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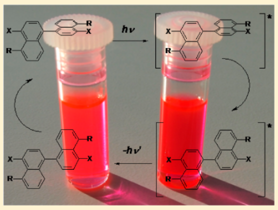
Controlling UV/vis Absorption and Stokes Shifts in Highly Fluorescent Chromophores by Molecular Dynamics in Targeted Construction of Dyads

Heinz Langhals* and Alexander Hofer

Department of Chemistry, LMU University of Munich, Butenandtstrasse 13, D-81377 Munich, Germany

Supporting Information

ABSTRACT: Perylenedicarboximides were interlinked in their free *peri*-position to form dyads where the UV/vis absorptivity was amplified by exciton effects and the strong fluorescence bathochromically shifted by molecular dynamics. Applications of this type of dye with such increased Stokes shifts were discussed.



INTRODUCTION

Rigid aromatic systems are preferred as basic structures for the development of highly fluorescent materials.[1] Small Stokes shifts are generally observed for such fluorophores because the electronic excitation does not induce significant geometric alterations and the conditions are similar in the electronic transitions both for absorption and fluorescence, respectively. On the other hand, strongly fluorescent materials with large Stokes shift are of interest for many fields such as laser dyes,[2] solar energy collectors,[3] analytics,[4] and many more applications because reabsorption of the fluorescent light is avoided. We intend to solve this problem with the development of dyads with dynamic interlinks. Moreover, the interaction of such proximate chromophores may cause exciton effects as a consequence of optical resonance where Davidov splitting and alterations of the absorptivities, respectively, can be additionally applied for the control of the UV/vis spectra.

RESULTS AND DISCUSSION

We estimated that peri-linked binaphthyls would be suitable structures for dynamically increased Stokes shifts according to Figure 1 where there is a tendency from steric effects for the two naphthyl units in the S_o ground state to be orthogonal. The light absorption ($\hbar\nu$) means a fast, vertical electronic transition to the S_1 state preserving the initial geometry. The subsequent relaxation to the S_1' state is fast enough not to affect the electronic excitation. Bathochromically shifted fluorescence ($-\hbar\nu'$) proceeds as a vertical electronic transition to the electronic ground state S_o' where a further relaxation closes the circle to the initial state S_o. One can expect that the S_1' state is more planar than the initial state S_o because the π-system is less firm as a consequence of the electronic excitation and the conjugation between the naphthalene units becomes more important, forcing the two systems in plane. Naphthalene is colorless because of UV absorption, and a bathochromic shift is necessary for light absorption in the visible region. As a consequence, we targeted dyads where X is an element of structure of a chromophore. A ring-closure from X to R allows the construction of rigid structures suitable for high fluorescence quantum yields.

We made suitable dyads with the perylene dye series[5,6] because of their high fluorescent quantum yields[7] and chemical and photochemical stability[8] and started synthesis with the perylene anhydride carboximides[9] **1** where the long chain *sec*-alkyl substituent R = 1-hexylheptyl (swallow-tail substituent) was used to increase solubility.[10] A copper-induced decarboxylation[11] allowed the direct preparation of **2a** in 30% yield in air-equilibrated solution; see Scheme 1. The alkyl chains of R at the nitrogen atoms were further extended to 1-nonyldecyl[12] in **2b** in order to increase the solubility and diminish the tendency of aggregation, respectively, in weakly solubilizing media; other derivatives of **2** were described previously in the literature as intermediates for syntheses,[13] however, without reporting any special photophysical properties.

Some **3** was formed as a product of reduction; **3** became the main product by thorough exclusion of oxygen where the quality of applied copper powder was essential for high yields; com pare to ref 12. **3** was additionally converted to **2** by bromination to form **4** and, finally, palladium-mediated coupling. Hydrolysis of **2** by means of KOH in *tert*-butyl alcohol[9] was not successful. On the other hand, such a hydrolysis of **4** proceeded to form **6**, and a palladium-mediated coupling allowed the preparation of **5**. Finally, the bromination of the well accessible[12,15] **7** was an alternative for the preparation of **6** and **5**, respectively. **5** and **7**, respectively, react with aqueous potassium hydroxide to form the water-soluble **8** and potassium perylene-3,4-dicarboxylate, respectively.

Furthermore, we expanded the perylene dye **9** laterally to the more bathochromically absorbing and highly fluorescent imidazolo derivative **10** according to Scheme 2 and hydrolyzed

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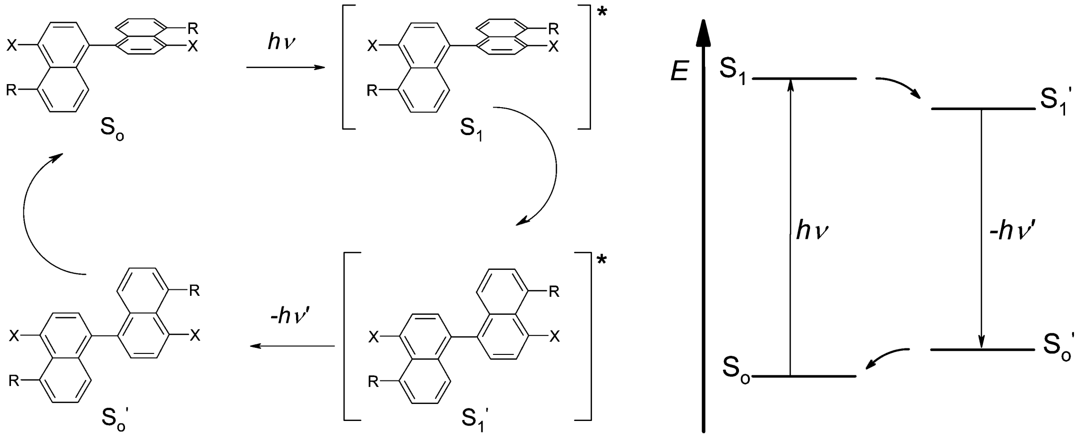
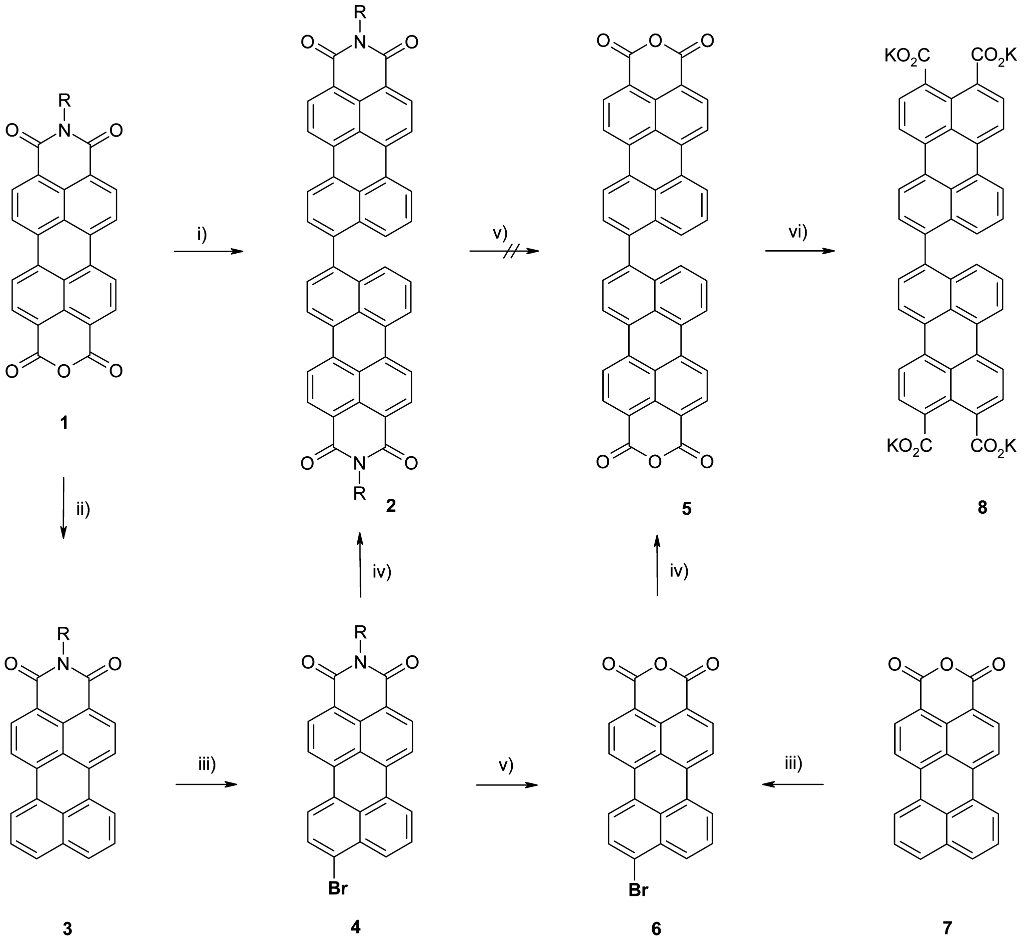


Figure 1. Left: Increase of the Stokes shift of fluorescent materials by fast dynamic processes in binaphthyls: Start with the initial state S_o, vertical electronic transition by light absorption ($\hbar\nu$) to the electronically excited state S_1, relaxation to the excited state S_1', bathochromic fluorescence ($-\hbar\nu'$) to the ground state S_o', and relaxation back to the initial state S_o. X, R: Structure elements of chromophores. Right: Schematic energy diagram (E) of electronic transitions and relaxation processes; overlaying vibronic processes are omitted because of clearness.

Scheme 1. Synthesis of the Dyad 2 (1a–4a: R = 1-hexylheptyl, 1b–4b: R = 1-nonyldecyl)[a]

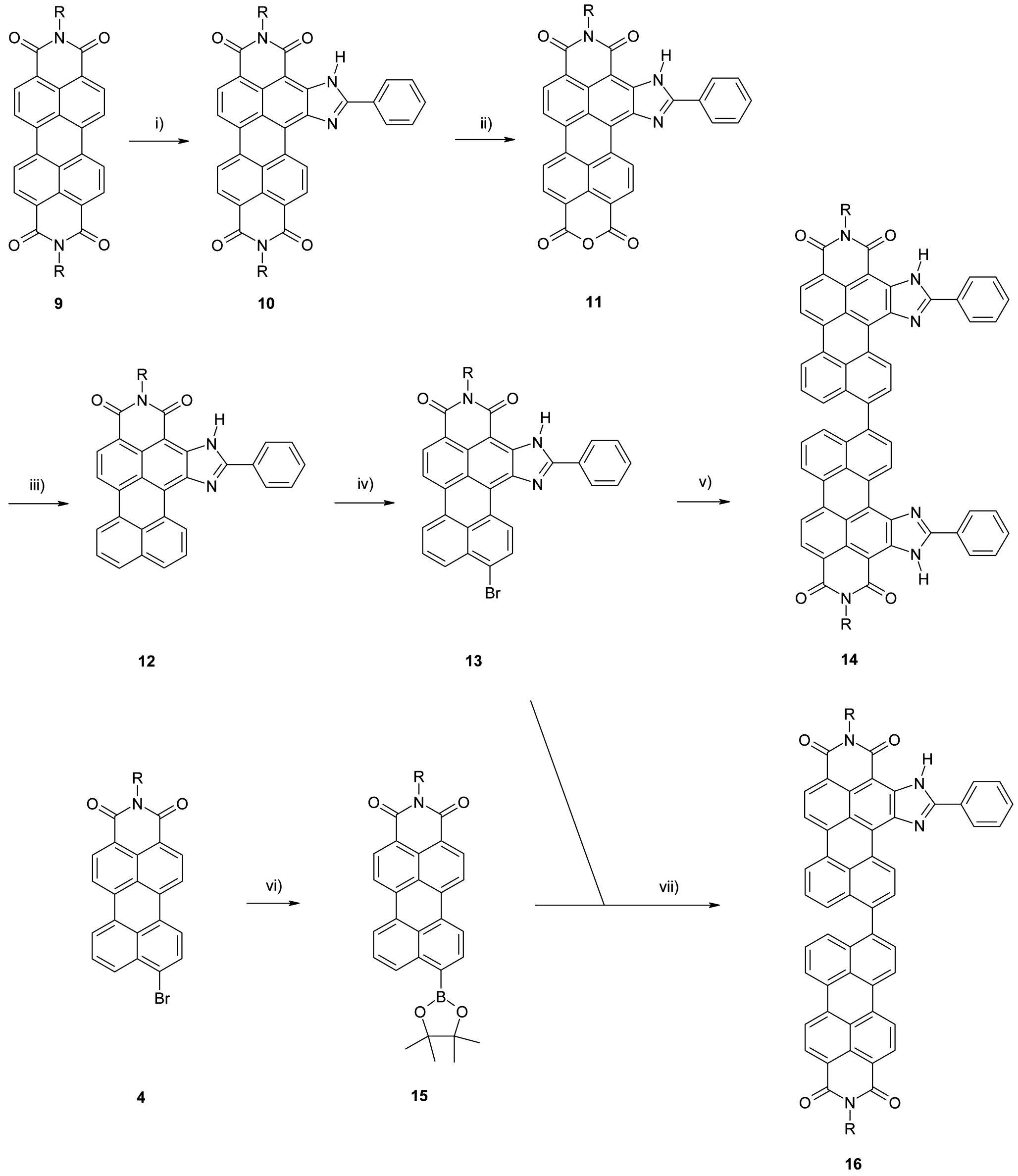


[a]Reagents and conditions: (i) Cu, 3-picoline, air-equilibrated, 28%; (ii) Cu, 3-picoline, exclusion of air and moisture; (iii) Br_2, I_2, H_2SO_4; (iv) $Pd(OAc)_2$, $(C_4H_9)_4NBr$, NEt_3, toluene, 34%; (v) (1) KOH, *tert*-butyl alcohol (2) HCl, (vi) KOH/H_2O.

one carboximide ring to obtain **11**.[14] A copper-mediated decarboxylation gave **12** where a coupling to **14** could not be detected (the yield of **12** depends on the quality of the copper powder). As an alternative, **12** was brominated to form **13** and, finally, palladium-induced coupled to the dyad **14**. The hetero dyad **16** was prepared starting with **4** and the exchange of the bromine atom by a pinacolyl boronic unit in **15**, where a cross coupling with **13** gave the hetero dyad **16**.

The UV/vis absorption spectrum of **3** is typical of perylene dicarboximides[12] with a double maximum and a strong yellow fluorescence (≈100% quantum yield); see Figure 2. The arrangement of two chromophores in **2** induces both a bathochromic

Scheme 2. Synthesis of the Dyad 14 and 16 (R = 1-hexylheptyl)[a]



[a]Reagents and conditions: (i) sodium amide, benzonitrile; (ii) KOH, *tert*-butyl alcohol; (iii) Cu, 3-picoline, 48%; (iv) Br_2, chloroform, 88%; (v) $Pd(OAc)_2$, $(C_4H_9)_4NBr$, NEt_3, toluene, 60%; (vi) pinacole diborane, $PdCl_2(dppf)$, KOAc, 1,4-dioxane, 63%; (vii) $Pd[P(C_6H_5)_3]_4$, 2 M aqueous Na_2CO_3, ethanol, toluene, 60%.

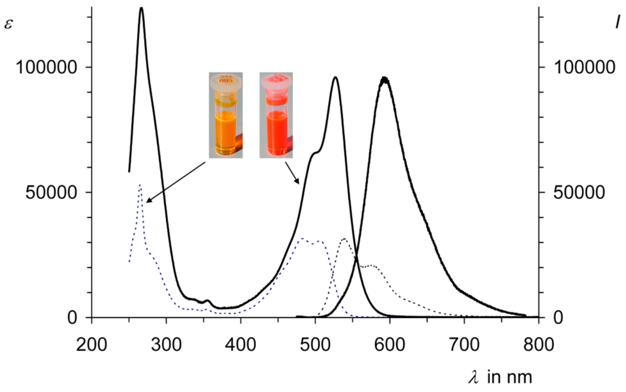


Figure 2. UV/vis absorption (left) and fluorescence spectra (right) of **2a** (solid lines) and **3a** (dotted lines) in chloroform.

shift and an appreciable amplification of the light absorption by co-operative exciton interactions, where the molar absorptivity ε was increased from 31600 L·mol·cm^{-1} of **3** to even 96000 for **2**, and the spectrum was dominated by a strong additional exciton band in **2**; only a doubling of the molar absorptivity would be expected for simple additive effects in the dyad, whereas exciton effects cause a further increase to more than three times the absorptivity of a single chromophore (compare to ref 16). Dye **3a** is highly fluorescent, where a quantum yield of ≈100% was found in chloroform. The high fluorescence quantum yield is preserved in the bichomophore **2a** (≈100%) and indicates that the mobile single bond between the chromophores does not interfere with high fluorescence quantum yields. The Stokes shift of **2a** is appreciably increased compared with the monochromophore **3a**. We interpret this photophysical effect in terms of a dynamic process of the

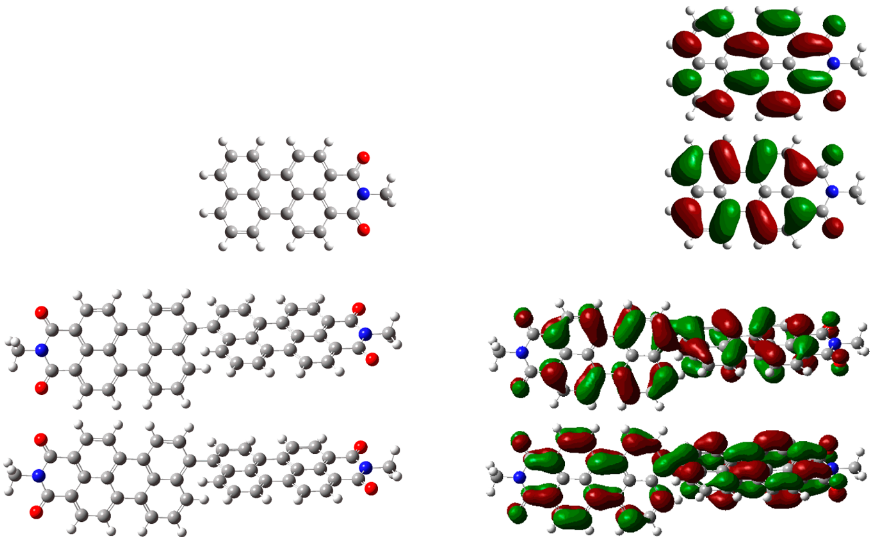


Figure 3. Left from top to bottom: The calculated geometries (DFT, B3LYP) of the ground state of **3**, the equilibrated LUMO of **2**, and the HOMO of **2**. Right from top to bottom: The LUMO of **3**, the HOMO of **3**, the equilibrated LUMO of **2**, and the HOMO of **2**.

electronically excited state of the dye molecules according to Figure 1. The ground state of **2** is characterized by steric effects as the driving force to an orthogonal arrangement of the two chromophores; this causes an electronic decoupling of the π-systems, however, leaves exciton effects unaffected. We calculated the geometry of **2** quantum chemically (DFT) and obtained a dihedral angle of 76° (C9a–C9–C9′–C9a′). The vertical electronic transition by light absorption preserves this geometry; however, the π-system becomes less firm because there is one additional nodal plane of the orbital occupying the excited electron and the interchromophore bond gets more π-character. As a consequence, the excited molecule relaxes to a more planar state with lower energy where the electronic transition of fluorescence becomes bathochromically shifted and the Stokes shift is increased, respectively. We calculated the geometry of the excited state (RTD-CAM-B3LYP-FC) and found a lowered interplanar angle of 53°. DFT calculations of the triplet state with a less firm π-system gave a similar result (46°); involved orbitals and geometries are shown in Figure 3.

We tested the more general applicability of the concept of Figure 1 and prepared the imidazoloperylene derivative **12** where the transversal extension by an imidazolo ring causes a bathochromic shift of the absorption compared with **3** and a bright red fluorescence with a quantum yield close to 100%; see Figure 4.

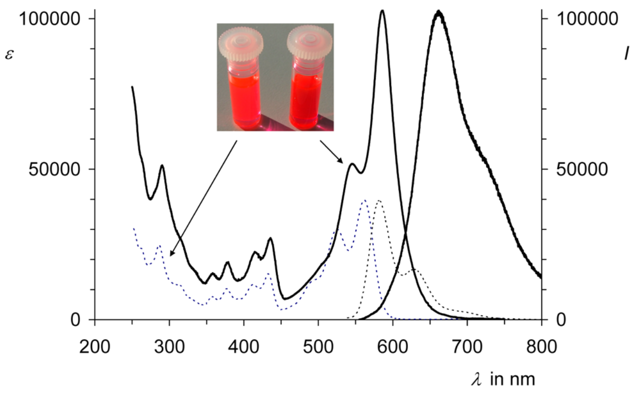


Figure 4. UV/vis absorption (left) and fluorescence spectra (right) of **14** (straight lines) and **12** (dotted lines) in chloroform.

The coupling of two chromophores in **14** causes a slight additional bathochromic shift and an appreciable increase of the absorptivity by exciton effects similarly to **2**. The strong fluorescence (close to 100% quantum yield) is bathochromically shifted such as in **2** and causes an increase of the Stokes shift, respectively, where we make the mechanism of Figure 1 responsible for this effect; the high fluorescence quantum yield indicates that there is no interference either by the dynamic of the flexible interlinking single bond or by the bathochromicity of fluorescence extending into the NIR. The bathochromic shift of the fluorescence is so pronounced that the visual fluorescence of **14** is weaker than that of **12** and **2**, respectively, because despite the high fluorescence quantum yield, an appreciable part of the fluorescence light is in the invisible and the spectral region and region of low eye sensitivity.

We calculated the geometry of both the ground state and the excited state in the same manner as for **2** and found a similar orthogonal geometry for the ground state of **14**: dihedral angle of 90° and only a slight change for the excited state; this may be a consequence of dipole–dipole interactions of the annelated heterocyclic rings. The anhydride **7** is strongly fluorescent (quantum yield close to 100%) and is of special interest because it consists only on C, H, and O and may be applied as a nitrogen-free fluorescent dye. As a consequence, we coupled two chromophores to obtain **5** in order to get a structure suitable for the mechanism according to Figure 1. The UV/vis spectra in Figure 5 indicate an amplified UV/vis absorption by exciton interactions and an increased Stokes shift by the dynamic process according to Figure 1 in complete analogy to the carboximides **2** and **14**, respectively; **7** exhibits a bright orange fluorescence with a quantum yield close to 100% in chloroform. Quantum chemical calculations (DFT, B3LYP) indicate a dihedral angle of 76° for the ground state and 48° for the first excited state (45° for the triplet), verifying the concept of the dynamic increase of the Stokes shift. The anhydride **7** can be ring-opened by means of diluted aqueous KOH to form the water-soluble **8**. The fluorescence quantum yield of such aqueous solutions is appreciably lower than for **2**, **14**, and **7**; however, the dynamics for the increase of the Stokes shift proceeds for this tetraanion in the aqueous phase in the same way as with the other dyads, indicating that

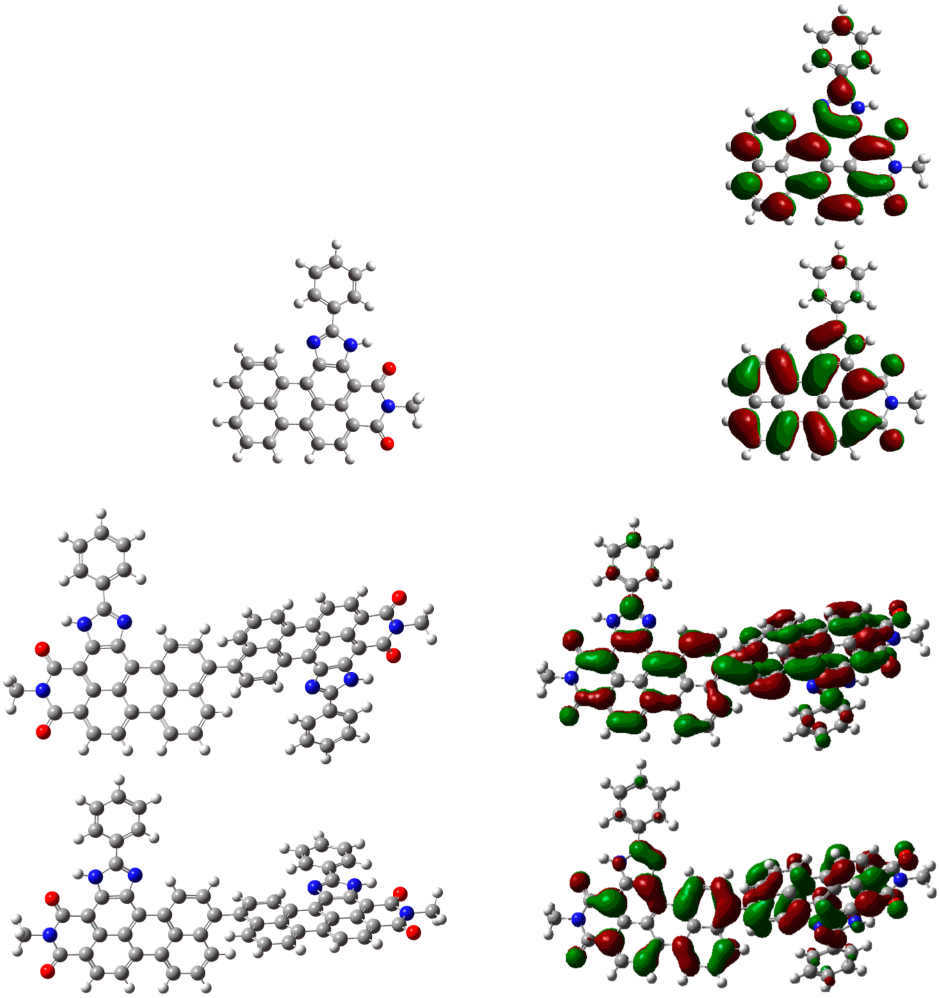


Figure 5. Left from top to bottom: The calculated geometries (DFT, B3LYP) of the ground state of **12**, the equilibrated LUMO of **14**, and the HOMO of **14**. Right from top to bottom: The LUMO of **12**, the HOMO of **12**, the equilibrated LUMO of **14**, and the HOMO of **14**.

the aqueous phase is generally suitable for dynamics according to Figure 1.

Finally, the concept for the increase of the Stokes shift by the dynamic of peri-linked dyads was extended to hetero dyads. This is of special interest because Förster resonance energy transfer (FRET) may proceed from the hypsochromically absorbing chromophore to the bathochromically absorbing and fluorescent chromophore where the dynamic process may increase the Stokes shift of the latter. As a consequence, one may construct broad-band absorbing dyads with increased Stokes shifts. Dyad **16** fulfills these conditions because of the linking of two highly fluorescent chromophores based on **3** and **12**. The UV/vis spectra reported in Figure 6 correspond to an addition of the spectra of **3** and **12** where the bathochromically absorbing chromophore of **12** seems to dominate in **16**. No hypsochromic fluorescence is observed even with the predominant electronic excitation of the more hypsochromically absorbing component based on **3**, indicating an efficient energy transfer according to Förster's mechanism (FRET). The Stokes shift of **16** is increased compared with **12**, indicating a dynamic process although the effect is not as pronounced as with the homo dyads. A dihedral angle of 78° was calculated for the ground state and a diminished angle for the excited state of 55°; this corresponds with the Stokes shift.

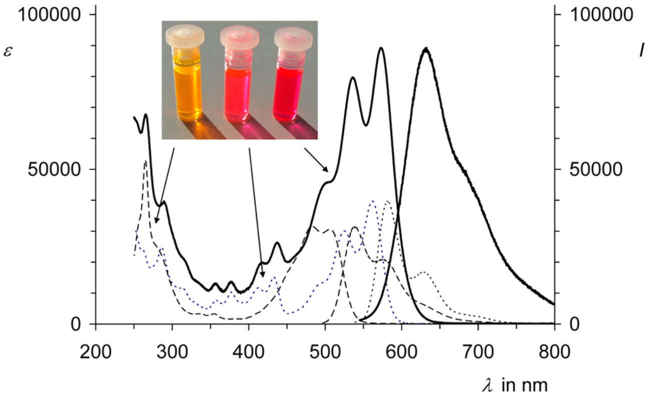


Figure 6. UV/vis absorption (left) and fluorescence spectra (right) of **3** (dashed lines), **12** (dotted lines), and **16** (straight lines) in chloroform.

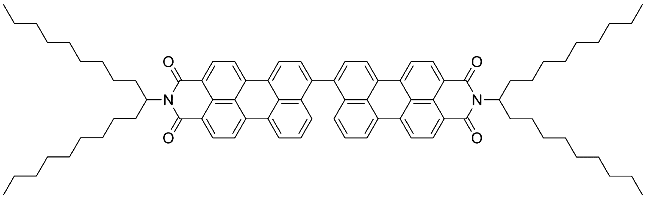
■ CONCLUSIONS

We conclude that the linking of aromatic systems in *peri*-positions to form dyads allows the construction of fluorescent dyes with increased Stokes shifts by molecular dynamics where the molecules undergo of a cyclic process to give high fluorescence quantum yields. Perylenedicarboximides linked in the free *peri*-position to dyads are good candidates for such fluorescent dyes because of their high photostability and fluorescence quantum yields where the extension of the aromatic system allows the adaption of the UV/vis spectra. Such systems with increased Stokes shifts may be of interest for applications where the reabsorption of the fluorescent light by the chromophore is problematic such as for laser applications,[2] for fluorescent planar solar-light concentrators[3,17] where the behavior in glassy matrixes has to be investigated, for analytical applications, and even for strong visual impressions of fluorescence.

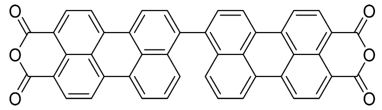
■ EXPERIMENTAL SECTION

General. All FAB spectra were recorded in 3-nitrobenzyl alcohol as the matrix. The interpretation of NMR signals was verified with carbon−proton and proton−proton correlation methods.

9,9′-Bis[perylene-3,4-dicarboxylic-3,4-(1-nonyldecylimide)] (2b). Copper powder (10.43 g, 164.17 mmol) was disperged in 3-picoline (1400 mL), stirred at 80 °C for 24 h, treated with *N*-(1-nonyldecyl)-3,4,9,10-perylenetetracarboxylic-9,10-anhydride-3,4-imide (21.6 g, 32.84 mmol), and stirred at 140 °C for 24 h. The mixture was allowed to cool and poured into 2 M HCl (4000 mL). The solid was collected by vacuum filtration (Büchner filter), dried at 110 °C in air, and purified by column separation (silica gel, chloroform; second, strongly reddish orange fluorescent band). Yield 3.55 g (28%) of a reddish orange solid, mp >250 °C. R_f (silica gel, chloroform/isohexane 1:1): 0.95. IR (ATR): $\tilde{\nu}$ = 3394.9 (w), 3297.6 (w), 3052.8 (w), 2952.5 (m), 2919.3 (s), 2850.6 (s), 2587.3 (w), 2238.9 (w), 1922.8 (w), 1688.8 (s), 1647.8 (s), 1594.1 (s), 1573.6 (s), 1501.6 (m), 1456.0 (m), 1404.7 (m), 1371.5 (w), 1343.9 (s), 1306.2 (m), 1285.2 (m), 1249.4 (m), 1217.9 (m), 1205.9 (m), 1171.3 (m), 1156.5 (m), 1132.5 (w), 1110.2 (w), 1044.5 (m), 963.5 (w), 945.2 (w), 898.9 (w), 850.2 (w), 836.6 (w), 803.7 (s), 788.5 (m), 747.4 (m), 731.8 (w), 720.7 (w), 669.7 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.84 (t, ^3J(H,H) = 7.0 Hz, 12 H), 1.21−1.37 (m, 56 H), 1.85−1.90 (m, 4 H), 2.24−2.30 (m, 4 H), 5.12−5.24 (m, 2 H), 7.48−7.57 (m, 4 H), 7.72 (d, ^3J (H,H) = 7.6 Hz, 2 H), 8.66−8.55 (m, 4 H), 8.58 (d, ^3J(H,H) = 8.1 Hz, 2 H), 8.45 (t, ^3J(H,H) = 8.0 Hz, 4 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ = 14.0, 22.6, 27.0, 29.3, 29.5, 31.8, 32.4, 54.5, 120.4, 120.5, 123.1, 123.8, 126.6, 127.3, 128.3, 129.2, 129.6, 129.6, 130.0, 131.2, 132.0, 133.7, 136.6, 140.4, 164.1, 165.1 ppm. UV/vis ($CHCl_3$): λ_{max} (E_{rel}) = 495.6 (sh, 0.68), 526.8 (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 495.6): λ_{max} (I_{rel}) = 597.1 (1.00). Fluorescence quantum yield (λ_{exc} = 495.6, $E_{491\ nm/1\ cm}$ = 0.0151, $CHCl_3$, reference **9a** with Φ = 1.00): ≈1.00. MS (FAB$^-$): *m/z* (%): 1173.7 $[M]^-$ (11). MS (FAB$^+$): *m/z* (%): 1173.7 $[M + H]^+$ (7). HRMS (FAB$^+$, quadrupole, $C_{82}H_{97}N_2O_4$, M^+ + H): Calcd 1173.7404, found 1173.7450, Δ = +0.0046. $C_{82}H_{96}N_2O_4$ (1172.7): Calcd C 83.92, H 8.24, N 2.39; C 83.93, H 8.28, N 2.38.



5: 9-Bromoperylene-3,4-dicarboxylic anhydride (**6**, 300 mg, 0.748 mmol) and freshly distilled and anhydrous toluene (40 mL) were heated at 70 °C with thorough exclusion of air and moisture (argon atmosphere) and treated with palladium(II) acetate (129 mg, 0.576 mmol) and tetrabutylammonium bromide (424 mg, 1.32 mmol). The mixture was heated at 100 °C, treated with triethylamine (2 mL), stirred at 120 °C for 12 h, allowed to cool, and treated with 2 M aqueous HCl. The precipitate was collected by vacuum filtration (D4 glass filter), washed with distilled water, dried at 110 °C for 16 h, and purified by column separation (silica gel, chloroform/acetic acid 100:1; second, red band). Yield 81.7 mg (34%) of a dark red solid, mp >250 °C. R_f (silica gel/chloroform): 0.12. IR (ATR): $\tilde{\nu}$ = 3091.2 (w), 3052.0 (w), 2922.4 (w), 2852.8 (w), 2348.5 (w), 1749.7 (vs), 1717.9 (s), 1653.8 (w), 1590.4 (s), 1568.6 (s), 1521.8 (w), 1498.7 (w), 1457.6 (w), 1408.9 (w), 1370.7 (w), 1339.6 (s), 1306.1 (w), 1282.3 (s), 1231.8 (w), 1191.5 (w), 1151.6 (w), 1130.3 (m), 1018.2 (s), 995.7 (s), 902.1 (w), 857.4 (w), 834.1 (w), 807.8 (s), 762.0 (m), 739.6 (s), 675.2 (w), 657.1 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.65−7.80 (m, 4 H), 7.94−7.99 (m, 2 H), 8.25−8.71 ppm (m, 12 H). ^{13}C NMR (150 MHz, $CDCl_3$ and trace of paraffin, 25 °C, TMS): δ = 123.1, 123.3, 123.4, 123.5, 126.5, 129.6, 130.0, 130.5, 131.2, 132.0, 134.3, 135.3, 136.5, 146.2, 146.9, 164.3 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 354.0 (16670), 489.0 (61300), 511.0 nm (59600). Fluorescence ($CHCl_3$, λ_{max} = 490.4 nm): λ_{max} (I_{rel}) = 548.5 (1.00), 586.8 nm (0.87). Fluorescence quantum yield (λ_{exc} = 490.4 nm, $E_{490.4\ nm/1\ cm}$ = 0.0192, $CHCl_3$, reference **9a** with Φ = 1.00): 0.78. MS (DEI$^+$, 70 eV) *m/z* (%): 643 (21) $[M^+ + H]$, 642 (45) $[M^+]$, 336 (23), 323 (26), 322 (100) $[M^+ - C_{22}H_8O_3]$, 278 (24), 250 (76), 249 (28), 248 (42), 128 (25), 125 (29), 124 (43), 97, (25), 85 (46), 83 (83), 82 (19), 71 (21), 70 (20), 69 (54), 57 (37), 55 (57), 43 (28), 41 (25). HRMS (DEI$^+$, 70 eV, $C_{44}H_{18}O_6$): Calcd *m/z*: 642.1103; found *m/z*: 642.1101, Δ = −0.0002.



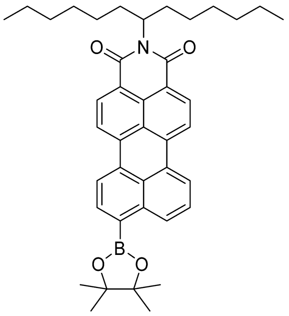
12: Copper powder (1.28 g, 20.1 mmol) in 3-picoline (160 mL) was stirred with the exclusion of moisture and air (nitrogen) at 85 °C for 5 h and treated with **11** (2.50 g, 4.02 mmol). The mixture was heated to reflux (165 °C bath) for 24 h, allowed to cool, and treated with 2 M aqueous HCl (500 mL). The solid was collected by vacuum filtration (D4 glass filter), dried at 110 °C for 16 h, and purified by column separation (silica gel, chloroform). Yield: 1.20 g (48%) of a violet solid, mp 167 °C. R_f (silica gel, chloroform): 0.85. IR (ATR): $\tilde{\nu}$ = 3422 (w), 2953.6 (m), 2920.0 (m), 2853.1 (m), 1725.5 (m), 1673.9 (s), 1635.9 (vs), 1619.6 (vs), 1564.2 (s), 1564.2 (m), 1534.5 (w), 1486.8 (w), 1486 (w), 1466.8 (m), 1453.8 (m), 1410.6 (w), 1397.0 (m), 1376.3 (w), 1340.2 (vs), 1318.2 (m), 1279.0 (s), 1250.1 (s), 1226.0 (m), 1155.9 (w), 1118.1 (m), 1068.4 (w), 1053.3 (m), 1025.4 (w), 1001.5 (w), 951.9 (w), 939.8 (w), 920.3 (w), 893.4 (w), 878.1 (w), 831.4 (m), 809.9 (s), 775.6 (m), 759.4 (s), 724.4 (w), 703.2(w), 682.2 (s) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.84 (t, ^3J = 7.0 Hz, 6 H), 1.20−1.48 (m, 16 H), 1.88−2.00 (m, 2 H), 2.28−2.40 (m, 2 H), 5.21−5.34 (m, 1 H), 7.58 (t, ^3J = 7.8 Hz, 2 H,), 7.85 (d, ^3J = 8.0 Hz, 2 H,), 8.32 (d, ^3J = 8.1 Hz, 2 H), 8.35 (d, ^3J = 7.4 Hz, 2 H), 8.50 (br, 2 H), 10.54 (d, ^3J(H,H) = 7.6 Hz, 1 H), 11.46 ppm (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.1, 27.2, 29.3, 29.7, 31.8, 32.4, 32.6, 118.3, 123.5, 123.8, 126.4, 127.3, 127.4, 128.2, 128.7, 129.2, 129.5, 130.5, 130.8, 131.5, 133.7 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 357.4 (7400), 376.4 (9900), 412.8 (11000), 432.8 (14500), 489.6 (11800), 525.6 (29900), 561.8 nm (39800). Fluorescence ($CHCl_3$, λ_{max} = 525.0 nm): λ_{max} (I_{rel}) = 581.8 (1.00), 633.0 (0.58), 692.6 nm (0.12). Fluorescence quantum yield (λ_{exc} = 525.0 nm, $E_{525.0\ nm/1\ cm}$ = 0.0168, $CHCl_3$, reference **9a** with Φ = 1.00): 0.96. MS (DEI$^+$, 70 eV): *m/z* (%): 620.3 (32.8) $[M + H]^+$, 619.3 (69.1) $[M^+]$, 438.1 (52.6), 437.1 (100), 322.1 (13.0), 321.1 (30.7). HRMS (DEI$^+$, $C_{42}H_{41}N_3O_2$): Calcd *m/z*: 619.3199, found *m/z*: 619.3185, Δ = −0.0014. $C_{42}H_{41}N_3O_2$ (619.3): Calcd C 81.37, H 6.67, N 6.78; found C 81.49, H 6.86, N 6.75.

13: **12** (540 mg, 0.871 mmol) was disperged in chloroform, heated at 40 °C, and treated with Br_2 (0.18 mL, 1.60 mmol). The mixture was stirred at 40−50 °C for 2.5 h and evaporated. The residue was purified by column separation (silica gel, chloroform). Yield: 536 mg (88%), mp 186−187 °C. R_f (silica gel, chloroform): 0.75. IR (ATR): $\tilde{\nu}$ = 3412.6 (w), 3073.6 (w), 2953.0 (m), 2920.2 (s), 2853.6 (s), 1730.3 (w), 1708.5 (w), 1678.3 (s), 1636.3 (vs), 1619.5 (vs), 1605.4 (vs), 1591.7 (s), 1560.3 (s), 1534.2 (m), 1520.2 (w), 1504.2 (w), 1485.8 (m), 1453.4 (s), 1408.2 (m), 1393.6 (w), 1341.7 (vs), 1321.9 (vs), 1294.2 (m), 1282.3 (w), 1255.6 (s), 1222.5 (m), 1204.9 (m), 1170.3 (w), 1157.0 (w), 1116.0 (w), 1054.3 (w), 968.2 (w), 951.8 (w), 917.7

(w), 881.9 (w), 835.7 (w), 821.5 (w), 802.9 (m), 775.2 (w), 749.8 (s), 706.2 (w), 684.2 (s) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.84 (t, ^{3}J = 7.0 Hz, 6 H), 1.21−1.42 (m, 16 H), 1.85−1.93 (m, 2 H), 2.23−2.31 (m, 2 H), 5.16−5.24 (m, 1 H), 7.45 (t, ^{3}J = 7.9 Hz, 1 H), 7.61 (d, ^{3}J = 8.0 Hz, 2 H), 7.81 (d, ^{3}J = 8.1 Hz, 1 H), 8.00 (d, ^{3}J = 8.0 Hz, 1 H), 8.02 (d, ^{3}J = 8.3 Hz, 1 H), 8.08 (d, ^{3}J = 8.0 Hz, 1 H), 8.09 (d, ^{3}J = 8.3 Hz, 1 H), 8.41 ppm (m br, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.1, 27.2, 29.3, 31.8, 32.4, 32.6, 118.7, 123.9, 127.4, 127.5, 129.2, 129.7, 129.8, 131.7 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 357.4 (6400), 376.4 (8300), 417.6 (11800), 438.2 (14600), 491.4 (12900), 526.6 (34000), 564.0 nm (47800). Fluorescence ($CHCl_3$, λ_{max} = 526.6 nm): λ_{max} (I_{rel}) = 581.8 (1.00), 633.0 (0.58), 692.6 nm (0.12). Fluorescence quantum yield (λ_{exc} = 525.0 nm, $E_{525.0\ nm/1\ cm}$ = 0.01681, $CHCl_3$, reference **9a** with Φ = 1.00): 0.96. MS (DEI$^+$, 70 eV): m/z (%): 700.2 (46.6), 699.2 (81.7) [M^+ + 2H], 698.2 (49.3) [M^+ + H], 697.2 (100) [M^+], 619.3 (12.2), 519.0 (18.4) 516.0 (59.9), 438.1 (14.7), 437.1 (24.7), 56.9 (14.1), 54.9 (24.9), 43.1 (20.1), 41.2 (16.6). HRMS (DEI$^+$, $C_{42}H_{40}BrN_3O_2$): Calcd m/z: 697.2304, found m/z: 697.2308, Δ = +0.0004. $C_{42}H_{40}BrN_3O_2$ (679.2): Calcd C 72.20, H 5.77, N 6.01; found C 71.95, H 5.76, N 6.03.

14: **13** (100 mg, 0.143 mmol) in a heat-degassed Schlenk vessel was flushed with argon, dissolved in warm toluene (8 mL), heated to 70 °C, and treated with tetrabutyl ammonium bromide (81.2 mg, 0.252 mmol) and Pd(OAc)$_2$(24.7 mg, 0.110 mmol). The mixture was heated at 100 °C, treated with triethylamine (1 mL), heated at 120 °C for 15 h, allowed to cool, treated with 2 M aqueous HCl (100 mL), and extracted with chloroform. The organic phase was dried with $MgSO_4$ and the reaction product purified by column separation (silica gel, chloroform). Yield: 53.1 mg (60.0%) of a violet solid, mp >250 °C. R_f (silica gel, chloroform): 0.70. IR (ATR): $\tilde{\nu}$ = 3413.9 (w), 2953.8 (m), 2924.7 (vs), 2854.0 (s), 2359.9 (w), 2339.3 (w), 2097.0 (w), 1734.3 (w), 1718.5 (w), 1683.9 (s), 1637.9 (vs), 1622.4 (vs), 1606.5 (s), 1562.4 (m), 1535.2 (w), 1486.8 (w), 1455.0 (m), 1408.0 (w), 1408.0 (w), 1375.5 (w), 1344.1 (vs), 1294.2 (w), 1256.7 (w), 1224.8 (w), 1207.0 (w), 1120.5 (w), 1053.8 (w), 1024.6 (w), 947.3 (w), 811.9 (w), 796.8 (w), 758.2 (w), 685.7 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.84 (t, ^{3}J = 7.0 Hz, 6 H), 1.20−1.48 (m, 16 H), 1.88−2.00 (m, 2 H), 2.28−2.40 (m, 2 H), 5.21−5.34 (m, 1 H), 7.58 (t, ^{3}J = 7.8 Hz, 2 H), 7.85 (d, ^{3}J = 8.0 Hz, 2 H), 8.32 (d, ^{3}J = 8.1 Hz, 2 H), 8.35 (d, ^{3}J = 7.4 Hz, 2 H), 8.50 (br, 2 H).10.54 (d, ^{3}J(H,H) = 7.6 Hz, 1 H), 11.46 ppm (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.1, 27.2, 29.3, 29.7, 31.8, 32.4, 32.6, 118.3, 123.5, 123.8, 126.4, 127.3, 127.4, 128.2, 128.7, 129.2, 129.5, 130.5, 130.8, 131.5, 133.7 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 358.2 (12400), 378.0 (16800), 415.4 (20600), 436.4 (25300), 545.2 (51300), 586.0 nm (10300). Fluorescence ($CHCl_3$, λ_{max} = 525.0 nm): λ_{max} (I_{rel}) = 581.8 (1.00), 633.0 (0.58), 692.6 nm (0.12). Fluorescence quantum yield (λ_{exc} = 525.0 nm, $E_{525.0\ nm/1\ cm}$ = 0.01681, $CHCl_3$, reference **9a** with Φ = 1.00): 0.96. MS (DEI$^+$, 70 eV): m/z (%): 620.3 (32.8) [M^+ + H], 619.3 (69.1) [M^+], 438.1 (52.6), 437.1 (100), 322.1 (13.0), 321.1 (30.7). HRMS (DEI$^+$, $C_{42}H_{41}N_3O_2$): Calcd m/z: 619.3199, found m/z: 619.3185, Δ = −0.0014. $C_{84}H_{80}N_6O_4$ (1236.6): Calcd C 81.52, H 6.79, N 6.52; found C 81.34, H 6.72, N 6.75.

15: *N*-(1-Hexylheptyl)-9-bromo-3,4-perylenedicarboximide (**4**, 770 mg, 1.32 mmol), bispinacolatodiborane (369 mg, 1.45 mmol), and potassium acetate (376 mg, 3.83 mmol) were dissolved in 1,4-dioxane (15 mL) with the exclusion of moisture and air (argon atmosphere) and treated with $PdCl_2$(dppf) (29.0 mg, 0.040 mmol). The mixture was heated at 70 °C for 17 h and evaporated in vacuo. The residue was purified by column separation (silica gel, chloroform). Yield: 524 mg (63%) of an orange solid, mp >179−181 °C. R_f (silica gel/chloroform): 0.79. IR (ATR): $\tilde{\nu}$ = 2953.4 (m), 2924.3 (m), 2855.6 (m), 1689.6 (s), 1650.4 (vs), 1616.1 (w), 1591.5 (s), 1577.0 (m), 1523.0 (w), 1507.8 (m), 1459.5 (m), 1411.4 (m), 1377.6 (m), 1351.3 (s), 1328.3 (vs), 1293.0 (m), 1272.5 (m), 1245.6 (m), 1207.1 (m), 1170.3 (m), 1137.1 (s), 1114.6 (s), 1068.0 (m), 1051.1 (m), 966.6 (m), 934.5 (w), 900.1 (w), 858.9 (m), 840.2 (m), 809.1 (s), 764.3 (m), 751.0 (s), 724.7 (w), 713.5 (w), 700.0 (m), 681.8 (m), 666.6 (w), 657.4 (w), 619.2 (w), 608.1 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.81 (t, ^{3}J(H,H) = 7.1 Hz, 6 H), 1.15−1.36 (m, 16 H), 1.45 (s, 9 H, 12 H), 1.80−1.88 (m, 2 H), 2.20−2.29 (m, 2 H), 5.14−5.22 (m, 1 H), 7.63 (t, ^{3}J(H,H) = 7.9 Hz, 1 H), 8.16 (d, ^{3}J(H,H) = 7.9 Hz 1 H), 8.35−8.43 (m, 4 H), 8.50−8.60 (m, 2 H) 8.38 (d, ^{3}J(H,H) = 8.3 Hz, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 25.0, 27.0, 29.2, 31.8, 32.4, 54.4, 84.2, 120.2, 120.7, 122.5, 123.4, 126.6, 127.2, 127.7, 129.0, 129.8, 131.5, 131.7, 136.2, 138.0 ppm. UV/vis ($CHCl_3$): λ_{max} (E_{rel}) = 488.6 (0.96), 514.8 nm (1.00). Fluorescence ($CHCl_3$, λ_{max} = 488.6 nm): λ_{max} (I_{rel}) = 546.5 (1.00), 587.5 nm (0.79). Fluorescence quantum yield (λ_{exc} = 488.6 nm, $E_{488.6\ nm/1\ cm}$ = 0.0115, $CHCl_3$, reference **9a** with Φ = 1.00): 0.82. MS (FAB$^+$): m/z (%):631.4 (9.2) [M^+ + 2H], 630.4 (42.8) [M^+ + H], 629.4 (100) [M^+], 628.4 (21.7), 448.2 (42.6), 447.2 (84.4), 446.2 (20.0), 348.1 (11.2), 347.1 (14.7), 84.9 (15.3), 82.9 (24.9). HRMS (FAB$^+$, $C_{41}H_{48}BNO_4$): Calcd m/z: 629.3676, found m/z: 629.3678, Δ = +0.0002.



16: *N*-(1-Hexylheptyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-perylenedicarboximide (**15**, 164 mg, 0.260 mmol) and **13** (200 mg, 0.286 mmol) were added to freshly distilled toluene (20 mL) with the exclusion of air (argon atmosphere), treated with 1 M aqueous Na_2CO_3 (16 mL) and ethanol (2 mL), heated at 80 °C, and treated with $Pd(PPh_3)_4$ (34.6 mg, 0.03 mmol). The mixture was stirred at 80 °C for 16 h and allowed to cool to room temperature. The organic phase was separated, dried with $MgSO_4$, and purified by column separation (silica gel, toluene). Yield: 53.1 mg (60.0%) of a violet solid, mp >250 °C. R_f (silca gel/chloroform): 0.72. IR (ATR): ν = 3410.8 (w), 2951.6 (w), 2923.0 (m), 2854.2 (w), 1690.4 (s), 1651.8 (s), 1638.6 (vs), 1605.7 (s), 1591.8 (s), 1571.2 (s), 1534.4 (w), 1485.9 (w), 1453.8 (m), 1408.2 (m), 1374.3 (w), 1346.3 (vs), 1324.3 (s), 1291.5 (m), 1246.0 (s), 1208.1 (m), 1171.6 (m), 1106.8 (w), 1053.3 (w), 955.2 (w), 917.6 (w), 843.0 (m), 811.9 (vs), 777.7 (w), 757.4 (s), 723.0 (w), 687.1 cm^{-1} (m). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, 12 H, ^{3}J(H,H) = 6.9 Hz, 12 H), 1.19−1.40 (m, 32 H), 1.83−1.97 (m, 4 H), 2.25−2.38 (m, 4 H), 5.18−5.35 (m, 2 H), 7.46−7.58 (m, 2 H), 7.60−7.63 (m, 3 H), 7.65−7.80 (m, 4 H), 7.87 (d, ^{3}J(H,H) = 7.7 Hz, 1 H), 8.22−8.37 (m, 2 H), 8.45−8.50 (m, 2 H), 8.50−8.57 (m, 2 H), 8.58−8.70 (m, 4 H), 10.78−10.84 (m, 1 H), 11.52−11.60 ppm (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 25.7, 27.0, 29.3, 31.8, 52.0, 54.4, 118.5, 120.0, 120.3, 122.0, 122.2, 123.7, 123.8, 124.0, 126.0, 126.1, 127.0, 127.9, 128.2, 130.1, 131.7, 147.6 ppm. UV/vis ($CHCl_3$): λ_{max} (ε) = 358.2 (12400), 378.0 (16800), 415.4 (20600), 436.4 (25300), 545.2 (51300), 586.0 nm (10300). Fluorescence ($CHCl_3$, λ_{max} = 545.2 nm): λ_{max} (I_{rel}) = 661.6 (1.00), 732.0 nm (0.49). Fluorescence quantum yield (λ_{exc} = 545.2 nm, $E_{545.2\ nm/1\ cm}$ = 0.0115, $CHCl_3$, reference **9a** with Φ = 1.00): ca. 0.65. MS (FAB$^+$): m/z (%): 1121.4 (8) [M^+ + H], 1120.4 (6) [M^+]. HRMS (FAB$^+$, $C_{77}H_{76}N_4O_4$): Calcd m/z: 1120.5867, found m/z: 1120.5924, Δ = +0.0057. $C_{77}H_{76}N_4O_4$ (1120.6): Calcd C 82.47, H 6.83, N 5.00; found C 82.62, H 6.91, N 4.66.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data of **8** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Langhals@lrz.uni-muenchen.de.

Notes

The authors declare no competing financial interest.

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