along the molecular long axis, we have obtained the higher homologues terrylenebis(dicarboximide) (**2**) and quaterryl-enebis(dicarboximide) (**3**; Figure 1). In comparison to the absorption maximum of perylenebis(dicarboximide) (**1**),
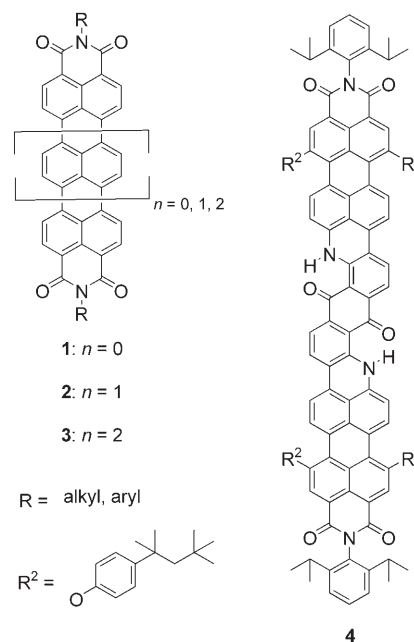

Figure 1. Chemical structures of rylenebis(dicarboximide)s and bis(rylenedicarboximide)-*a,d*-1,5-diaminoanthraquinone.

NIR Dyes

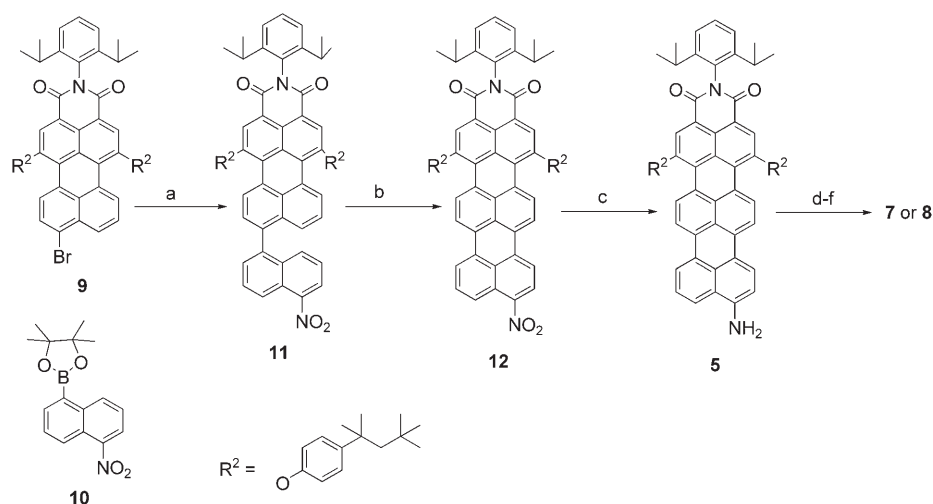# Pentarylene- and Hexarylenebis(dicarboximide)s: Near-Infrared-Absorbing Polyaromatic Dyes**

*Neil G. Pschirer, Christopher Kohl, Fabian Nolde, Jianqiang Qu, and Klaus Müllen**

Although a large variety of dyes are commercially available today, there is an ongoing need for new chromophoric systems[1–3] and low-band-gap materials.[4] For example, near-infrared (NIR) emission has received increased attention for applications in bioassays and medicine[5] while NIR absorption is demanded for laser-welding of plastics or efficient blocking of heat rays. Most of the commercially available NIR materials are not suitable for such purposes owing to their insufficient stability.[6] Over the last decade we have developed several NIR-absorbing polyaromatic dyes.[7–9] By extending the π system of perylenebis(dicarboximide)s

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those of **2** and **3** are shifted bathochromically. Quaterrylene-bis(dicarboximide) (**3**) is a deeply colored dye with a strong absorption in the NIR region.[9] Both chromophores exhibit high thermal, chemical, and photochemical stabilities together with high extinction coefficients.[8–11] Recently we introduced an alternative and surprisingly facile approach toward NIR absorbers by the coupling and fusion of a perylenedicarboximide with a 1,5-diaminoanthraquinone to afford bis(perylenedicarboximide)-*a,d*-1,5-diaminoanthra-quinone (**4**), a NIR absorber with a remarkably strong absorption around 1100 nm and extraordinary thermal and photochemical inertness.[7]

If we take into consideration the outstanding role of quaterrylenebis(dicarboximide) (**3**), then the extension of the framework of rylenebis(dicarboximide)s appears a logical next step to induce a narrowing of the HOMO–LUMO gap, thereby causing a further bathochromic shift in the absorption spectrum.[12] Herein, we describe the synthesis and attractive optical properties of homologous ladder-type chromophores, namely the pentarylenebis(dicarboximide)s **6** and **7** as well as the hexarylenebis(dicarboximide) **8**.

We selected two different construction concepts for the penta- and hexarylenebis(dicarboximide)s **6**, **7**, and **8**: 1) The "nitronaphthalene method" in which one nitronaphthalene unit is attached to a perylenedicarboximide, the bisaryl product is fused, and the nitro group is replaced by a halide to provide a halogen-substituted terrylenedicarboximide as a precursor for the penta- or hexarylenebis(dicarboximide)s **7** and **8** (Scheme 1); or 2) the "bisbromorylene method" in

Scheme 1. Reagents and conditions: a) [Pd(PPh$_3$)$_4$], K$_2$CO$_3$ (aq), ethanol/toluene, 80°C, 16 h, 100%; b) DBN, NaO*t*Bu, diglyme, 70°C, 2 h 35%; c) Pd/C, H$_2$, ethanol/CHCl$_3$, room temperature, 15 h, 78%; d) NaNO$_2$, HCl, THF, Et$_2$O, MeCN, −10°C, NaI; e) for **8**: B(OR)$_2$, [Pd(PPh$_3$)$_4$], KOAc, toluene; for **7**: **9**, K$_2$CO$_3$ (aq), [Pd(PPh$_3$)$_4$], ethanol/toluene; f) K$_2$CO$_3$, ethanolamine, 135°C. DBN = 1,5-diazabicyclo-[4.3.0]non-5-ene.

which two perylenedicarboximides are coupled to a bisbromo-monaphthalene or -perylene and fused in a one-step (**6**) or two-step (**7** and **8**) sequence to form the corresponding penta- or hexarylenediimide (Schemes 2 and 3).
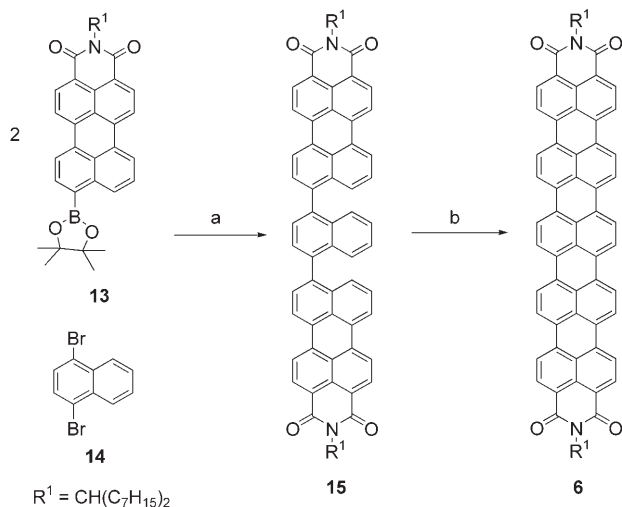
Scheme 2. Reagents and conditions: a) [Pd(PPh$_3$)$_4$], K$_2$CO$_3$ (aq), ethanol/toluene, 80°C, 72%; b) AlCl$_3$, chlorobenzene, 75°C, 20 min, 24%.

The nitronaphthalene method requires the boronic ester of 1-bromo-5-nitronaphthalene (**10**) which was prepared according to the procedure of Miyaura et al.[13] with bis(pinacolato)diboron and [PdCl$_2$(dppf)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene). The boronic ester was coupled to the diphenoxy-substituted 9-bromoperylenedicarboximide (**9**) under standard Suzuki conditions to form the terrylene precursor **11** in quantitative yield (Scheme 1). In the subsequent step, **11** was cyclized with sodium *tert*-butoxide/1,5-diazabicyclo[4.3.0]non-5-ene as base in diglyme to give 11-

nitroterrylenedicarboximide (**12**) in 35% yield, after isolation and purification by column chromatography.

11-Nitroterrylenedicarboximide (**12**) is readily soluble in all common organic solvents (120 mg mL^{-1} CH$_2$Cl$_2$) at room temperature and serves as a starting material for the preparation of **7** and **8**. Reduction of **12** with Pd/C and hydrogen gave 11-aminoterrylene (**5**) in 78% yield. Attempts to produce a halogenated terrylene by the Sandmeyer reaction delivered the non-halogenated terrylene as the major product and only small quantities of the desired compound. The amount obtained, however, was sufficient for the homocoupling of the iodinated terrylenemonoimide or the Suzuki coupling of the monoimide with perylenemono-imide **9** to form the bis(terrylenemonoimide) or perylenemonoimide-terrylenemonoimide bichromophores, respectively, which were then directly cyclized (without isolation) through an oxidative cyclodehydrogenation to yield **8** or **7** in high purity and yield (last step) after purification.

To obtain these higher rylenediimides in an improved overall yield, a second approach was investigated. Extension of the framework by introducing a naphthalene or perylene unit between two perylenemonoimides (the bisbromorylene method) involves the palladium-catalyzed coupling reaction of perylenemonoimides with a bisbromo-functionalized naphthalene or perylene followed by a final bond closure to a double-stranded rylene structure. To avoid the use of toxic stannyl compounds as intermediates in the Stille coupling reaction, the boronic esters of 9-bromoperylenedicarboximide (**13**) and **9** were subjected to Suzuki coupling with 1,4-bisbromonaphthalene (**14**) to give the bisperylenylnapthalene derivatives **15** and **17** in good yields (**15** 72%, **17** 75%). The boronic ester of **9** was coupled with 1,9(10)-bisbromoperylene (**16**) to provide **18** in 79% yield (Scheme 3).

The final cyclization steps were carried out through an oxidative cyclodehydrogenation. Several dehydrogenation methods to form rylene structures from polynaphthalene and/or polyperylene units are described in the literature. Clar et al. applied successfully an aluminum chloride/sodium chloride melt to "cake" polynaphthalene derivatives together.[14, 15] We developed milder conditions for the cyclization to oligorylenes under the influence of AlCl$_3$/CuCl$_2$ and FeCl$_3$.[16]

While both 2,6-diisopropylphenyl and 1-heptyloctyl substituents at the imide structure improve the synthesis of pentarylenediimide by enhancing the solubility, the alkyl substitution has the advantage that no dealkylation has to be feared during the Lewis acid assisted cyclization step. To obtain the fully annulated ladder-type structure **6**, the bisperylenyl(naphthalene) derivative **15** was allowed to react with aluminum chloride in chlorobenzene to afford **6**, which was obtained as a black–green precipitate in 24% yield. The pentarylenediimide **6** is only slightly soluble in organic
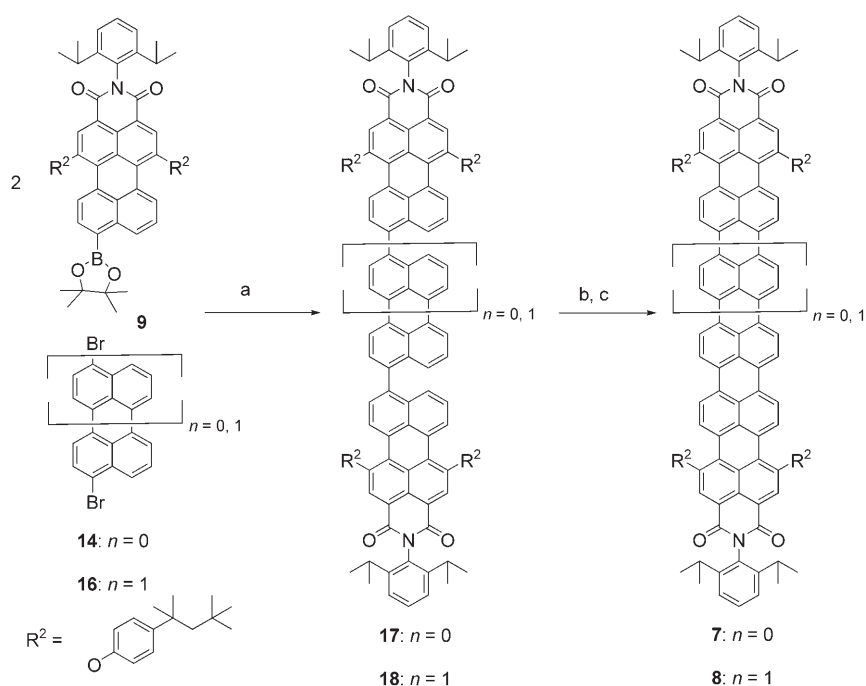
Scheme 3. Reagents and conditions: a) [Pd(PPh$_3$)$_4$], K$_2$CO$_3$ (aq), ethanol/toluene, 80 °C; b) FeCl$_3$/nitromethane, CH$_2$Cl$_2$, room temperature, 24 h; c) K$_2$CO$_3$, ethanolamine, 135 °C, 4 h.

against the inverse squared length of the π system, where the length L is taken as the N–N distance of the force-field geometries of rylenes **1**, **2**, **3**, **7**, and **8**, an ideal particle-in-the-box behavior ($E \approx 1/L^2$) was indeed observed (see Figure 3).

In the case of the pentarylene derivatives **6** and **7**, the absorption maximum is additionally influenced by the number of phenoxy substituents in the bay region of the chromophore. The maximum absorption of the unsubstituted pentarylene **6** lies at 831 nm, whereas that for the tetrasubstituted pentarylene **7** lies at 877 nm. This is a consequence of the destabilization of the HOMO by antibonding contributions of the phenoxy groups. The bathochromic shift of the first electronic transition upon phenoxy substitution in the bay position of **6** is best reproduced by ZINDO/s calculations, which give values of 745 nm for **6** and 777 nm for **7**. These calculations show a bathochromic shift of approxi-
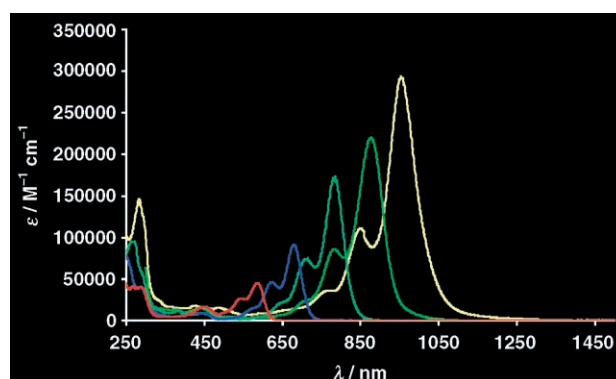
solvents (< 0.5 mg mL^{-1} CH$_2$Cl$_2$) at room temperature and is better regarded as a pigment than a dye.

It was then of particular interest to see if we could synthesize, through the bisbromorylene method the more-soluble tetraphenoxy-substituted derivatives **7** and **8**, which were already obtained by the nitronapthalene method. The cyclization of **17** and **18** to the tetraphenoxy-pentarylene **7** and -hexarylene **8** was achieved under milder conditions in a two-step process to avoid the undesirable dealkylation of phenoxy and imide substituents by strong Lewis acids. The first cyclization of **17** and **18** was obtained with FeCl$_3$/nitromethane in CH$_2$Cl$_2$ at room temperature. After hydrolysis and washing, the target compounds were formed by a mild base-promoted cyclization with K$_2$CO$_3$/ethanolamine. This method provides the NIR absorbers **7** and **8** in an overall yield of over 25 %.

As a result of the substitution with four *tert*-octylphenoxy groups in the bay positions, penta- and hexarylene derivative **7** and **8** are soluble in all common organic solvents (> 1 mg mL^{-1} CH$_2$Cl$_2$). The synthesized penta- and hexarylenediimides were characterized by mass spectrometry and IR and UV/Vis/NIR spectroscopy, while the measurement of ^{1}H NMR spectra was only successful in the case of **7**. The absorption spectra of penta- and hexarylene derivatives **7** and **8** demonstrate a strong bathochromic shift of the absorption maximum with an increasing degree of annulation (Figure 2). The absorption maximum of **7** is found at 877 nm whereas that for **8** lies at 953 nm. By examining the entire rylenediimide series (perylenediimide **1** to hexarylenediimide **8**), it is apparent that the energy of the absorption maximum is shifted to lower energies upon increasing the length of the π system, as is to be expected from a simple particle-in-a-box picture. When the maximum absorption energy was plotted

Figure 2. Absorption spectra of the entire tetraphenoxy-substituted rylenediimide series in CHCl$_3$: perylenebis(dicarboximide) (red), terrylenebis(dicarboximide) (blue), quaterrylenebis(dicarboximide) (turquoise), pentarylenebis(dicarboximide) **7** (green), and hexarylenebis(dicarboximide) **8** (yellow).

mately 100 nm compared to the observed values, a typical effect of gas-phase calculations. In each case, the absorption bands exhibit a similar vibrational structure, which is typical for rylenediimides.

As a result of the extension of the aromatic π system along the molecular long axis, not only does a bathochromic shift become apparent but the absorption coefficients increase also: $\varepsilon = 235$ M^{-1}cm^{-1} for the pentarylenediimide **7**, $\varepsilon = 293$ M^{-1}cm^{-1} for the hexarylenediimide **8**. Such absorption coefficients are phenomenal and, to our knowledge, are the highest reported among all the known organic dyes in this region of the NIR spectrum. Theoretic elucidation of the electronic transition properties of penta- and hexarylene as
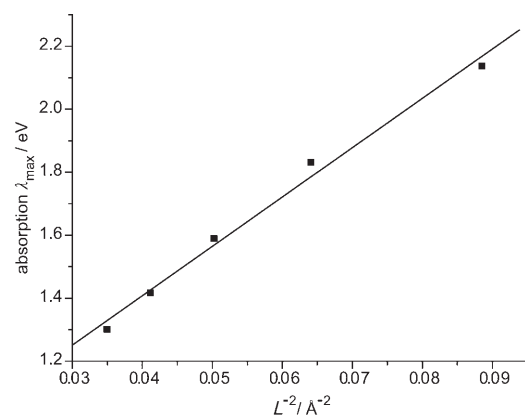
Figure 3. Correlation between the maximum absorption energy and the inverse squared length of the π system (see text). A particle-in-the-box behavior is observed ($E \approx 1/L^2$). Plotted points represent the tetraphenoxy-substituted rylene dyes (left to right) **8**, **7**, **3**, **2**, and **1**.

extended π-conjugated derivatives of perylenediimide substantiate these excellent spectral properties. Compounds **6**, **7**, and **8** display an impressive stability and their solutions remained unchanged over weeks in sunlight. The photostability of **8** was compared with its lower homologue, the quaterrylenediimide **2**, whose excellent photochemical stability was reported previously.[10] Exposure of solutions of **8** and **2** in THF ($10^{-6}\,\text{M}^{-1}$) in quartz cuvettes to UV light ($\lambda = 365$ nm) for 9 h led to no significant changes in their absorption intensities. From a practical point of view, it is important to mention the almost colorless solutions of the penta- and hexarylenediimide derivatives **6**, **7**, and **8**. A negligible absorption in the visible region together with their extraordinary high extinction coefficients in the NIR, which is only comparable to a few squarylium dyes,[17] predestine them for many technological applications, such as security printing.

In conclusion, two synthetic approaches give access to an extended homologous series of NIR-absorbing rylenebis(dicarboximide)s. The absorption spectra of pentarylenediimide **6** and **7** as well as hexarylenediimide **8** are characterized by an extremely intense absorption between 830 and 960 nm. In addition to these remarkable photophysical properties, the penta- and hexarylene derivatives still display good chemical and thermal stability, as already observed for their smaller homologues, the perylene-, terrylene-, and quaterrylenediimides.

[1] M. Linke-Schätzel, A. D. Bhise, H. Gliemann, T. Koch, T. Schimmel, T. S. Balaban, *Thin Solid Films* **2004**, *451*, 16–21.
[2] F. Würthner, S. Ahmed, C. Thalacker, T. Debaerdemaeker, *Chem. Eur. J.* **2002**, *8*, 4742–4750.
[3] P. Coppo, M. Duati, V. N. Kozhevnikov, J. W. Hofstraat, L. De Cola, *Angew. Chem.* **2005**, *117*, 1840–1844; *Angew. Chem. Int. Ed.* **2005**, *44*, 1806–1810.
[4] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, *Adv. Mater.* **2000**, *12*, 481–494.
[5] V. Mantareva, D. Petrova, L. Avramov, I. Angelov, E. Borisova, M. Peeva, D. Wöhrle, *J. Porphyrins Phthalocyanines* **2005**, *9*, 47–53.
[6] P. Gregory, *High-Technology Applications of Organic Colorants*, Plenum, New York, **1991**.
[7] C. Kohl, S. Becker, K. Müllen, *Chem. Commun.* **2002**, *23*, 2778–2779.
[8] F. Holtrup, G. Müller, H. Quante, S. de Feyter, F. C. De Schryver, K. Müllen, *Chem. Eur. J.* **1997**, *3*, 219–225.
[9] H. Quante, K. Müllen, *Angew. Chem.* **1995**, *107*, 1487–1489; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1323–1325.
[10] Y. Nagao, H. Iwawaki, K. Kozawa, *Heterocycles* **2002**, *56*, 331–340.
[11] Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Böhm, K. Müllen, *J. Mater. Chem.* **1998**, *8*, 2357–2369.
[12] M. Adachi, Y. Nagao, *Chem. Mater.* **1999**, *11*, 2107–2114.
[13] T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508–7510.
[14] E. Clar, *Chem. Ber.* **1948**, *81*, 52–63.
[15] E. Clar, W. Kelly, R. M. Laird, *Monatsh. Chem.* **1956**, *87*, 391.
[16] K.-H. Koch, K. Müllen, *Chem. Ber.* **1991**, *124*, 2091–2100.
[17] J. Fabian, R. Zahradnik, *Angew. Chem.* **1989**, *101*, 693–710; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 677–694; J. Fabian, M. Nakazumi, T. J. Matsuoka, *Chem. Rev.* **1992**, *92*, 1197–1226.