

Novel Core-Expanded Rylenebis(Dicarboximide) Dyes Bearing Pentacene Units: Facile Synthesis and Photophysical Properties

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Abstract: Two synthetic routes for the benzannulation in the “bay”-region of rylenebis(dicarboximide)s leading to new π -system-expanded chromophores are described. The first route follows a two-step approach: Suzuki coupling of bromo-substituted perylenebis(dicarboximide) with 2-bromophenylboronic acid, followed by palladium-catalysed dehydrobromination. The second route

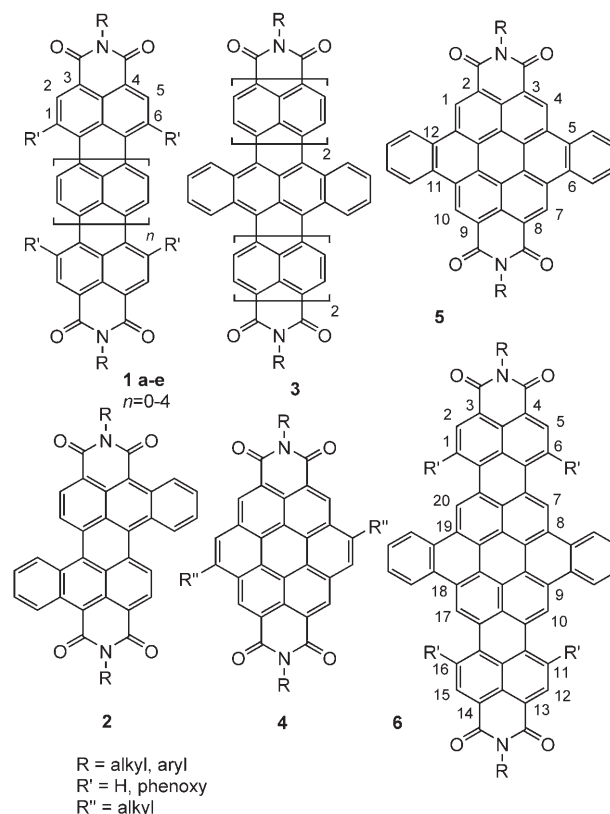
is best described as a palladium-assisted cycloaddition of benzyne, formed in situ, to the bay-region of the bromo-substituted rylene core. Two new types of core-expanded rylene dyes were syn-

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thesised: yellow dibenzocoronenebis(dicarboximide)s, absorbing at 490 nm, and a green dinaphthoquaterylenebis(dicarboximide), which absorbs at 700 nm. These new chromophores are characterised by significant hypsochromic shifts of absorption, compared to their parent rylenebis(dicarboximide)s, excellent photostabilities and high fluorescence quantum yields.

Introduction

Rylenebis(dicarboximide) chromophores **1** possess exceptional chemical, thermal and photochemical stabilities with high extinction coefficients.^[1] Their use has been explored for demanding applications such as optoelectronic^[2] and photovoltaic^[3] devices, thermographic processes,^[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- (PDI), **1a** ($n=0$), to terylene- (TDI), **1b** ($n=1$)^[8] and quaterylenebis(dicarboximide)s (QDI), **1c** ($n=2$)^[9] induced a bathochromic shift of about 100 nm per additional naphthalene unit reaching an absorbance maximum of 780 nm for the quaterylene **1c** and a nearly linear increase of the extinction coefficient up to $170\,000\text{ M}^{-1}\text{ cm}^{-1}$. Very recently, the syntheses of two higher rylene homologues, which each have an intensive absorption in the NIR region, were reported: pentarylene- (**1d**, $n=3$, $\lambda_{\text{max}}=877\text{ nm}$) and hexarylenebis(dicarboximide)s (**1e**, $n=4$, $\lambda_{\text{max}}=950\text{ nm}$).^[10]



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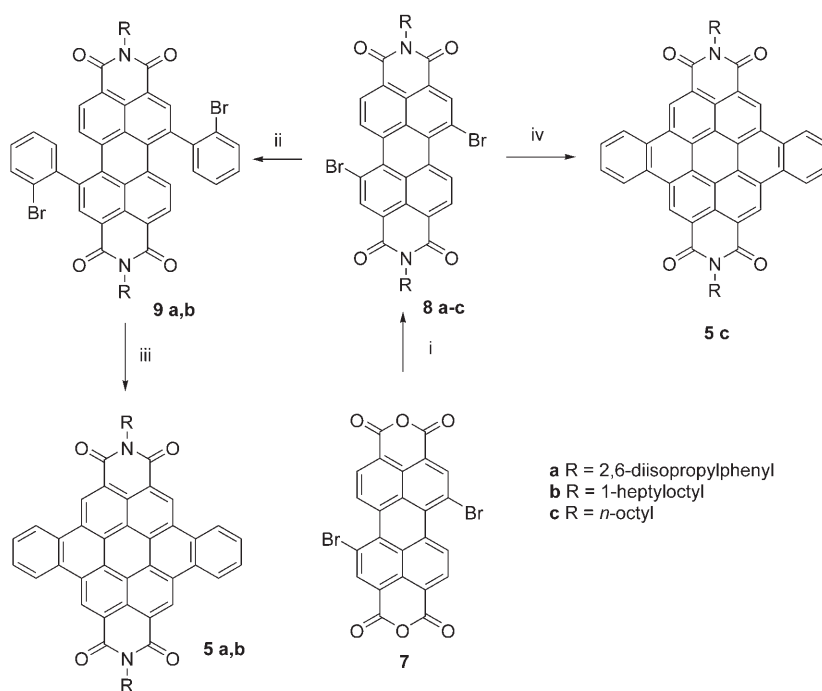
A bathochromic shift of the absorption was also obtained by expanding the π system of perylenebis(dicarboximide)s along the short molecular axis. Benzannulation in the “bay”-region of rylenees with the introduction of anthracene (**2**, $\lambda_{\text{max}}=701$ nm) or tetracene (**3**, $\lambda_{\text{max}}=1018$ nm) elements resulted in significant bathochromic shifts of the absorption maximum, presumably due to the nonplanarity of the molecules formed.^[11–13] The absorption of dibenzoperylenebis(dicarboximide)^[11] **2** and dibenzopentarylenebis(dicarboximide)^[13] **3** was shifted by about 180 nm relative to the perylene **1a** ($\lambda_{\text{max}}=524$ nm) and pentarylene **1d** ($\lambda_{\text{max}}=830$ nm) derivatives, respectively.^[10] However, enlargement of the π system did not always promote a shift to longer wavelengths. The coronenebis(dicarboximide)s (CDI) **4** can be regarded as perylenebis(dicarboximide)s expanded along the short molecular axis. Their absorbances were hypsochromically shifted by 20–100 nm, relative to that of the perylene **1a**, to a maxima at 511 (low intensity band) and 428 nm (high intensity band), leading to a yellow colour.^[14] Stable, yellow chromophores with high molar extinction coefficients are generally difficult to obtain as the extinction coefficient often increases with the size of the aromatic system, which generally necessitates that these dyes absorb more bathochromically.^[1c] Basic chemical modification of the red perylene core facilitates a hypsochromic shift of the absorption to the yellow. Diverse methodologies to functionalise 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. Perylenebis(dicarboximide)s, functionalised in one bay-region, through cycloaddition reactions followed by reduction or mono-nitration and cyclisation, are known.^[15] An additional core-expansion from coronenebis(dicarboximide)s **4** to dibenzocoronenebis(dicarboximide)s **5** shifted the absorption to the red.^[16] However, the yellow colour in solution remained and became brighter due to the absence of residual absorption above 500 nm.

Herein, we report two synthetic routes to enlarge the aromatic π system of available rylene derivatives, leading to two novel chromophores with hypsochromically shifted absorption, namely the dibenzocoronenebis(dicarboximide) **5**, and dinaphthoquaterrylenebis(dicarboximide) **6**. Both represent a new class of core-expanded derivatives of the rylene dyes.

Results and Discussion

Syntheses

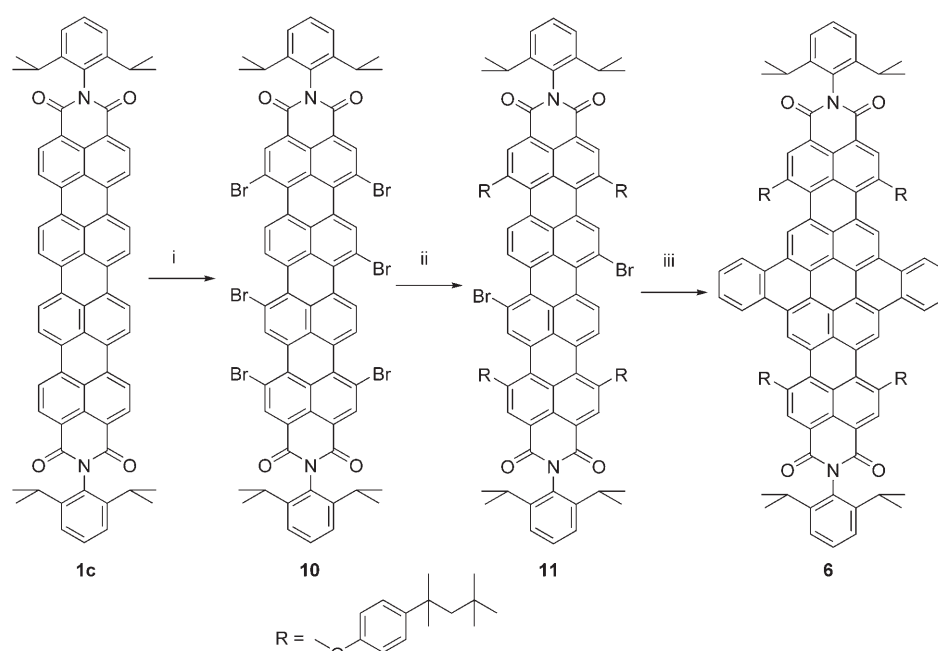
Two-step benzannulation of PDIs: The two-step benzannulation of 1,7-dibromoperylenebis(dicarboximide) **8** has been previously reported:^[16] bromination of perylene 3,4:9,10-bis-anhydride led to 1,7-dibromoperylene bisanhydride **7**, which contains various amounts of the corresponding 1,6-isomer depending on the reaction conditions.^[17] In contrast to the coronenebis(dicarboximide) synthesis,^[18] both isomers reacted to form the same desired product in the case of benzannulation, which is a major advantage of this synthesis. The 1,7-dibromoperylenebis(dicarboximide)s **8a–c** were obtained by imidisation of the anhydride **7** with aryl or alkyl amines.^[14,18] The reaction of 1,7-dibromoperylenebis(dicarboximide)s **8a,b** with 2-bromophenylboronic acid under Suzuki conditions afforded the perylene derivatives **9a,b** in 53 % yield (Scheme 1). Self-reaction of 2-bromophenylboronic acid is known not to occur under these conditions.^[19] One- and twofold debrominated products of **9** were observed in minor amounts (less than 10%), but this mixture



Scheme 1. Reagents, conditions and yields: i) 1-heptyloctylamine, NMP, 150 °C, 4 h, 39%; ii) 2-bromophenylboronic acid, $[\text{Pd}(\text{Ph}_3\text{P})_4]$, K_2CO_3 (aq), toluene, ethanol, 75 °C, 12 h, 53%; iii) $[\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2]$, DBU, DMA, 160 °C, overnight, 46%; iv) 2-(trimethylsilyl)phenyl trifluoromethanesulfonate, $[\text{Pd}(\text{dba})_2]$, $\text{P}(\text{o-tolyl})_3$, CsF, 110 °C, 24 h, 80%.

was directly used for the next step successfully. The palladium-catalysed dehydrohalogenation^[20] with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in dimethylacetamide (DMA) furnished dibenzocoronenebis(dicarboximide)s **5a,b** in 46 % yield as yellow solids.

One-step benzannulation of PDI: The appeal of these new yellow chromophores is slightly diminished by the moderate yields during their syntheses. The Suzuki coupling in the first step is accompanied by side reactions, even under mild conditions, whereas a high yield in the second step is prevented by the drastic conditions of the palladium-induced dehydrobromination. Simplification of the procedure was achieved by the core-extension of the bay-region of PDI by means of a one-step Diels–Alder cycloaddition.^[21] Recently, an effective route for the benzannulation of 2-halobiaryls, with in situ generation of arynes, was described.^[22] This reaction was successfully applied for the synthesis of carbo- and heterocyclic polyaromatic molecules in good yields. The bay-region of



Scheme 2. Reagents, conditions and yields: i) Br_2 , chloroform, 55 °C, 60 h, 84%; ii) *tert*-octylphenol, K_2CO_3 , NMP, 48 h, 85%; iii) 2-(trimethylsilyl)phenyl trifluoromethanesulfonate, $[\text{Pd}(\text{dba})_2]$, $\text{P}(\text{o-tolyl})_3$, CsF, 95 °C, 24 h, 46%.

dibromoPDIs **8** is apparently synthetically equivalent to the 2-halobiaryls. The reaction of the commercially available 2-(trimethylsilyl)phenyl trifluoromethanesulfonate and *N,N'*-diocetyl-1,7-dibromoperylenebis(dicarboximide) (**8c**)^[18] under the conditions described above^[22] afforded dibenzocoronene bis(dicarboximide) **5c** in high yield (80%) as a light-brown solid. The product **5c** precipitated almost quantitatively from the reaction mixture upon cooling to room temperature, which opens the possibility for the industrial application of the benzannulation of 1,7-dibromoPDIs, since these compounds are readily accessible.^[17,18]

Core extension of quaterylenebis(dicarboximides): Quaterylene bis(dicarboximides) are known as green NIR dyes that possess high thermal and photochemical stabilities as well as high molar absorptivities.^[9] However, their fluorescence quantum yields and solubilities are quite low. An increase of solubility could be achieved by the bromination of bay-region and subsequent phenoxylation of the bromides.^[8] Bromination of QDI **1c** with an excess of molecular bromine afforded the hexabrominated product **10** (Scheme 2). The hexabromide **10** possesses an enhanced solubility relative to **1c**, but a lower photochemical stability. It was found that only bromides closest to the imide positions (1,6,11,16) were substituted with the phenoxy groups upon phenoxylation. The two “inner” bromides remained even after the long reaction times and drastic conditions. The dibromoQDI **11** is synthetically analogous to the PDIs **8**; therefore, the bromides are suitable for the palladium-promoted benzannulation. The core expansion of **11** under the same conditions as for **8** afforded core-modified QDI **6** in 46% yield. It

should be noted that precursor **11** was more susceptible to the basic conditions upon heating than **8**. As such, a lower reaction temperature was used (95 °C instead of 110 °C for the PDI **8**) in order to avoid debromination of **11**.

Photophysical properties

Dibenzocoronenebis(dicarboximides): Both coronene derivatives **4** and **5** 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 the dibenzoCIDI **5** 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 **4** is broad (Figure 1). Only one band with the typical perylene vibronic structure is seen at

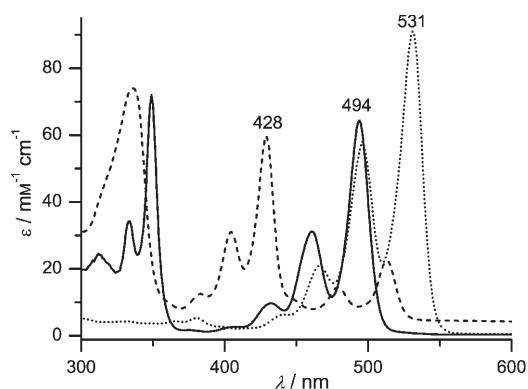


Figure 1. Absorption spectra of coronenebis(dicarboximide) **4** (dashed line), dibenzocoronenebis(dicarboximide) **5a** (solid line) and PDI **1a** (dotted line).

longer wavelength with an absorbance maximum at 494 nm ($\epsilon = 66000 \text{ M}^{-1} \text{ cm}^{-1}$), giving rise to the yellow colour. The yellow solution of dibenzoCDI **5a** appears brighter and greener than that of the CDI **4**, given that there is no absorbance above 515 nm for **5**. The value of ϵ for **5** at 494 nm is similar to that of **4** at 428 nm ($\epsilon = 62000 \text{ M}^{-1} \text{ cm}^{-1}$).^[18] Dibenzocoronenebis(dicarboximide)s **5a,b** have a bright fluorescence with a quantum yield of 80% (see Experimental Section), high with respect to other yellow fluorophores; for example, acridine yellow, which has a fluorescence quantum yield of 47%.^[23] The emission spectrum of the dibenzoCDI **5c** (Figure 2) shows the mirror symmetry with the absorption spectrum, and a Stokes shift of 13 nm.

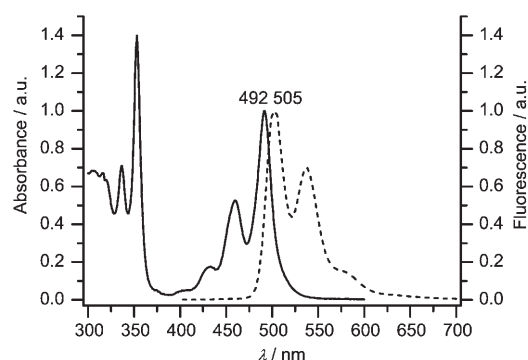


Figure 2. Absorption (solid line) and emission (dashed line) spectra of dibenzocoronenebis(dicarboximide) **5c** (solvent: chlorobenzene, $T = 373 \text{ K}$).

Dinaphthoquaterrylenebis(dicarboximide): A comparison of the absorption spectra of the newly synthesised dinaphthoQDI **6** (Figure 3) shows a significant hypsochromic shift of ab-

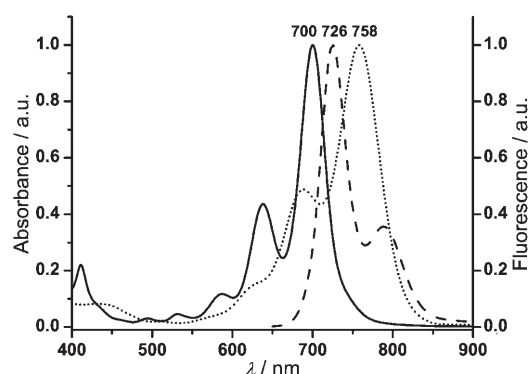


Figure 3. Absorption (solid line) and emission (dashed line) spectra of dinaphthoquaterrylenebis(dicarboximide) **6** and absorption spectrum of its precursor **11** (dotted line, solvent: toluene).

sorption maximum as compared to the precursor **11** (from 758 to 700 nm). This phenomenon is accompanied by a blue-green appearance in solution (chloroform, toluene). The value of the extinction coefficient is lower than for the precursor, but still remains high ($\epsilon = 143000 \text{ M}^{-1} \text{ cm}^{-1}$). As

was reported for the parent QDI,^[9] the absorption of such dyes is additionally influenced by the phenoxy substitution in the bay. The bathochromic shift for tetraphenoxyQDI **1c** is 19 nm with respect to the unsubstituted dye. Therefore, the λ_{max} for the parent dinaphthoQDI, bearing no phenyl ether moieties, is expected to be near 680 nm. The peak at 411 nm is caused by the four phenyl ethers that affect the slight nonplanarity of the polyaromatic macrocycle, similar to the parent QDI.^[9] Dinaphthoquaterrylenebis(dicarboximide)s **6** shows a strong emission with a maximum at 726 nm and a quantum yield of 40%.

Electronic properties: The absorption properties of the described rylene derivatives can be understood with support of semiempirical quantum mechanical calculations (Table 1).

Table 1. Calculated HOMO–LUMO energy levels^[a] and λ_{max} values^[a,b] for dyes **1a**, **1b**, **1c**, **4**, **5** and **6**.

	HOMO	LUMO	HOMO–LUMO gap	λ_{max} calcd ^[a,b]	λ_{max} exptl
1a	−8.85	−3.12	5.72	509	524
1b	−8.17	−3.12	5.05	603	650
1c	−7.86	−3.25	4.61	693	760
4	−9.01	−2.75	6.26	455	511
5	−8.65	−2.86	5.79	492	494
6	−7.93	−3.13	4.80	622	701 ^[c]

[a] HyperChem 6, PM3. [b] Single excited state, 20 occupied and 20 unoccupied orbitals. [c] Tetraphenoxy substituted.

Within the homologous series of rylenebis(dicarboximide)s, the energy level of the LUMO is barely influenced by the extension of the aromatic system, whereas the HOMO energy is increased with each additional naphthalene unit, leading to a smaller HOMO–LUMO gap and a bathochromically shifted absorption maximum. This increase in energy of the HOMOs is attributed to the increasing number of antibonding connections between the naphthalene moieties.^[24] The calculated frontier orbitals of coronenebis(dicarboximide) show already that CDI cannot be regarded as a simple analogue of rylenebis(dicarboximide)s (Figure 4).

The formal fusion of a perylenebis(dicarboximide) with two ethylenes in the bay-region leads to a totally different appearance of the HOMO orbital coefficients of CDI compared to PDI, whereas the LUMO of CDI matches the LUMO of PDI. Regarding the orbitals of the pure hydrocarbon coronene, it becomes evident that the HOMO of CDI is comparable with the HOMO of coronene. As previously mentioned, the absorption spectrum of a CDI shows two main bands in the region above 350 nm, instead of only one as in the case for PDI. Hence, this absorption behaviour is a result of a mixture of perylenebis(dicarboximide)- and coronene-like orbitals: the band at 511 nm, corresponding to the HOMO–LUMO transition according to the calculation, is therefore caused by a transition from a coronene-like HOMO to a perylene-like LUMO. The second band at 429 nm shows the typical vibronic fine structure of perylenebis(dicarboximide)s, as this band is related to the transition between the perylene-like NHOMO and the perylene-like

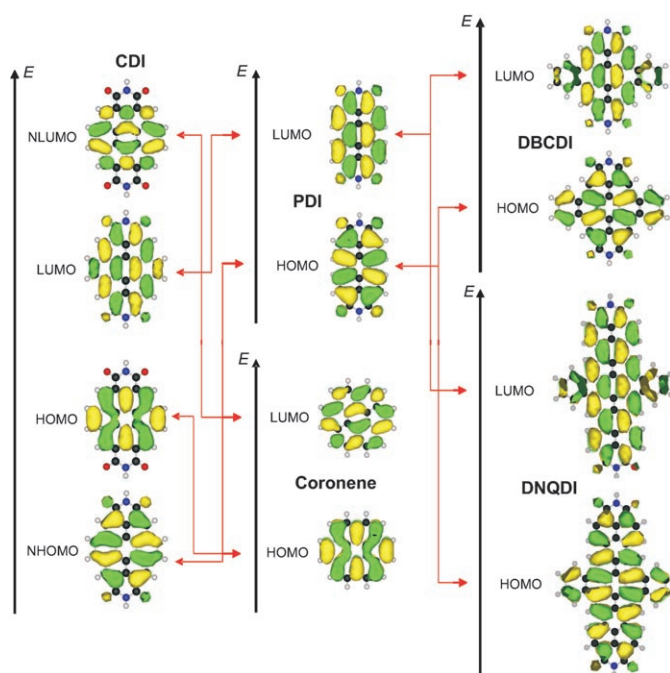


Figure 4. Molecular orbitals (PM3) of coronenebis(dicarboximide) (CDI), coronene, perylenebis(dicarboximide) (PDI), dibenzocoronenebis(dicarboximide) (DBCDI) and dinaphthoquaterylene bis(dicarboximide) (DNQDI). Abbreviations for molecular orbitals (MO): HOMO=highest occupied, NHOMO=next highest occupied, LUMO=lowest unoccupied, NLUMO=next lowest unoccupied.

LUMO.^[25] The theoretical calculations clearly reproduce the hypsochromically shifted absorption, as the energy value of the HOMO of CDI is lower relative to PDI, whereas the LUMO energy is increased, thus leading to a larger HOMO–LUMO gap.

The calculated orbitals of the new dibenzocoronene and dinaphthoquaterylene derivatives (Figure 4) are similar to those of the corresponding rylene, showing a similar UV absorption behaviour with only one main band. The determined HOMO–LUMO band gaps of **5** and **6** are slightly increased relative to the perylene- and quaterylenebis(dicarboximide)s, respectively, causing a hypsochromic shift in absorption, in good agreement with the experimental data.

Photochemical stabilities: The photochemical stability of the dibenzoCDI **5** is much higher than that of CDI **4**: the absorption of **4** in the chloroform under UV irradiation^[26] dropped to 34% of its initial value after 10 h. The benzanulated derivatives **5** still showed absorption of 76% under the same conditions. Presumably, the bonds between the 5- and 6-positions and the 11- and 12-positions in the coronenebis(dicarboximide) **4** have some double bond character, which makes them less stable. These bonds are part of other aromatic π systems in the dibenzocoronenebis(dicarboximide) **5** (Figure 4), leading to the higher stability. The photochemical stability of the core-extended QDI **6** is even higher than that for dibenzoCDI **5**. The absorption spectrum of **6** remained the same after 12 h of UV irradiation.^[26]

Conclusion

The syntheses of two novel chromophores are detailed, namely the dibenzocoronenebis(dicarboximide)s **5** and the dinaphthoquaterylenebis(dicarboximide) **6**, by short and facile routes. The palladium-catalysed ring annulation reaction enabled the enlargement of the aromatic π system and has thereby led to new chromophores based on core-extended rylene dyes. The optical properties of the newly synthesised dyes are in good agreement with the results of semiempirical quantum mechanical calculations. Sharp absorption bands between 400 and 500 nm led to a brilliant greenish-yellow appearance with an intensive fluorescence characterise the UV/Vis spectrum of dibenzocoronenebis(dicarboximide) **5**. The optical properties are in good agreement with the results of the semiempirical calculations. Insoluble derivatives of **5** may be useful as new stable yellow pigments. Further, one can envision their use in optoelectronic devices such as field effect transistors, as good phase forming ability is expected when decorated with long alkyl chains.^[27] The UV/Vis spectrum of dinaphthoquaterylenebis(dicarboximide) **6** is characterised by the intensive absorption between 600 and 750 nm and a bluish-green colour in a solution. The intensive fluorescence with the quantum yield of 40% makes the new dye **6** useful as a red absorbing fluorophore that possesses an extremely high photostability. The latter makes it a promising dye for biolabelling and multichromophoric systems for energy and electron transfer.

Experimental Section

General: Melting points were performed on a Büchi melting point apparatus and are not corrected. ¹H NMR and ¹³C NMR spectra were recorded in deuterated solvents on a Bruker AMX 300 and Bruker Avance 700, with the residual proton resonance or the carbon signal of the solvent as the internal standard. For ¹³C *J*-modulated spin-echo NMR measurements, the abbreviations q and t represent quaternary carbons, CH₂, and CH₃, CH groups, respectively. Infrared spectra were obtained on a Nicolet FT-IR 320. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer at room temperature. Fluorescence spectra were recorded on a Spex Fluorolog 3 spectrometer. Fluorescence quantum yields were determined by the relative method using the following compounds as references: acridine yellow for dibenzoCDI **5** and Rhodamine 800^[28] for dinaphthoQDI **6**. FD mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD. The elemental analyses were carried out by the Microanalytical Laboratory of Johannes Gutenberg University, Mainz. 1,7-Dibromo-3,4,9,10-perylene tetracarboxydianhydride (**7**) and *N,N'*-bis(2,6-diisopropylphenyl)quaterylene-3,4:13,14-bis(dicarboximide) (**1c**) were provided by the BASF AG. All other starting materials were purchased from Aldrich, Acros, ABCR, or Lancaster, and used as received.

***N,N'*-Bis(2,6-diisopropylphenyl)-1,7-bis(2-bromophenyl)perylene-3,4,9,10-bis(dicarboximide) (9a):** A Schlenk flask was charged with compound **8a** (1.00 g, 1.15 mmol), 2-bromophenylboronic acid (500 mg, 2.49 mmol), tetrakis(triphenylphosphine)palladium(0) (150 mg, 0.130 mmol), toluene (75 mL), ethanol (5 mL) and a 2 M solution of potassium carbonate (25 mL) under argon. The mixture was heated to 75 °C with vigorous stirring for 12 h. It was then cooled to room temperature and the organic phase separated and washed twice with water. After drying with magnesium sulphate, the solvent was removed in vacuo. The crude product was dissolved in methylene chloride and filtered over silica gel. Evaporation

of the solvent gave 620 mg (53%) of red crude product, which was used without further purification.

***N,N'*-Bis(2,6-diisopropylphenyl)-5,6:11,12-dibenzocoronene-2,3:8,9-bis(dicarboximide) (5a):** dichloridobis(triphenylphosphine)palladium(II) (15 mg, 0.021 mmol) was added to a solution of compound **9a** (100 mg, 0.098 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (60 mg, 0.39 mmol) in dry dimethylacetamide (3 mL) under argon. The mixture was heated to 160°C with stirring for 24 h, was cooled to room temperature and was diluted with methylene chloride. The mixture was washed twice with water and dried over magnesium sulfate and the solvent removed in vacuo. The crude product was purified by column chromatography (silica gel, methylene chloride) to yield 40 mg (46%) of a yellow solid. M.p. 240°C (decomp); ¹H NMR (700 MHz, C₂D₂Cl₄, 20°C, TMS): δ = 10.66 (s, 4H), 9.56 (m, 4H), 8.22 (m, 4H), 7.53 (dd, ³J = 7.7 Hz, ⁴J = 2.1 Hz, 2H), 7.40 (d, ³J = 8.5 Hz, 4H), 2.99 (sept, ³J = 6.8 Hz, 4H), 1.26 ppm (d, ³J = 6.8 Hz, 24H); ¹³C NMR (*J*-modulated spin-echo; 175 MHz, C₂D₂Cl₄, 100°C, TMS): δ = 164.77 (q, C=O), 146.39 (q), 131.67 (q), 130.12 (q), 129.76 (t), 129.68 (t), 129.35 (q), 125.24 (q), 125.22 (q), 124.96 (t), 124.87 (t), 124.31 (t), 124.01 (q), 29.73 (CH), 24.29 ppm (CH₃); IR (KBr): $\tilde{\nu}$ = 2962, 2927, 2869, 1698, 1663, 1655, 1581, 1541, 1459, 1363, 1351, 1278, 1214, 1175 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (ϵ) = 432 (10000), 460 (32000), 494 nm (66000 M⁻¹ cm⁻¹); MS (8 kV): *m/z* (%): 859.2 (100) [*M*⁺], 429.3 (23) [*M*²⁺]; elemental analysis calcd (%) for C₆₀H₄₆N₂O₄: C 83.89, H 5.40, N 3.26; found: C, 83.66; H, 5.38; N, 3.12.

***N,N'*-Bis(1-heptyloctyl)-1,7-dibromoperylene-3,4:9,10-bis(dicarboximide) (8b):** The mixture of compound **7** (500 mg, 0.909 mmol) and 1-heptyloctylamine (750 mg, 3.298 mmol) in *N*-methylpyrrolidone (NMP; 50 mL) was stirred at 150°C. After 4 h the mixture was allowed to cool down to room temperature and was then poured into diluted hydrochloric acid (400 mL). The precipitate was collected by filtration, was washed with water and methanol several times and was dried under reduced pressure at 80°C. The crude product was purified by column chromatography (silica gel, petrol ether/methylene chloride 3:2) to yield 340 mg (39%) of a red wax. ¹H NMR (300 MHz, CD₂Cl₂, 20°C, TMS): δ = 9.53 (s, 1H), 9.50 (s, 1H), 8.89 (brs, 2H), 8.66 (d, ³J = 7.2 Hz, 2H), 5.20–5.12 (m, 2H), 2.25–2.20 (m, 4H), 1.86–1.80 (m, 4H), 1.28–1.22 (m, 40H), 0.85–0.81 ppm (m, 12H); ¹³C NMR (*J*-modulated spin-echo; 175 MHz, C₂D₂Cl₄, 100°C, TMS): δ = 162.55 (C=O), 138.21, 137.13, 132.86, 132.66, 131.52, 130.10, 129.28, 128.48, 127.18, 120.61, 54.75 (CH), 41.08 (CH₂), 31.77 (CH₂), 29.44 (CH₂), 29.18 (CH₂), 26.85 (CH₂), 22.59 (CH₂), 13.79 ppm (CH₃); IR (KBr): $\tilde{\nu}$ = 2956, 2925, 2854, 1703, 1660, 1589, 1381, 1329, 1240, 810, 748 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (ϵ) = 390 (6000), 460 (15000), 490 (37000), 526 nm (55000 M⁻¹ cm⁻¹); MS (FD, 8 kV): *m/z* (%): 971.3 (100) [*M*⁺].

***N,N'*-Bis(1-heptyloctyl)-1,7-bis(2-bromophenyl)perylene-3,4:9,10-bis(dicarboximide) (9b):** A Schlenk flask was charged with compound **8b** (600 mg, 0.619 mmol), 2-bromophenylboronic acid (250 mg, 1.238 mmol), tetrakis(triphenylphosphine)palladium(0) (72 mg, 0.062 mmol), toluene (50 mL), ethanol (2 mL) and a 2M solution of potassium carbonate (25 mL) under argon. The mixture was heated to 75°C with vigorous stirring for two days. It was then cooled to room temperature and the organic phase separated and washed twice with water. After drying with magnesium sulphate, the solvent was removed in vacuo. The crude product was dissolved in petrol ether/methylene chloride (3:2) and filtered over silica gel. Evaporation of the solvent gave 600 mg (87%) of red crude product, which was used without further purification.

***N,N'*-Bis(1-heptyloctyl)-5,6:11,12-dibenzocoronene-2,3:8,9-bis(dicarboximide) (5b):** Dichloridobis(triphenylphosphine)palladium(II) (10 mg, 0.014 mmol) was added to a solution of compound **9b** (80 mg, 0.071 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (43 mg, 0.284 mmol) in dry dimethylacetamide (3 mL) under argon. The mixture was heated to 160°C with stirring for 18 h, cooled to room temperature and diluted with methylene chloride. The mixture was washed twice with water and dried over magnesium sulfate and the solvent removed in vacuo. The crude product was purified by column chromatography (silica gel, toluene) to yield 44 mg (65%) of a yellow solid. M.p. > 350°C; ¹H NMR (300 MHz, C₂D₂Cl₄, 100°C, TMS): δ = 9.78 (s, 4H), 9.06 (m, 4H), 8.16 (m, 4H), 5.36 (quint, ³J = 6.7 Hz, 2H), 2.54–2.44 (m, 4H), 2.23–2.14 (m,

4H), 1.55–1.30 (m, 40H), 0.84 ppm (t, ³J = 6.9 Hz, 12H); ¹³C NMR (125 MHz, C₂D₂Cl₄, 100°C, TMS): δ = 165.00 (C=O), 129.59, 129.17, 128.37, 124.67, 124.14, 123.86, 122.51, 122.35, 106.90, 55.67 (CH), 33.08 (CH₂), 32.06 (CH₂), 29.96 (CH₂), 29.44 (CH₂), 27.56 (CH₂), 22.77 (CH₂), 14.16 ppm (CH₃); IR (KBr): $\tilde{\nu}$ = 2956, 2926, 2854, 1703, 1660, 1606, 1437, 1315, 810, 741 cm⁻¹; UV/Vis (CHCl₃): λ_{max} (ϵ) = 334 (42000), 350 (78000), 431 (12000), 459 (33000), 493 nm (65000 M⁻¹ cm⁻¹); MS (8 kV): *m/z* (%): 957.6 (100) [*M*⁺].

***N,N'*-Bis(*n*-octyl)-1,7-dibromoperylene-3,4:9,10-bis(dicarboximide) (8c):** This compound was synthesised as described in literature.^[18]

***N,N'*-Bis(*n*-octyl)-5,6:11,12-dibenzocoronene-2,3:8,9-bis(dicarboximide) (5c):** Compound **8c** (260 mg, 0.34 mmol), [Pd(dba)₃] (50 mg), P(*o*-tolyl)₃ (35 mg), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (400 mg) and CsF (300 mg) were stirred at 95°C in the mixture of toluene (40 mL) and acetonitrile (4 mL) for 24 h under argon. The resulting mixture was allowed to stand overnight at room temperature. The precipitate formed was filtered, rinsed with methanol and crystallised from toluene to yield 205 mg (80%) of a yellow solid. M.p. 346°C (decomp); ¹H NMR (500 MHz, C₂D₂Cl₄, 100°C, TMS): δ = 9.62 (s, 4H), 8.90 (m, 4H), 8.01 (m, 4H), 4.31 (t, ³J = 7.5 Hz, 4H), 1.61–1.57 (m, 4H), 1.53–1.47 (m, 4H), 1.42–1.25 (m, 16H), 0.93 ppm (t, ³J = 6.9 Hz, 6H); IR (KBr): $\tilde{\nu}$ = 2955, 2922, 2846, 1697, 1661, 1607, 1440, 1326, 1255, 811, 742 cm⁻¹; UV/Vis (chlorobenzene, 100°C): λ_{max} (ϵ) = 337 (32500), 353 (64100), 433 (8100), 460 (24000), 492 nm (45800 M⁻¹ cm⁻¹); MS (MALDI-TOF): *m/z* (%): 763 (100) [*M*⁺]; elemental analysis calcd (%) for C₅₂H₄₆N₂O₄: C 81.86, H 6.08, N 3.67; found: C 81.66, H 6.18, N 3.58.

***N,N'*-Bis(*N*-2,6-diisopropylphenyl)-1,6,8(9),11,16,18-hexabromoquaterylene-3,4:13,14-bis(dicarboximide) (10):** Compound **1c** (3 g, 3.0 mmol) and bromine (65 mL, 1.26 mol) was stirred in chloroform (1.3 L) at 55°C for 60 h. The reaction mixture was cooled to room temperature and added to a vigorously stirred solution of KOH (15 g) and Na₂SO₃ (15 g) in water (2 L). Then Na₂SO₃ was added to the stirred solution until the aqueous layer became colourless. The organic layer was separated, dried with anhydrous sodium sulfate and evaporated. The residue was purified by the column chromatography on silica gel with dichloromethane as eluent to give **10** as a green powder (3.6 g, 84%). M.p. > 350°C; ¹H NMR (250 MHz, CD₂Cl₂, 20°C, TMS): δ = 9.71 (s, 1H), 9.68 (s, 1H), 9.53 (d, ³J = 8.7 Hz, 1H), 9.48 (d, ³J = 8.7 Hz, 1H), 9.38 (d, *J* = 8.75 Hz, 1H), 9.33 (d, ³J = 8.7 Hz, 1H), 9.00 (s, 1H), 8.99 (s, 1H), 8.89 (s, 1H), 8.92 (s, 1H), 7.54 (t, ³J = 8.2 Hz, 2H), 7.38 (d, ³J = 7.8 Hz, 4H), 2.77 (sept, ³J = 6.9 Hz, 4H), 1.18 ppm (d, ³J = 6.8 Hz, 24H); ¹³C NMR (67 MHz, CD₂Cl₂, 20°C, TMS): δ = 161.7, 161.4, 145.0, 133.5, 131.8, 129.8, 129.5, 129.1, 128.6, 128.5, 128.4, 128.3, 126.1, 125.5, 121.5, 120.9, 119.6, 119.5, 28.5, 23.1 ppm; IR (KBr): $\tilde{\nu}$ = 2961, 2927, 2867, 1717, 1713, 1705, 1674, 1590, 1573, 1468, 1386, 1348, 1233, 1197, 1172, 1152, 1051, 842, 815, 794, 724 cm⁻¹; UV/Vis (toluene): λ_{max} (ϵ) = 752 (113000), 686 nm (59300 M⁻¹ cm⁻¹); MS (8 kV): *m/z* (%): 1431.6 (100) [*M*⁺]; elemental analysis calcd (%) for C₆₈H₄₄Br₆N₂O₄: C 56.71, H 3.10, N 1.96; found: C 56.07, H 3.13, N 1.99.

***N,N'*-Bis(*N*-2,6-diisopropylphenyl)-1,6,11,16-tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]-8(9),18-dibromoquaterylene-3,4:13,14-bis(dicarboximide) (11):** Compound **10** (1.43 g, 1 mmol), *tert*-octylphenol (0.845 g, 4 mmol) and K₂CO₃ (0.3 g, 2.2 mmol) were suspended in NMP (150 mL) in a 250 mL Schlenk flask and flushed with argon. The mixture was stirred at 110°C for 48 h under argon. After cooling to room temperature, the mixture was poured into a mixture of 6M HCl (100 mL) and ice (200 g). The green precipitate was filtered, rinsed with water and dried under vacuum. Compound **11** was isolated after column chromatography on silica gel with toluene as eluent. Yield 1.44 g (85%); M.p. > 350°C; ¹H NMR (500 MHz, CD₂Cl₂, 20°C, TMS): δ = 9.78 (s, 3H), 9.57 (d, ³J = 8.95 Hz, 2H), 9.18 (d, ³J = 8.80 Hz, 2H), 8.23 (s, 4H), 7.50 (m, 9H), 7.33 (d, ³J = 7.74 Hz, 4H), 7.16 (d, ³J = 8.65 Hz, 8H), 2.50 (sept, ³J = 6.80 Hz, 4H), 1.70 (s, 8H), 1.35 (s, 24H), 1.10 (d, ³J = 6.79 Hz, 24H), 0.70 ppm (s, 36H); ¹³C NMR (125 MHz, CD₂Cl₂, 20°C, TMS): δ = 163.47, 155.61, 154.92, 153.74, 153.53, 153.39, 153.29, 147.42, 147.25, 147.15, 146.48, 135.95, 131.55, 120.58, 130.13, 129.81, 129.69, 129.09, 128.61, 128.58, 128.34, 127.97, 127.84, 126.00, 125.55, 124.46, 123.68, 123.40, 122.84, 122.51, 120.62, 119.27, 119.17, 118.73, 118.60, 118.55, 57.50, 38.74, 38.72, 32.65, 31.91, 31.71, 29.51, 24.13 ppm; IR (KBr): $\tilde{\nu}$ = 2957, 1707, 1670,

1595, 1503, 1334, 1210 cm^{-1} ; UV/Vis (toluene): λ_{max} (ϵ) = 758 (157900), 688 nm ($77000 \text{ M}^{-1} \text{ cm}^{-1}$); MS: m/z (%): 1934.2 (100) [M^+]; elemental analysis calcd (%) for $\text{C}_{124}\text{H}_{128}\text{Br}_2\text{N}_2\text{O}_8$: C 83.84, H 7.38, N 1.58; found: C 83.67, H 7.29, N 1.50.

***N,N'*-Bis-(*N*-2,6-diisopropylphenyl)-1,6,11,16-tetrakis[4-(1,1,3,3-tetramethylbutyl)phenoxy]-8,9:18,19-dinaphthoquaterylene-3,4:13,14-bis(dicarboximide) (6):** Compound **11** (1.94 g, 1 mmol), $[\text{Pd}(\text{dba})_2]$ (60 mg), $\text{P}(\text{o-tolyl})_3$ (30 mg), 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.5 g) and CsF (460 mg) were stirred at 95°C in the mixture of toluene (90 mL) and acetonitrile (10 mL) for 48 h under argon. The resulting mixture was cooled and washed with water. The organic layer was separated, evaporated under vacuum and purified by column chromatography on silica gel with toluene as eluent. Yield 0.89 g (46%); M.p. $>350^\circ\text{C}$; ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100°C , TMS): δ = 11.18 (s, 4H), 8.74 (brs, 4H), 8.54 (s, 4H), 7.59 (brs, 4H), 7.43–7.45 (m, 10H) 7.28–7.30 (m, 12H), 2.84 (sept, 3J = 6.68 Hz, 4H), 1.71 (s, 8H), 1.38 (s, 24H), 1.10 (d, 3J = 6.71 Hz, 24H), 0.69 ppm (s, 36H); ^{13}C NMR (175 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100°C , TMS): δ = 163.37, 154.35, 154.01, 147.03, 146.18, 132.47, 131.50, 129.83, 129.51, 128.40, 128.20, 127.94, 127.68, 126.80, 125.69, 125.27, 124.18, 124.15, 123.999, 123.96, 123.91, 122.93, 122.55, 118.02, 57.59, 38.70, 32.44, 31.98, 31.63, 29.56, 24.22 ppm; IR (KBr): $\tilde{\nu}$ = 2958, 2919, 2863, 1707, 1663, 1590, 1501, 1355, 1311, 1503, 1205, 1160 cm^{-1} ; UV/Vis (toluene): λ_{max} (ϵ) = 700 (142900), 638 (62800), 589 (16000), 411 (31000), 389 nm ($21500 \text{ M}^{-1} \text{ cm}^{-1}$); MS (FD): m/z (%): 1926 (100) [M^+]; elemental analysis calcd (%) for $\text{C}_{136}\text{H}_{134}\text{N}_2\text{O}_8$: C 84.88, H 7.02, N, 1.46; found: C 84.74, H 7.11, N 1.50.

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