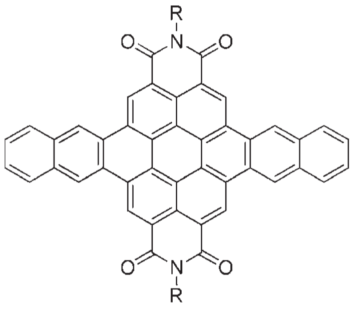

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Two novel coronenediimide (CDI) derivatives, CDI 2 and dinaphtho-CDI 4, were synthesized via straightforward synthetic routes completing the homologous series of coronene tetracarboxdiimides, which show remarkable optical properties with absorption wavelengths ranging from 380 to 600 nm, high absorption coefficients, and high fluorescence quantum yields.

Coronene dyes, both the pure hydrocarbon derivatives and coronene tetracarboxdiimides (CDIs), have been the focus of research for many years. Thus various synthetic routes to coronene and core-expanded analogs are known,[1] but most of them suffer from numerous reaction steps and low yields.[2] Furthermore only a few reactions are known for the preparation of CDIs,[3] which can be regarded as bay-extended perylene tetracarboxdiimides (PDIs),[4] and for this reason most syntheses start from the latter. Particularly the enlargement of the π-system along the short molecular axis of PDI (**1**) attracts huge interest[5] and offers access to various biological[6] as well as organic electronic applications[7] such as light-emitting diodes[3c] and field-effect transistors.[8] Herein we present the straightforward syntheses of two novel chromophores,

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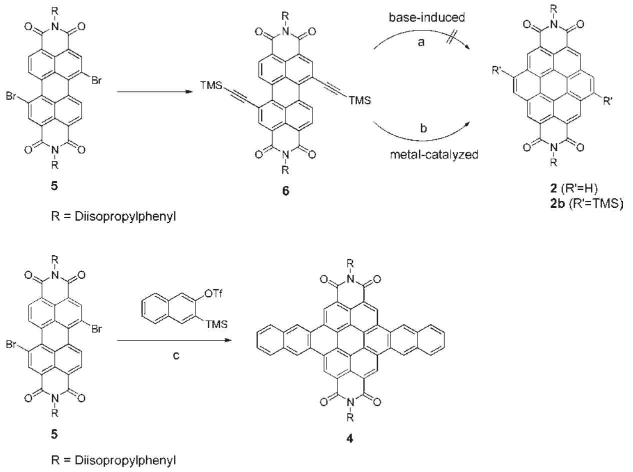
namely coronene tetracarboxdiimide **2** and dinaphthocoronene tetracarboxdiimide **4** (Scheme 1). In combination with the already known dibenzo-CDI **3**[9] we are now able to present a new homologous series of symmetrically extended coronene tetracarboxdiimides by a stepwise enlargement of the perylene core.

Scheme 1. Synthesis of CDI **2** and Dinaphtho-CDI **4**[a]



[a] (a) DBU, toluene, 60 °C-reflux, 6–24 h; (b) $PtCl_2$, toluene, 90 °C, 48 h; (c) $Pd(dba)_2$, $P(o\text{-tol})_3$, CsF, toluene, CH_3CN, reflux, 18 h.

Both synthetic routes start from the corresponding 1,7-dibromoperylene tetracarboxdiimide **5** which usually contains various amounts of the 1,6-isomer, but for symmetry reasons even the mixture of isomers is suitable to form the appropriate products. In the case of the formation of the CDI **2** the dibromo-PDI **5** was coupled under Sonogashira conditions with bis-(trimethylsilyl)-acetylene as the first step to afford **6** in 74% yield. Unfortunately the second step including the application of DBU (1,8-diazabicyclo-[5.4.0]undec-7-ene) to cyclize the ethinyl-precursor **6** resulting in **2** as already described for its alkyl substituted congener was not successful in this case.[10] Neither the bis-(trimethylsilyl)-coronenediimide **2b** nor the requested CDI **2** itself could be obtained. Instead a $PtCl_2$ catalyzed carbocyclization[11] of the trimethylsilylethinyl groups in toluene proved to be the right choice to achieve **2** in a reasonable yield, while the trimethylsilyl groups were cleaved within this process.

In contrast to the preparation of CDI **2**, the synthesis of dinaphtho-CDI **4** was carried out in one step according to the analogous procedure for the synthesis of dibenzo-CDI via *o*-(trimethylsilyl)phenyl triflate recently described by us.[9] It appeared in this case that using the dibromo-PDI **5** together with the commercially available 3-(trimethylsilyl)naphthyl-trifluormethane-sulfonate in a mixture of toluene and acetonitrile at reflux furnished the desired product **4** in 46% yield.

Table 1. Optical and Electrochemical Properties According UV and CV Measurement

Compound	λ_{max}/nm (log ε)	λ_{em}/nm (Φ)	ΔE_{opt}/eV[a]	E_{LUMO}/eV[b]
PDI **1**	458 (4.1)	540	2.00	−3.86
	489 (4.5)	575		
	525 (4.7)[12]	(0.98)[12]		
CDI **2**	397 (4.4)	498	2.46	−3.62
	421 (4.7)	534		
	494 (4.2)	(0.69)		
Dibenzo-CDI **3**	460 (4.5)	505	2.42	−3.75
	494 (4.8)[13]	(0.80)[13]		
Dinaphtho-CDI **4**	496 (4.4)	584	2.07	−3.84
	530 (4.4)	(0.42)		
	573 (4.4)			

[a] Optical band gap according UV/vis absorption (onset method). [b] Energy level of lowest unoccupied molecular orbital according cyclovoltammetry.

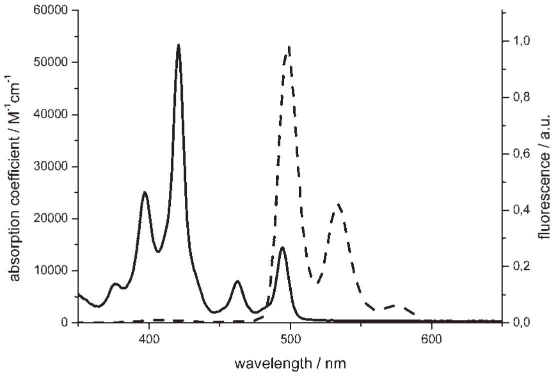


Figure 1. Absorption (solid line) and emission spectrum (dashed line, λ_{ex} = 410 nm) of CDI **2** in toluene.

It is already known from the established CDIs and dibenzo-CDIs that an extension of the core of perylene tetracarboxdiimides in some cases induces a shift to shorter wavelengths in their absorption spectra, which is in contrast to the extension along their long molecular axis.[4] Nevertheless starting from CDI **2** (λ_{max} = 421 nm) (Figure 1) leading to dibenzo-CDI **3** (λ_{max} = 494 nm)[9] and dinaphtho-CDI **4** (λ_{max} = 496, 530, 573 nm) (Figure 2), a stepwise bathochromic shift can be observed for each extension along the short molecular axis. It is noteworthy at this point that the novel dinaphtho-CDI **4** on its own shows a broad absorption from 450 to 600 nm and an

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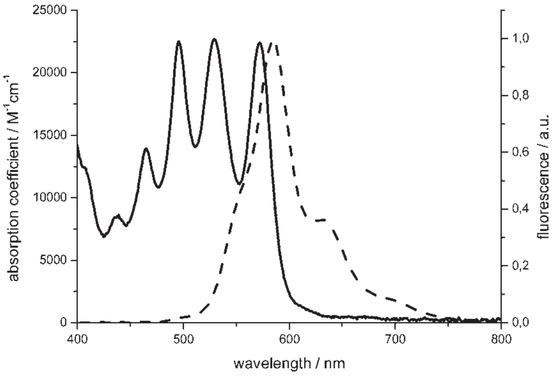

Figure 2. Absorption (solid line) and emission spectrum (dashed line, $\lambda_{ex} = 510$ nm) of Dinaphtho-CDI **4** in toluene.

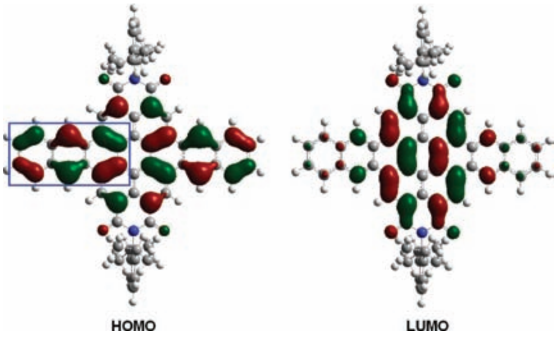

Figure 3. Molecular orbitals of Dinaphtho-CDI **4**. Abbreviations: (HOMO) highest occupied molecular orbital, (LUMO) lowest unoccupied molecular orbital (Gaussian 03W, AM1).

absorption coefficient of 22 700 M^{-1} cm^{-1} giving the substance a bright purple-red appearance. Furthermore its absorption spectrum does not exhibit the typical perylene vibronic fine structure, as this is observed for most perylene and coronene tetracarboxdiimides. Instead it shows an anthracene-like absorption behavior.[14] An explanation for this can be given from the respective frontier orbital calculations (Gaussian 03W, AM1), which reveal the influence of the anthracene HOMO on the electronic structure of **4** (Figure 3). As expected, the absorption spectrum of the coronene tetracarboxdiimide **2** resembles that of the alkyl substituted CDI, which was already described earlier.[10] The small Stokes shifts of about 5–15 nm, which are typically observed for perylene and coronene tetracarboxdiimides, lead to fluorescence maxima of 498 and 534 nm with a quantum yield of 69% for CDI **2** and an emission at 584 nm ($\Phi = 42\%$) for the dinaphtho-CDI **4** (Table 1).

In summary we presented the syntheses of CDI **2** and dinaphtho-CDI **4** as two novel derivatives in the series of coronene tetracarboxdiimides. Both compounds are available via short and straightforward routes in reasonable overall yields starting from the well-known dibromo-PDI **5**. With this knowledge we are now able to tune the properties of perylene and coronene tetracarboxdiimides not only by the extension at their long molecular axis but also at their short axis. Additionally, the coronene tetracarboxdiimides of the presented series show versatile absorption and emission behavior with high absorption coefficients and fluorescence quantum yields. Especially the dinaphtho-CDI **4** offers interesting optical properties, as its absorption spectrum covers a broad range of the visible light. Additionally the similarity of the LUMO energy levels of **4** and the established PDI **1**[7] makes compound **4** a promising dye for organic photovoltaics. In analogy to known perylene dyes[15] one can furthermore envision its use as a red emitting dye in organic light emitting diodes due to its strong fluorescence at 584 nm. Finally the reaction leading to dinaphtho-CDI **4** opens the possibility to achieve even larger extended coronene diimides.

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Supporting Information Available. Full experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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