

Angular Benzoperylenetetracarboxylic Bisimides

Heinz Langhals,* Bernd Böck, Tanja Schmid, and Alexey Marchuk^[a]

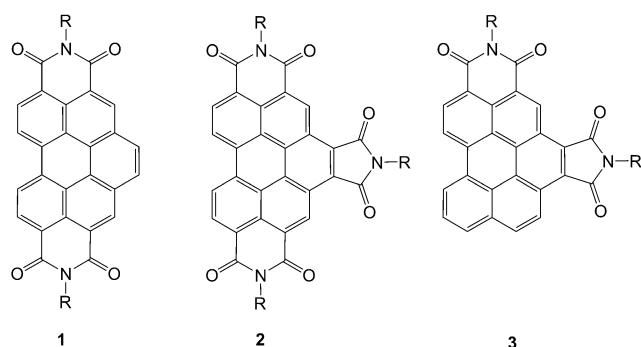
Abstract: Benzoperylene derivatives with two angularly attached dicarboxylic imide rings, which were prepared by the Diels–Alder-Reaction, exhibit strong fluorescence and their free *peri* positions allow either control of the UV/Vis spectra through their substituents or form anchor positions for the attachment of functional units. The angular chromophore **3** may be used both for fluorescent labeling such as for primary amines or enzymes or as building blocks for more complex assemblies where they may act as energy donors for FRET or electron acceptors in PET such as for photovoltaic solar cells.

Keywords: electron transfer • enzymes • fluorescence spectroscopy • FRET • heterocycles

Introduction

Benzoperylene derivatives such as tetracarboxylic bisimides^[1] **1** and hexacarboxylic trisimides **2** (Scheme 1) receive increasing interest as energy donors^[2] for FRET^[3] (Förster resonance energy transfer)^[4] processes.

The hitherto unknown angular isomer **3** of **1** offers new possibilities such as an orthogonal arrangement of the substituents R and the possibility of the extension of the structure at the unsubstituted *peri*-positions. Thus, it forms an interesting building block for more complex molecular architectures where the orthogonal arrangement of chromophores^[2,5] allows the special management of the energy of optical excitation.

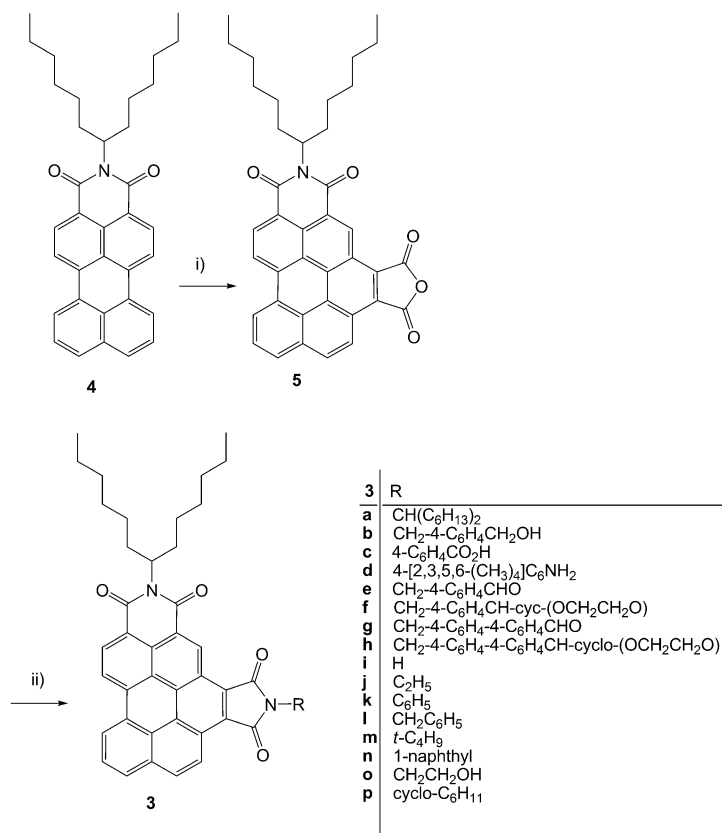


Scheme 1. Benzoperylenetetracarboxylic bisimides (**1**), benzoperylenehexacarboxylic trisimides (**2**) and angular benzoperylenetetracarboxylic bisimides (**3**).

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Results and Discussion

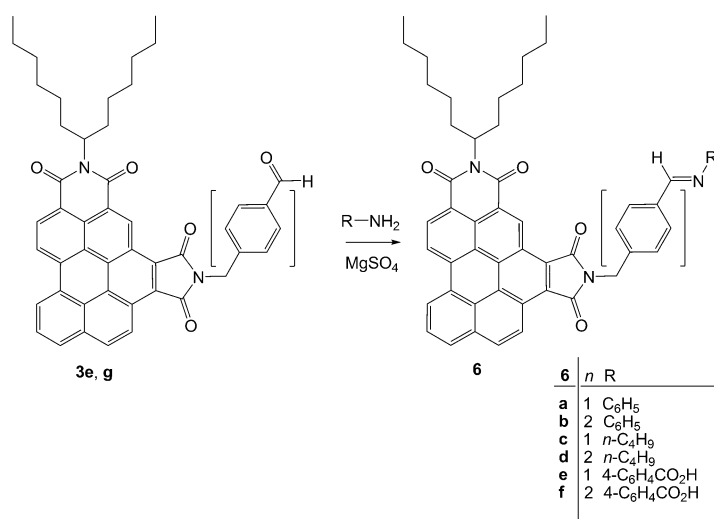
We started the synthesis of **3** with perylene-3,4-dicarboxylic imide^[6] (**4**) where the solubilising 1-hexylheptyl swallow-tail substituent was attached to the nitrogen atom and allowed for a reaction with maleic anhydride and the aromatizing reagent *p*-chloranile according to the Clar variant^[7] of the Diels–Alder-reaction. We obtained the readily soluble anhydride carboximide **5** in 87% yield (see Scheme 2). Com-



Scheme 2. Preparation of the angular perylenebiscarboximides **3**. i) Maleic anhydride, *p*-chloranile. ii) R-NH₂, quinoline and imidazole, respectively.

pound **5** forms a key intermediate for further synthesis and has not been described before; another low soluble and difficult to purify derivative of the basic chromophore of **5** has been reported, however, with different spectroscopic data.^[8] Compound **5** was condensed with primary amines to prepare **3** where the two swallow-tail substituents in **3a** made the material very readily soluble. The introduction of the bulky *tert*-butyl substituent in **3m** or the rigid cyclohexyl substituent in **3p** proceeded without problems. Moreover, functionalities such as for labeling can be introduced by means of a substituent R in **3**. For example, a hydroxy group can be incorporated by condensation of **5** with aminohydroxy-*p*-xylene to form **3b**, a carboxyl group by the condensation of 4-aminobenzoic acid to prepare **3c** and a basic and nucleophilic amino group, respectively, in **3d** where the latter is a suitable building block for the synthesis of even more complex structures by condensation. The introduction of an aldehyde group (**3e** and **3g** with differently long aromatic spacers) offers many possibilities for the labeling of biologically active materials with primary amino groups. A direct condensation of aminoaldehydes with **5** is problematic because of polymerisation. Thus, we protected the aldehyde group as the ethylene acetal according to ref. [9] and prepared either aldehyde **3e** directly by means of the corresponding amino acetals and acidic workup or acetal **3f** if acid was excluded. The former (**3e**) is more appropriate for direct labeling such as in the condensations with primary amines, whereas the latter is useful as a protected compound as it allows for the long-term storage of the comparably reactive aldehyde. The oxidation of **3b** is an alternative for the preparation of **3e**. The even longer spacer in **3g** and **3h**, respectively, allows more distance between the chromophore and the labelled position and lowers interference by the labeling.

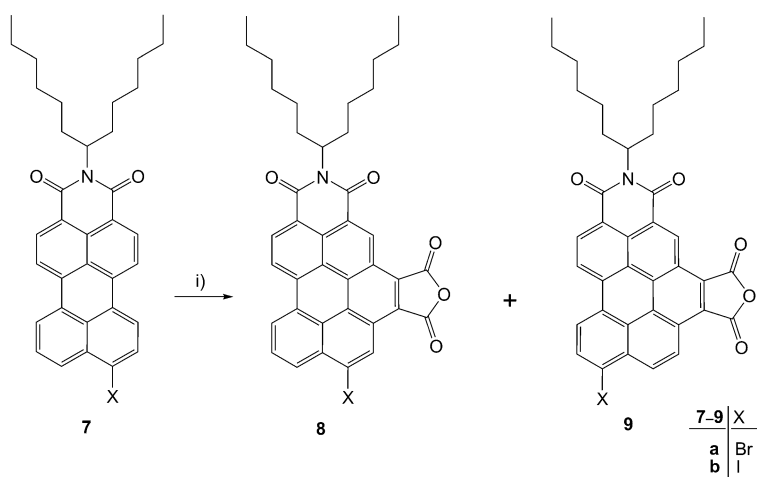
The condensation of **3e** and **3g** with aromatic amines **6a** and **6b**, respectively, is as simple as the reaction with simple aliphatic amines **6c** and **6d** and amino acids **6e** and **6f**; see Scheme 3. The labeling of natural polypeptides requires a suitable solvent for both the peptide and the labeling agent **3e** and **3g**. We applied bovine serum catalase as a typical biologically active substrate and investigated **3e** and **3g** in various solvents where NMP gives comparably good results. The catalase is labelled in both cases, which is indicated by its coloration, and remains catalytically active. Good results were also obtained in DMF, *N,N*-dimethylacetamide and *N*-methylpiperidone. DMPU, DMEU and *N*-methylformanilide are not useful for labeling, although



Scheme 3. Synthesis of azomethines **6** by means of the aldehydes **3e** ($n=1$) and **3g** ($n=2$), respectively.

they do not interfere with the catalytic activity of catalase, whereas DMSO favors labeling indicated by a yellow coloration, though it destroys the catalytic activity. Best results were obtained with NMP giving an efficient labeling and preserving the enzymatic activity indicated by a vigorous evolution of oxygen from hydrogen peroxide. Other aldehyde-linked chromophores gave similar results so that NMP seems to be an ideal solvent for the labeling of enzymes and other peptides with lipophilic aldehydes-linked chromophores.

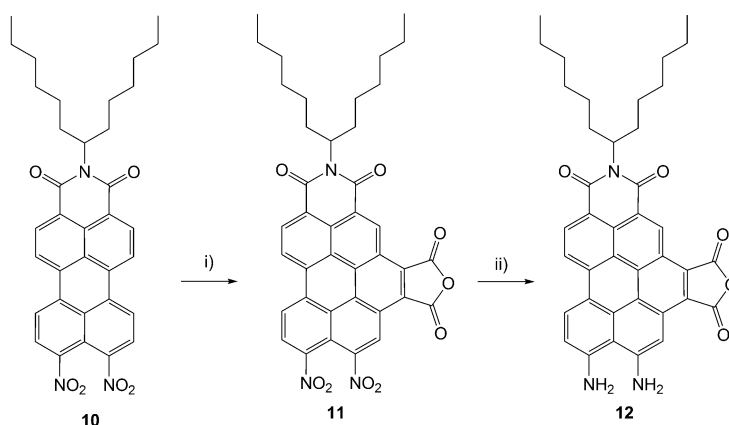
The free *peri* position in **3** and **5**, respectively, can be applied for the construction of even more complex assemblies. Bromination of **3** gave a complex mixture, which was difficult to separate. Better results were obtained if **4** was firstly halogenated to form **7** and then extended by means of the Clar reaction to form **8** and **9** (Scheme 4). Clearly, only



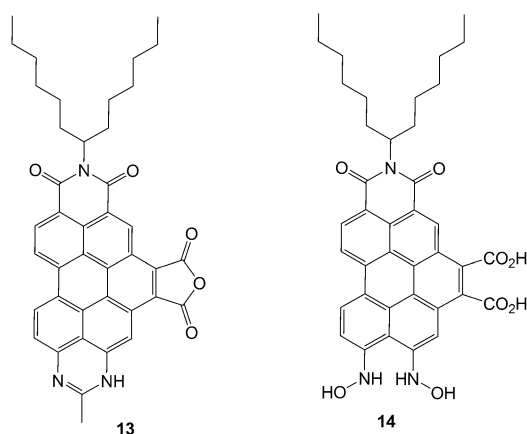
Scheme 4. Synthesis of the *peri*-halogenated compound **7**. i) Br₂, K₂CO₃, and chlorobenzene for **7a** and I₂, H₃IO₆, HOAc and H₂SO₄, CHCl₃ for **7b**.

these two isomers were formed, however they could not be separated, neither the bromine derivative **8a** and **9a**, respectively, nor the iodine derivatives **8b** and **9b**. The purification problems could be overcome by a double substitution in the *peri* position.

We then nitrated **4** with nitric acid and acetic anhydride to dinitro derivative **10** where the Clar reaction with maleic anhydride to form **11** proceeded more slowly than the reaction with **4** because of electron deficiency; the conversion to **11** was successful without any problems. Compound **12** (Scheme 5) was expected as the product of reduction of **11** by means of metallic iron and HCl/ethanol (Bechamp reduction), although amidine **13** was obtained instead and did not undergo further reduction (see Scheme 6). Finally, a reduction of **11** to **12** was successful by means of H₂ and Pd/C where hydroxylamine **14** was the main product in a 70:30 mixture with **12**.



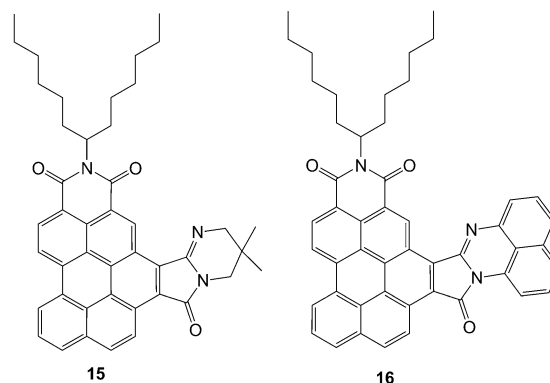
Scheme 5. Synthesis of the *peri*-dinitrated compound **11** and the diamine **12**. i) Maleic anhydride, chloranile. ii) H₂, Pd/C.



Scheme 6. Amidine **13** was obtained from the nitro compound **11** and Fe/HCl, whereas the hydroxylamine **14** and the amino compound **12** (70:30) from the catalytic reduction (H₂/Pd).

The anhydride group in **5** was used for a further extension of the chromophore. A condensation with 1,3-diamino-2,2-dimethylpropane gave amidine **15** analogously to ref. [10],

where the structure was stabilized by the incorporation into a six-membered ring and the application of geminal methyl groups. No oxidation of the aliphatic structure was found as observed in ref. [10]; on the other hand, the condensation was carried out with a strict exclusion of atmospheric oxygen. The chromophore was further extended by the condensation of **5** with 1,8-diaminonaphthalene to form **16** (Scheme 7).



Scheme 7. Amidines **15** and **16**.

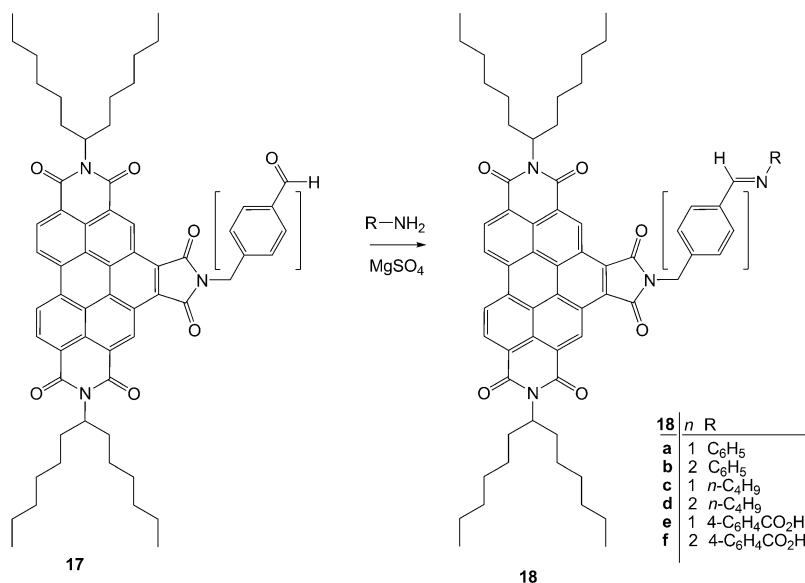
The successful labeling of amines with **3g** and **3e**, respectively, was extended to the chromophore of **2**. As a consequence, we prepared aldehyde **17a** for $n=1$ and **17b** for $n=2$ both as the free aldehydes and protected as the ethylene acetals (**17c** and **17d**, respectively) and condensed the aldehydes to form azomethines **18** similar to **6**; see Scheme 8. Catalase could be labelled with **17** and NMP can be recommended analogously to **3e** and **3g**. Moreover, we prepared the dicarboxylic imide aldehydes **19a** for $n=1$ and **19b** for $n=2$ where a labeling was successful even without the solubilising *sec*-alkyl group; see Scheme 9. Red compounds **20** were obtained both from simple primary amines and catalase.

Finally, two chromophores of **3** were interlinked by condensation of 1,4-diaminotetramethyl benzene where a mixture of **21** and **22** was obtained which was difficult to separate even in TLC (Scheme 10).

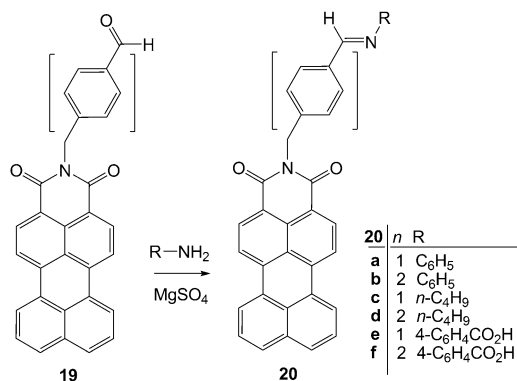
The UV/Vis absorption spectrum of **5** is hypsochromically shifted compared with **1** and structured differently (see Figure 1). The vibronic structure of **5** is less pronounced, however, there are several optical transitions in the visible where the most bathochromic is not the most intense one. The fluorescence spectrum is slightly structured with a fluorescence quantum yield of 64%.

The UV/Vis spectra of tetracarboxylic bisimide **3a** resemble the spectra of **5**, are slightly more structured and differ completely from the spectra of isomeric **1** where vibronic bands are dominating. On the other hand, several electronic transitions can be seen in Figure 2 where the most bathochromic is not the most intense one. The fluorescence quantum yield of **3a** is 31% and thus, is about the half that of **5**, however, still gives a strong visible impression in day light.

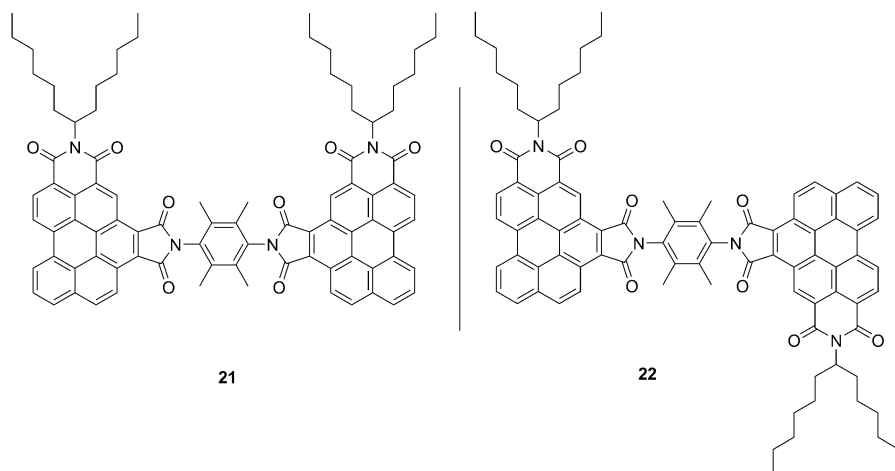
The labeling of primary amines and proteins with the derivatives **3e** and **3g**, respectively, influences the UV/Vis spectra insignificantly compared with **3a**.



Scheme 8. Synthesis of azomethines **18** by means of the aldehydes **4e** and **4g**, respectively.



Scheme 9. Synthesis of azomethines **20** by means of the aldehydes **19**.



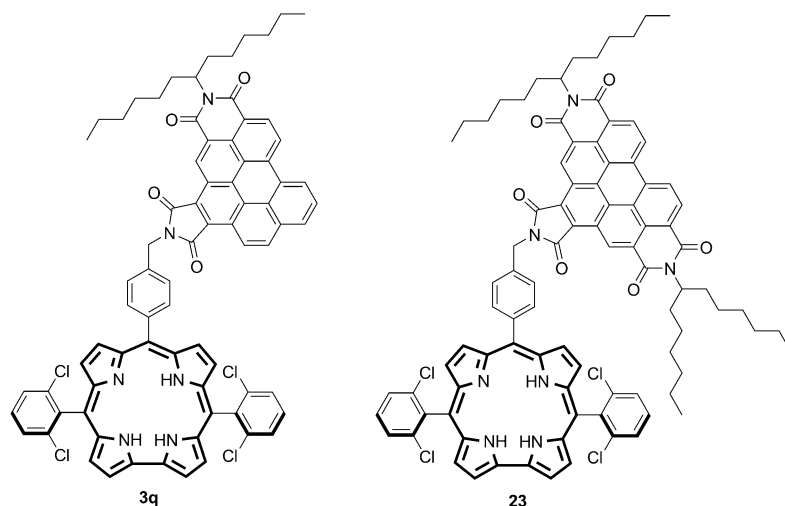
Scheme 10. Dyads **21** and **22**.

The introduction of the electron-withdrawing nitro groups into the *peri*-position of **3** to form **11** shifts the UV/Vis spectra only slightly, induces a stronger vibronic structure and diminishes the fluorescence quantum yield to 12%, whereas the electron-donating amino groups in **12** and the hydroxylamino groups in **14** cause strongly bathochromic shifts so that dark purple solutions were obtained. Amidine **13** is strongly solvatochromic both in absorption and fluorescence. Bathochromic shifts were also induced by the introduction of the aromatic amidine units in **16**; see Figure 3. The linking of two units of **3** to form the dyads **21** and **22**, respectively, causes weak exciton interactions with slightly altered spectra and a nearly unaffected fluorescence quantum yield of 36%.

Photophysical properties of the preylene derivatives were reported in Table 1. The fluorescence lifetimes of **3** are in the order of 6–7 ns and correspond to the absorptivities of 30 000–40 000. There is a pronounced inter-system crossing (ISC) in **3a** competing with fluorescence so that phosphorescence can be observed and efficient formation of singlet oxygen with a quantum yield as high as 68%; for more details see ref. [11].

Chromophore **3** is an interesting building block for even more complex arrangements of optical units. As a consequence, we used aldehyde **3e**, allowed an acid-catalysed reaction with the corresponding dipyrrolomethane and a subsequent oxidation with *p*-chloranile and isolated the corrole dyad **3q** (Figure 4); for corroles see ref. [12]. A similar reaction was successful with benzoperylene aldehyde **17a** to form **23**.

The UV/Vis absorption spectrum of **3q** is dominated by the strong absorption of the benzoperylene and the Q-band of the corrole unit below 500 nm and indicated the formation of the dyad with its appreciably weaker bathochromic absorption of the corrole with the Soret bands; see Figure 4. Efficient energy transfer from the hypsochromically absorbing benzoperylene proceeds to the corrole with a fluorescence quenching of the former. The fluorescence of the corrole unit of **3q** is comparably weak



where about 3% was found in chloroform solution. There is an efficiently competing photo-induced electron transfer process (PET) from the electron-rich corrole to the benzoperylene unit; compare ref. [13]. A similar behaviour was observed for the dyad **23** (Figure 5). An efficient energy transfer proceeds from the benzoperylene-triscarboximide to the corrole where only a weak fluorescence is observed for the latter with a fluorescence quantum yield below 1%; ob-

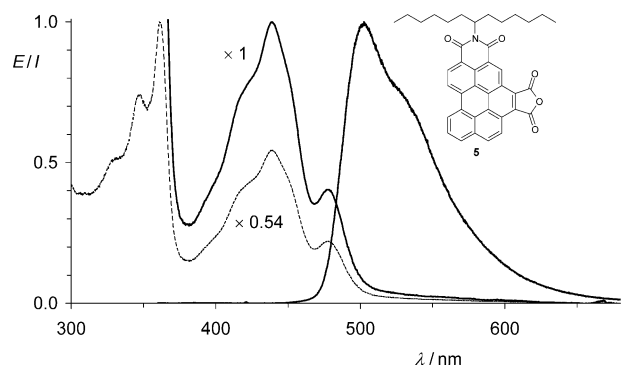


Figure 1. UV/Vis absorption (left) and fluorescence (right) spectra of **5** in chloroform.

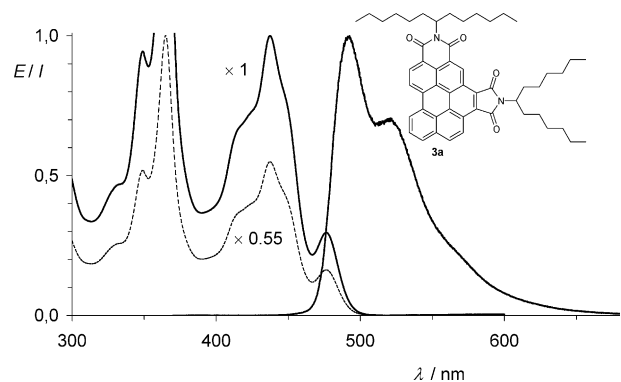


Figure 2. UV/Vis absorption (left) and fluorescence (right) spectra of **3a** in chloroform.

viously, the even more electron depleted benzoperylene triscarboximide causes in **23** a more efficient PET than in **3q**. Such PET processes cause light-induced charge separation^[14] and are of interest for photovoltaics in solar cells^[15] where the charge separation by **3q** and **23** is induced by a purely organic assembly.

Conclusion

The angular isomers **3** of the benzoperylene-tetracarboxylic bisimides **1** enlarge not only the variety of perylene derivatives, but also open many novel possibilities in this field. They exhibit strong fluorescence and their free *peri* positions allow either the controlling of UV/Vis spectra by means of substituents or form anchor positions for the attachment of functional units. The angular chromophore **3** may be used both for fluorescent labeling such as for primary amines or enzymes or as building blocks for more complex assemblies

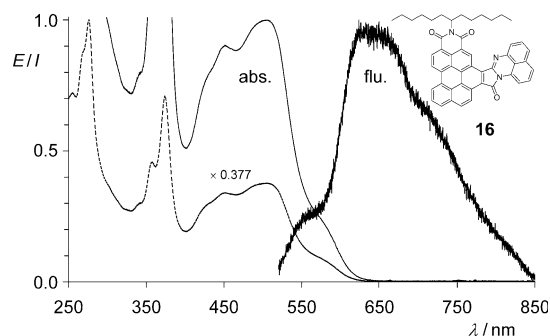


Figure 3. UV/Vis absorption (left) and fluorescence (right) spectra of **16** in chloroform.

Table 1. Photophysical properties of perylene derivatives. Molar absorptivities in the visible (ϵ), fluorescence quantum yields (ϕ) and fluorescence lifetimes (τ).

Compound	$\epsilon^{[a]}$	$\phi^{[b]}$	$\tau^{[c]}$	Solvent
3a	28 400	0.31	6.7	CH ₂ Cl ₂ ^[d]
3e	31 300	0.30	7.1	CHCl ₃
3i	22 900	0.38	6.1	CHCl ₃
3k	43 600	0.21	6.4	CHCl ₃
4	32 000	≈ 1.00	6.1	CHCl ₃
5	25 500	0.64	6.6	CHCl ₃
10	56 000	≈ 1.00	5.3	CHCl ₃
11	39 000	0.12	2.4	CHCl ₃
17a	60 200	0.17	7.0	CHCl ₃
19a	24 000	0.91	6.3	CHCl ₃
21/22		0.36	5.0	CHCl ₃

[a] Molar absorptivity in mol L⁻¹ cm⁻¹. [b] Fluorescence quantum yield. [c] Fluorescence lifetime in ns. [d] See ref. [11b]

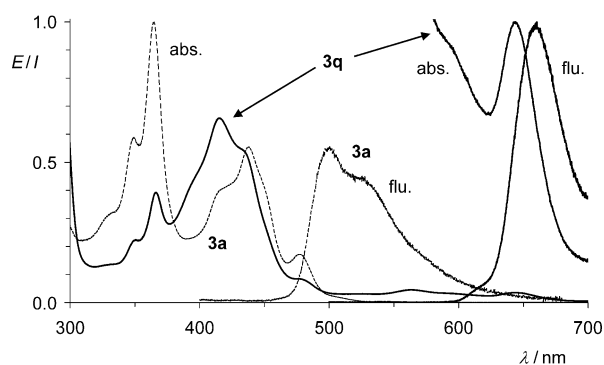


Figure 4. UV/Vis absorption (left) and fluorescence (right) spectra of **3q** in chloroform (—), compared with **3a** (-----).

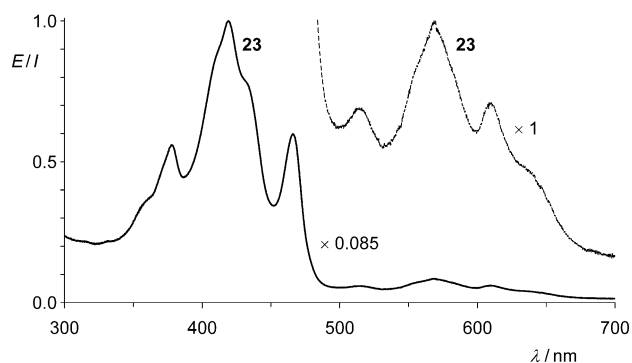


Figure 5. UV/Vis absorption spectrum of **23** in chloroform.

where they may be energy donor for FRET or electron acceptors in PET such as for photovoltaic solar cells.

Experimental Section

General methods: See Supporting Information.

10-[N-(1-Hexylheptyl)-N'-(benzyl)benzo[ghi]perylene-3,4,6,7-bis(dicarboximide)]-5,15-bis(2,6-dichlorophenyl)corrole (3q**):** *N*-(1-Hexylheptyl)-*N'*-(4-formylbenzyl)benzo[ghi]perylene-3,4,6,7-bis(dicarboximide) (**3e**, 200 mg, 280 μmol) and 2,6-dichlorophenyldipyrromethane (163 mg, 560 μmol) were dissolved with the exclusion of light in dichloromethane (7.00 mL), treated with trifluoroacetic acid (TFA, 12.8 mg, 112 μmol, dissolved in 0.25 mL of CH₂Cl₂), stirred at room temperature for 20 min, treated with triethylamine (11.3 mg, 112 μmol) and then *p*-chloranile (207 mg, 840 μmol), stirred at room temperature for 24 h, evaporated in vacuo, purified by column separation (silica gel 63–200 μm, CH₂Cl₂, first green band, and then silica gel, CH₂Cl₂/*n*-hexane 10:1), dissolved in a small amount of CH₂Cl₂ and precipitated with *n*-pentane. Yield 35.0 mg (10%) green solid, m.p. > 400 °C. *R*_f (silica gel, CH₂Cl₂) = 0.85; ¹H NMR (600 MHz, CDCl₃): δ = -2.91–2.79 (brs, 3H, NH), 0.81 (t, ³*J* = 7.0 Hz, 6H, CH₃), 1.22–1.27 (m, 16H, CH₂CH₂CH₂CH₂CH₃), 1.95–2.03 (m, 2H, CHCH₂), 2.32–2.44 (m, 2H, CHCH₂), 5.26–5.37 (m, 2H, NCH₂), 5.41 (s, 1H, NCH), 7.65 (d, ³*J* = 7.9 Hz, 2H, H_{Cl-phenyl}), 7.69–7.77 (m, 2H, H_{MIM-BP}), 7.83–7.89 (m, 1H, H_{arom}), 8.03–8.12 (m, 3H, H_{arom}), 8.22 (d, ³*J* = 4.3 Hz, 1H, H_{arom}), 8.32–8.35 (m, 1H, H_{arom}), 8.36–8.40 (m, 1H, H_{arom}), 8.45–8.49 (m, 1H, H_{arom}), 8.51–8.54 (m, 1H, H_{arom}), 8.60 (d, ³*J* = 4.8 Hz, 1H, H_{arom}), 8.68 (d, ³*J* = 4.7 Hz, 1H, H_{arom}), 8.75 (d, ³*J* = 4.3 Hz, 1H, H_{arom}), 9.09–9.11 (m, 1H, H_{arom}), 8.99–9.07 (m, 2H, H_{arom}), 9.13–9.17 (m, 2H, H_{arom}), 9.30 (d, ³*J* = 8.7 Hz, 1H, H_{MIM-BP}), 10.32 ppm (s, 1H, CCHCO); IR (ATR): $\tilde{\nu}$ = 3854.1 (w), 3676.0 (w), 2951.1 (s), 2923.5 (vs),

2854.3 (s), 2361.6 (vs), 2337.7 (vs), 1702.1 (s), 1661.5 (s), 1605.4 (m), 1558.4 (m), 1457.7 (m), 1428.4 (m), 1396.0 (m), 1325.3 (m), 1111.7 (w), 796.0 (w), 667.9 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (*E*_{rel}) = 350.8 (0.31), 366.0 (0.52), 413.0 (1.00), 433.8 (0.83), 473.9 (0.13), 567.2 (0.11), 608.0 (0.08), 639.6 (0.06), 715.6 nm (0.01); fluorescence (CHCl₃, λ_{exc} = 366 nm): λ_{max} (*E*_{rel}) = 535.8 (0.03), 663.1 (1.00), 720.4 nm (0.36); fluorescence quantum yield (CHCl₃, λ_{exc} = 565 nm, *E*_{565 nm/1 cm} = 0.0111, reference S-13 with Φ = 1.00): Φ = 0.0212. Fluorescence quantum yield (CHCl₃, λ_{exc} = 350 nm, *E*_{350 nm/1 cm} = 0.0307, reference S-13 with Φ = 1.00): Φ = 0.018. MS (FAB⁺): *m/z* (%): 1274 (1) [M+H]⁺, 1273 (2) [M]⁺, 1272 (2) [M-H]⁺, 1271 (1), 1092 (0.3) [M+H-C₁₃H₂₆]⁺, 1091 (0.3) M-C₁₃H₂₆⁺, 1090 (0.3) [M-H-C₁₃H₂₆]⁺, 675 (0.5) [corrole+benzyl spacer]⁺; HMRS (FAB⁺): calcd for C₇₇H₅₀Cl₄N₆O₄ [M+H]⁺: 1273.3345, found 1273.3331, Δ = 0.0014.

10-[N,N'-Bis(1-hexylheptyl)-N'-(benzyl)benzo[ghi]perylene-1',2':3,4:9,10-tris(dicarboximide)]-5,15-bis(2,6-dichlorophenyl)corrole (23**):** *N,N'*-Bis(1-hexylheptyl)-*N'*-(4-formylbenzyl)benzo[ghi]perylene-1',2':3,4:9,10-tris(dicarboximide) (**17a**, 134 mg, 139 μmol), 2,6-dichlorophenyldipyrromethane (81.0 mg, 278 μmol), dichloromethane (5.00 mL), TFA (6.34 mg, 55.6 μmol in 0.20 mL CH₂Cl₂), triethylamine (5.63 mg, 55.6 μmol in 0.25 mL CH₂Cl₂) and *p*-chloranile (103 mg, 417 μmol) were allowed to react analogously to **3q**, purified by column separation (silica gel 63–200 μm, CH₂Cl₂, first green fraction), dissolved in a small amount of CHCl₃ and precipitated with methanol. Yield 35.0 mg (16.5%) green solid, m.p. ≈ 250 °C; *R*_f (silica gel, CH₂Cl₂) = 0.80; ¹H NMR (600 MHz, CDCl₃): δ = -2.94–2.78 (brs, 3H, NH), 0.80 (t, ³*J* = 7.0 Hz, 12H, CH₃), 1.17–1.34 (m, 32H, CH₂CH₂CH₂CH₂CH₃), 1.89–1.98 (m, 4H, CHCH₂), 2.28–2.39 (m, 4H, CHCH₂), 5.25–5.36 (m, 2H, NCH₂), 5.46 (s, 2H, NCH), 7.63–7.70 (m, 2H, H_{arom}), 7.71–7.82 (m, 3H, H_{arom}), 8.04 (d, ³*J* = 8.3 Hz, 2H, H_{arom}), 8.19–8.29 (m, 2H, H_{arom}), 8.50–8.77 (m, 5H, H_{arom}), 9.08 (s, 1H, H_{arom}), 9.11–9.25 (m, 4H, H_{arom}), 9.36–9.42 (m, 1H, H_{arom}), 9.44 (d, ³*J* = 8.3 Hz, 2H, H_{BP}), 10.57 ppm (s, 2H, H_{BP}); IR (ATR): $\tilde{\nu}$ = 3357.9 (m), 3077.4 (w), 2953.6 (s), 2926.3 (vs), 2856.4 (s), 1770.1 (w), 1709.9 (s), 1689.3 (vs), 1679.4 (vs), 1664.4 (vs), 1595.3 (w), 1572.3 (m), 1557.9 (w), 1428.1 (w), 1414.5 (w), 1397.0 (w), 1364.3 (w), 1318.2 (m), 1238.0 (w), 1111.3 (m), 812.0 (w), 756.1 (w), 712.5 cm⁻¹ (w); UV/Vis (CHCl₃): λ_{max} (*E*_{rel}) = 272.4 (0.34), 377.6 (0.55), 418.7 (1.00), 431.0 (0.79), 467.1 (0.61), 567.6 (0.08), 606.4 (0.05), 717.2 nm (0.02); fluorescence (CHCl₃, λ_{exc} = 378 nm, very weak fluorescence): λ_{max} (*E*_{rel}) = 476.7 (1.00), 512.2 (0.76), 550.1 (0.29), 651.1 (0.22), 723.8 nm (0.23); fluorescence (CHCl₃, λ_{exc} = 419 nm, very weak fluorescence): λ_{max} (*E*_{rel}) = 477.6 (1.00), 508.6 (0.70), 651.4 (0.65), 720.9 nm (0.79); fluorescence quantum yield (CHCl₃, λ_{exc} = 569 nm, *E*_{569 nm/1 cm} = 0.0079, reference S-13 with Φ = 1.00): Φ = 0.0014. Fluorescence quantum yield (CHCl₃, λ_{exc} = 378 nm, *E*_{378 nm/1 cm} = 0.0439, reference S-13 with Φ = 1.00): Φ = 0.0021. MS (FAB⁺): *m/z* (%): 1525 (1) [M+H]⁺, 1524 (1) [M]⁺, 1523 (1) [M-H]⁺, 1343 (0.3) [M+H-C₁₃H₂₆]⁺, 1342 (0.3) [M-C₁₃H₂₆]⁺, 1160 (0.2) [M-2 × C₁₃H₂₆]⁺, 1159 (0.2) [M-H-2 × C₁₃H₂₆]⁺, 675 (0.4) [corrole+benzyl spacer]⁺; HMRS (FAB⁺): calcd for C₉₂H₈₄Cl₄N₇O₆ [M+H]⁺: 1524.5237, found 1524.5215, Δ = 0.0022; elemental analysis (%) calcd for C₉₂H₈₄Cl₄N₇O₆ (1524.5): C 72.48, H 5.49, Cl 9.30, N 6.43; found C 72.00, H 5.62, Cl 8.86, N 6.19.

The other compounds including characterization can be found in the Supporting Information.

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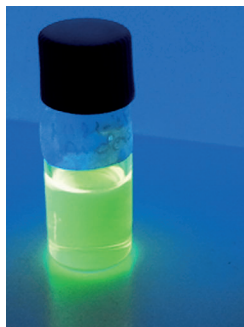
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Fluorescent Labels

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**Angular Benzoperylenetetracarboxylic
Bisimides**



Two angular rings: Benzoperylene derivatives with two angularly attached dicarboxylic imide rings, which were prepared by the Diels–Alder–Reaction, are strongly fluorescent (see figure) and were applied both for fluorescence labeling (e.g., enzymes) and as components in FRET and PET systems.