Facile synthetic approach to novel core-extended perylene carboximide dyes†

Sibylle Müller and Klaus Müllen*

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The straightforward synthesis of two new classes of core-extended perylene chromophores, dibenzocoronene tetracarboxdiimide and indenoperylene dicarboxmonoimide, proves that directional enlargement of the aromatic π-system leads to tailored bathochromic and hypsochromic shifts.

Rylene tetracarboxdiimides **1–3** as chromophores with an extended aromatic π-system display exceptional chemical, thermal, and photochemical stability with high extinction coefficients.[1] Their use has been explored for such demanding applications as optoelectronic devices,[2] thermographical processes,[3] photovoltaic devices,[4] energy transfer cascades,[5] light emitting diodes,[6] and NIR absorbing systems.[7] Extension of the aromatic system along the long molecular axis from perylene-, **1**, to terrylene-, **2**,[8] and quaterrylene tetracarboxdiimides, **3**,[9] (Fig. 1) induces a large bathochromic shift reaching an absorbance maximum at 780 nm for **3** and a linear increase of the extinction coefficient up to 170,000 M^{-1} cm^{-1}. However, enlargement of the π-system does not always cause a shift to longer wavelengths. The coronene tetracarboxdiimides **4** can be regarded as perylene tetracarboxdiimides expanded along the short molecular axis. Their absorbance is hypsochromically shifted by 100 nm to a maximum at 428 nm compared with that of the perylene derivative, leading to a yellow colour.[10] Stable, yellow chromophores with high molar extinction coefficients are generally difficult to obtain, as ε often increases with the size of the aromatic system, but these usually absorb more bathochromically.[1c] Basic chemical modification of the red or orange perylene core facilitates a shift of colour to either direction, yellow or violet.

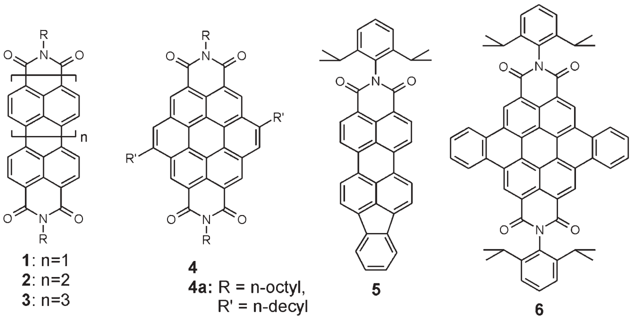
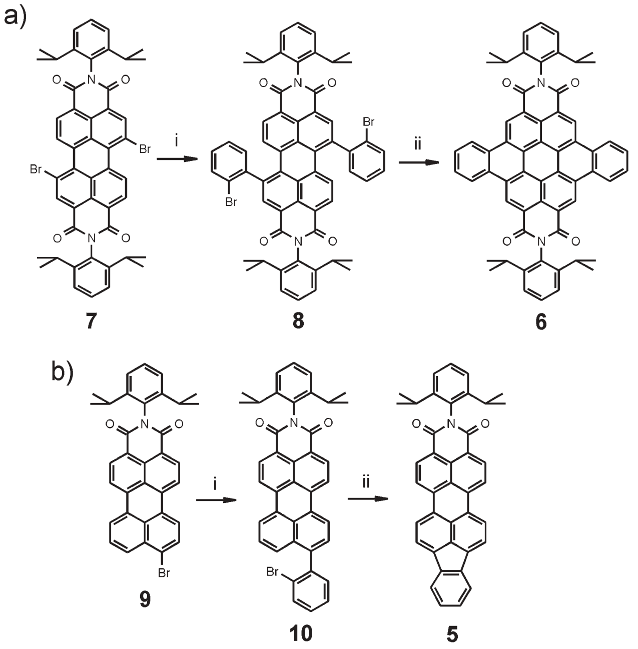


Fig. 1 Rylene- and coronene carboximide derivatives.

Diverse methodologies to functionalize the perylene aromatic core are a topic of current research to extend the range of application of these chromophores as functional dyes or improve their performance in devices. Perylene tetracarboxdiimides, functionalized in one bay-region using Diels–Alder reactions followed by reduction or mono-nitration and cyclization are known.[11] Diindenoperylenes are commercially available pigments which are synthesized by intermolecular oxidative coupling of fluoranthene units.[12]

Herein, we report a straightforward, two-step synthesis to enlarge the aromatic π-system of available perylene derivatives, leading to two novel chromophores, namely the indenoperylene dicarboxmonoimide **5** and the dibenzocoronene tetracarboxdiimide **6**. Both represent a new class of benzo-condensed derivatives of the perylene core.

1,7-Dibromoperylene tetracarboxdiimide **7** usually contains various amounts of the corresponding 1,6-isomer.[13] An advantage of this synthesis is that both isomers react to form the same desired product. The reaction of 1,7-dibromoperylene tetracarboxdiimide **7** with 2-bromophenylboronic acid under Suzuki conditions afforded **8** in 53% yield (Scheme 1). Self-reaction of



Scheme 1 *Reagents, conditions and yields:* a) (i) 2-bromophenylboronic acid, $(Ph_3P)_4Pd$, K_2CO_3 (aq), toluene, ethanol, 75 °C, 12 h, 53%; (ii) $(Ph_3P)_2PdCl_2$, DBU, DMA, 160 °C, overnight, 46%; b) (i) 2-bromophenylboronic acid, $(Ph_3P)_4Pd$, K_2CO_3 (aq), toluene, ethanol, 75 °C, 4 h, 85%; (ii) $(Ph_3P)_2PdCl_2$, DBU, DMA, 160 °C, overnight, 30%.

Max-Planck-Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany. E-mail: muellen@mpip-mainz.mpg.de; Fax: +49 6131 379350; Tel: +49 6131 379150

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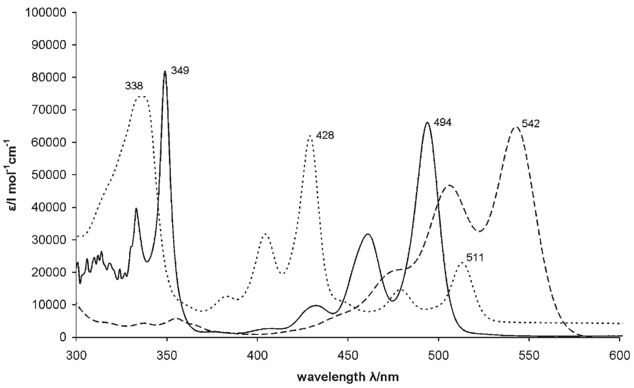

Fig. 2 Absorption spectra of **6** (solid line), **4a** (dotted line) and **5** (dashed line) in $CHCl_3$.

2-bromophenylboronic acid is known to not occur under these conditions.[14] One- and two-fold debrominated products of **8** were observed in minor amounts (*ca.* 10%) but this mixture was directly used successfully for the next step, in which palladium-catalyzed dehydrohalogenation[15] with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dimethyl acetamide (DMA) furnished dibenzocoronene tetracarboxdiimide **6** in 46% yield. Analogously, the 9-bromoperylene dicarboxmonoimide **9** was Suzuki coupled with 2-bromophenylboronic acid under the same conditions and yielded **10** in 85% (also containing *ca.* 10% of debrominated **10**). Treatment of this mixture with DBU and a palladium catalyst promoted cyclization to a five-membered ring, resulting in the indenoperylene dicarboxmonoimide **5** with a yield of 30%.

Both coronene derivatives **6** and **4a** are soluble in common organic solvents such as dichloromethane, chloroform, or toluene. In the region of shorter wavelengths, up to 400 nm, the spectrum of **6** shows a sharp band with a defined structure at 349 nm; whereas, the band with a maximum absorbance of 338 nm in the spectrum of **4a** is broad (Fig. 2). Only one band with the typical perylene vibronic structure can be seen at longer wavelength with an absorbance maximum at 494 nm (ε = 66,000 M^{-1} cm^{-1}) which gives rise to the yellow colour. The extinction coefficient of **6** at 494 nm is comparable with the extinction coefficient of **4a** at 428 nm (ε = 62,000 M^{-1} cm^{-1}).[13] The photochemical stability of **6** is much higher than that of **4a**: the extinction coefficient of a chloroform solution of **4a** under UV-irradiation[16] dropped to 34% of its initial value after 10 h. Dibenzocoronene **6** still showed an extinction coefficient maximum of 76% under the same conditions. Presumably, the aromatic bonds between the 5- and 6-positions and the 11- and 12-positions in the coronene tetracarboxdiimides **4** have some double bond character, which makes them less stable. These bonds are stabilized in the dibenzocoronene tetracarboxdiimide **6**, leading to the higher stability.

The yellow solution of **6** appears brighter and greener than that of **4a**, given that there is no absorbance above 515 nm for **6**. Dibenzocoronene **6** has a bright fluorescence with a quantum yield of 80%, high compared with other yellow fluorophores, *e.g.* acridine yellow, which has a fluorescence quantum yield of 47%.[17] The indenoperylene **5** has an absorption band with a maximum at 542 nm (ε = 65,000 M^{-1} cm^{-1}) which also shows the typical perylene vibronic structure, causing a violet appearance of the powder and a reddish-violet hue in chloroform solution. The indeno-substitution causes a bathochromic shift of the absorbance maximum by 15 nm compared to the perylene tetracarboxdiimide. The fluorescence maximum of **5** is at 565 nm.

In summary, the synthesis of two novel classes of chromophores was detailed, namely the dibenzocoronene tetracarboxdiimides and the indenoperylene dicarboxmonoimides, *via* a short and facile route. The palladium-catalyzed ring annulation reaction has opened the way to the enlargement of the aromatic π-system and has thereby led to new chromophores based on core-extended perylene dyes. The UV/vis spectrum of dibenzocoronene tetracarboxdiimide **6** is characterized by sharp absorption bands between 400 nm and 500 nm, leading to a brilliant greenish-yellow appearance. Insoluble derivatives of this new class of chromophore may be useful as new stable yellow pigments. Further, one can envision use in optoelectronic devices such as field effect transistors, as good phase forming ability is expected when decorated with long alkyl chains. The class of indenoperylene dicarboxmonoimide **5** with an absorbance maximum of 542 nm represents a new class of violet dyes and pigments. The application of **5** for frequency doubling in laser welding will be investigated. Both chromophores have a high photochemical stability and a bright fluorescence.

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