FRET in Dyads with Orthogonal Chromophores and Minimal Spectral Overlap

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Supporting Information

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1. Experimental
1.1 Materials

Reference Materials: Fluorescence quantum yields $\phi$ were determined by means of reference materials: (i) S-13\(^1\) (CAS registry number RN 110590-84-6), $\phi = 1.0$; (ii) 3,4,9,10-perylenetetramethylester\(^1\) (RN 53159-49-2), $\phi = 1.0$; (iii) C25\(^2\) (RN 335458-21-4), $\phi = 1.0$; S-19terrylenetetracarboxdiimide\(^3\) (RN 1029894-60-7), $\phi = 0.94$; perylene-terrylene dyad\(^3\) (RN 1313052-90-2), $\phi = 0.86$.

![Diagram](image)

2-(1-Nonyldecyl)-1H-beno[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (7):\(^4\)

Copper powder (7.43 g, 117 mmol) under argon atmosphere and 3-picoline (500 mL) were stirred at 90°C for 4 h, treated with 9-(1-nonyldecyl)-1H-isochromeno[6',5',4':10,5,6]anthra[2,1,9-def]isoquinoline-1,3,8,10(9H)-tetraon\(^5\) (RN 130296-48-9) (15.3 g, 23.3 mmol) stirred at 175°C for and 10 h, allowed to cool, precipitated with 2 m aqueous HCl (1300 mL), stirred at room temperature for 60 min, collected by vacuum filtration (D4 glass filter), washed with 2 m aqueous HCl (800 mL) and distilled water (2000 mL), dried at 90°C for 2 d and purified by column separation (silica gel, chloroform). Yield 10.5 g (76 %) bright red solid, m.p. 144°C (ref.\(^4\) 143-143.5°C). $R_f$ value (silica gel, CHCl\(_3\)): 0.8. IR (ATR): $\tilde{\nu} = 2952$ (m), 2923 (m), 2855 (m), $\tilde{\nu} ~ 2363$ (w), 1697 (s), 1659 (s), 1593 (s), 1578 (m), 1506 (w), 1483 (w), 1465 (w), 1430 (w), 1404 (w), 1352 (m), 1340 (s), 1305 (w), 1252 (m), 1202 (w), 1175 (w), 1125 (w), 1106 (w), 1018 (w), 964 (w), 854 (w), 811 (m), 747 (m), 731 (w), 694 (w), 667 cm\(^-1\) (w).

$^1$H NMR (600 MHz, CDCl\(_3\), 27.0°C, TMS): $\delta = 8.27$ (d, $^3$J(H,H) = 7.9 Hz, 2 H, CH\(_{arom.}\)), 7.97 (d, $^3$J(H,H) = 7.6 Hz, 2 H, CH\(_{arom.}\)), 7.92 (d, $^3$J(H,H) = 7.6 Hz, 2 H, CH\(_{arom.}\)), 7.63 (d, $^3$J(H,H) = 8.0 Hz, 2 H, CH\(_{arom.}\)), 7.36 (dd, $^3$J(H,H) = 7.7 Hz, $^3$J(H,H) = 7.7 Hz, 2 H, CH\(_{arom.}\)), 5.21-5.16 (m, 1 H, CH), 2.30-2.23 (m, 2 H, $\beta$-CH\(_2\)), 1.94-1.88 (m, 2 H, $\beta$-CH\(_2\)), 1.41-1.16 (m, 28 H, 14-CH\(_2\)), 0.83 ppm (t, $^3$J(H,H) = 7.1 Hz, 6 H, 2\(_x\)CH\(_3\)). $^{13}$C NMR (150 MHz, CDCl\(_3\), 27.0°C): $\delta = 165.0, 164.0, 134.2, 131.7, 130.6, 130.4, 129.4, 128.7, 127.4, 126.6, 126.0, 123.0, 121.3, 120.5, 119.6, 54.3, 32.4, 31.9, 29.7, 29.6, 29.3, 27.1, 22.7, 14.1 ppm. UV/VIS (CHCl\(_3\)): $\lambda_{max}$ ($\varepsilon$) = 482.8 (31900), 506.2 nm (31500). Fluorescence (CHCl\(_3\)): $\lambda_{max}$ ($I_{rel}$) = 537.9 (1.00), 578.4 nm (0.83). Fluorescence quantum yield (CHCl\(_3\), $\lambda_{exc} = 482$ nm, $E_{482\ nm, 1\ cm} = 0.0161$, reference: S-13 with $\Phi = 1.00$): 0.95.
MS (DEP/EI) m/z (%): 587 (84) [M*], 322 (100) [M* – C19H38]. HRMS (C41H49NO2) m/z: Calcd. 587.3763, found 587.3759; Δ = – 0.0004. C41H49NO2 (587.4): Calcd. C 83.77, H 8.40, N 2.38; found C 83.78, H 8.48, N 2.33.

2-(4-Amino-2,3,5,6-tetramethylphenyl)-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d’e’f’]diisoquinoline-1,3,8,10(2H,9H)-tetrone: ² 2,3,5,6-Tetramethylbenzene-1,4-diamine⁷ (RN 3102-87-2) (197 mg, 1.20 mmol), 9-(1-hexylheptyl)-1H-isochromeno[6’,5’:4’:10,5,6]anthra[2,1,9-def]diisoquinoline-1,3,8,10(9H)-tetrone (RN 130294-37-6) (230 mg, 400 µmol), zincacetate (14.8 mg, 80 µmol) and quinoline (4 mL) under argon atmosphere were stirred at 210°C 4 h (dark red mixture), allowed to cool, still warm and with vigorous stirring was dropped into 2 M aqueous HCl (300 mL) stirred for 2 h, allowed to stand for 16 h, collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl (300 mL), hot distilled water (300 mL) and a mixture of methanol and water (300 mL, 1:1), dried in vacuo at 110°C for 2 d, purified by column separation (basic alumina, CHCl₃/methanol 80:1 and then silica gel, CHCl₃/methanol 40:1). Yield 250 mg (87 %) red solid, m.p. > 300°C. Rf value (silica gel, CHCl₃/methanol 40:1): 0.4.

IR (ATR): ν = 3482 (w), 3395 (w), 2953 (m), 2924 (m), 2856 (m), 2363 (w), 1698 (s), 1653 (s), 1592 (s), 1577 (s), 1507 (w), 1458 (w), 1432 (m), 1405 (m), 1346 (m), 1328 (s), 1250 (m), 1198 (w), 1174 (m), 1138 (w), 1107 (w), 962 (w), 855 (w), 839 (w), 810 (m), 748 (m), 722 (w), 671 cm⁻¹ (w). ¹H NMR (600 MHz, CDCl₃, 27.0°C, TMS): δ = 8.78-8.66 (m, 8 H, CH aromatic perylene), 5.22-5.16 (m, 1 H, CH), 3.71 (br, 2 H, NH₂), 2.29-2.21 (m, 2 H, β-CH₂), 2.16 (s, 6 H, 2×CH₃), 2.06 (s, 6 H, 2×CH₃), 1.91-1.83 (m, 2 H, β-CH₂), 1.38-1.19 (m, 16 H), 0.83 ppm (t, 3J(H,H) = 6.7 Hz, 6 H, 2×CH₃). ¹³C NMR (150 MHz, CDCl₃, 27.0°C): δ = 163.5, 143.4, 135.0, 134.5, 132.0, 131.2, 130.8, 130.1, 129.6, 126.8, 126.5, 124.3, 123.4, 123.2, 123.1, 118.9, 54.8, 32.4, 31.8, 29.2, 26.9, 22.6, 15.1, 14.0, 13.9 ppm. UV/VIS (CHCl₃): λ_max (E_rel) = 458.6 (0.22), 490.6 (0.60), 527.2 nm (1.00). Fluorescence (CHCl₃): λ_max (Irel) = 535.8 (1.00), 575.7 nm (0.56). Fluorescence quantum yield (CHCl₃, λ_exc = 491 nm, E₄₉₁ nm, cm⁻¹ = 0.0164, reference: S-13 with Φ = 1.00): < 0.01. MS (DEP/EI) m/z (%): 719 (100) [M⁺], 538 (40) [M⁺+H – C₁₃H₂₆], 391 (29) [M⁺+H – C₁₄H₂₆ – C₁₀H₁₄N]. HRMS (C₄₇H₄₀N₃O₄) m/z: Calcd. 719.3723, found 719.3729; Δ = 0.0006. C₄₇H₄₀N₃O₄ (719.4): Calcd. C 78.41, H 6.86, N 5.84; found C 78.22, H 6.89, N 5.78.
2,10-Bis(1-hexylheptyl)-6[4'-{(3,8,9,10-tetrahydro-9-(1-hexylheptyl)-1,3,8,10-tetraoxoanthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-2(1H)-yl][2,3,5,6-tetramethylphenyl]-1H-pyrrolo[3'4':4,5]pyreno[2,1,10-def;7,8,9-d'e'f']diisoquinoline-1,3,5,7,9,11 (2H,6H,10H)-hexone (1): 6-(4-Amino-2,3,5,6-tetramethylphenyl)-9-(1-hexylheptyl)anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone (RN 1089735-50-1) (150 mg, 208 µmol), 2,10-bis(1-hexylheptyl)furo[3',4':4,5]pyreno[2,1,10-def;7,8,9-d'e'f']diisoquinoline-1,3,5,7,9,11(2H,10H)-hexone (RN 130296-37-6) (100 mg, 118 µmol) and quinoline (3 mL) were heated at 230°C for 15 h by means of 250 W microwave radiation (dark red mixture), allowed to cool, precipitated with vigorous stirring with 2 M aqueous HCl (200 mL), stirred for 3 h, collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl (300 mL) and distilled water until colorless washings (300 mL), dried at 110°C for 2 d and purified by column separation (silica gel, CHCl₃/methanol 60:1 and then neutral alumina, CHCl₃). Yield 108 mg (59 %) bright red solid, m.p. > 300°C. Rᵣ value (CHCl₃/methanol 80:1): 0.7. IR (ATR): ν = 2953 (m) 2924 (s), 2855 (m), 2361 (w), ~2340 (w), 1774 (w), 1721 (s), 1661 (s), 1626 (w), 1594 (m), 1578 (w), 1522 (w), 1484 (w), 1457 (m), 1431 (w), 1415 (w), 1405 (m), 1363 (m), 1336 (s), 1253 (w), 1204 (w), 1175 (w), 1123 (w), 1018 (w), 963 (w), 851 (w), 810 (m), 767 (w), 746 (m), 722 (w), 667 cm⁻¹ (w). ¹H NMR (600 MHz, CDCl₃, 27.0°C, TMS): δ = 10.62 (s, 1 H, CHₐrom. benzoperylene), 10.58 (s, 1 H, CHₐrom. benzoperylene), 9.47 (d, 3J(H,H) = 8.4 Hz, 2 H, CHₐrom. benzoperylene), 9.26-9.17 (m, 2 H, CHₐrom. benzoperylene), 8.84 (d, 3J(H,H) = 7.8 Hz, 2 H, CHₐrom. perylene), 8.76-8.70 (m, 2 H, CHₐrom. perylene), 5.38-5.28 (m, 2 H, 2×CH), 5.23-5.18 (m, 1 H, CH), 2.42-2.31 (m, 4 H, 2×β-CH₂), 2.30 (s, 6 H, 2×CH₃), 2.29-2.22 (m, 2 H, β-CH₂), 2.21 (s, 6 H, 2×CH₃), 2.00-1.91 (m, 4 H, 2×β-CH₂), 1.91-1.85 (m, 2 H, β-CH₂), 1.46-1.20 (m, 48 H, 24×CH₃), 0.85-0.82 ppm (m, 18 H, 6×CH₃). ¹³C NMR (150 MHz, CDCl₃, 27.0°C): δ = 167.1, 162.8, 135.4, 134.2, 132.9, 132.5, 130.2, 128.4, 127.5, 125.3, 124.2, 123.6, 123.4, 123.2, 55.3, 54.8, 32.4, 31.8, 29.7, 29.2, 27.0, 26.9, 22.6, 15.9, 15.4, 14.0 ppm. UV/VIS (CHCl₃): λ_max (ε): 376.8 (41100), 410.6 (16500), 436.0
(43900), 465.8 (76700), 490.4 (57100), 527.2 nm (93900). Fluorescence (CHCl₃): \( \lambda_{\text{max}} \) (\( I_{\text{rel}} \)): 534.8 (1.00), 577.2 nm (0.51). Fluorescence quantum yield (CHCl₃, \( \lambda_{\text{exc}} = 490 \) nm, \( E_{490 \text{ nm}, 1 \text{ cm}} = 0.0162 \), reference: C25 with \( \Phi = 1.00 \)): 1.00. Fluorescence quantum yield (CHCl₃, \( \lambda_{\text{exc}} = 436 \) nm, \( E_{436 \text{ nm}, 1 \text{ cm}} = 0.0123 \), reference: C25 with \( \Phi = 1.00 \)): 1.00.

Fluorescence quantum yield (CHCl₃, \( \lambda_{\text{exc}} = 436 \) nm, \( E_{436 \text{ nm}, 1 \text{ cm}} = 0.0124 \), reference: 3,4,9,10-pyrenetramethylester with \( \Phi = 1.00 \)): 1.00.

MS (DEP/EI): \( m/z \) (%):
1550 (14) \[ M^+ \], 1368 (39) \[ M^+ + H – C_{13}H_{26} \], 1186 (50) \[ M^+ + H – 2 \cdot C_{13}H_{26} \], 1004 (74) \[ M^+ + H – 3 \cdot C_{13}H_{26} \]. MS (FAB+) \( m/z \): 1550 \[ M^+ \], 1368 \[ M^+ – C_{13}H_{26} \], 1186 \[ M^+ – 2 \cdot C_{13}H_{26} \], 1004 \[ M^+ + 1 – 3 \cdot C_{13}H_{26} \]. HRMS (C₁₀₁H₁₀₇N₅O₁₀): \( m/z \): Calcd. 1550.8135, found 1550.8051; \( \Delta = 0.0084 \). C₁₀₁H₁₀₇N₅O₁₀ (1549.8): Calcd. C 78.21, H 6.95, N 4.52; found C 77.84, H 7.03, N 4.35.

6-(4-Amino-2,3,5,6-tetramethylphenyl)-2,10-bis(1-hexylheptyl)-1H-pyrrolo[3′:4:5]pyrreno[2,1,10-def:7,8,9-d'ef']diisoquinoline-1,3,5,7,9,11 (2H,6H,10H)-hexone (3):⁸ 2,3,5,6-Tetramethylbenzene-1,4-diamine (RN 3102-87-2) (49 mg, 0.30 mmol), 2,10-bis(1-hexylheptyl)furo[3′,4′:4,5]pyrreno[2,1,10-def:7,8,9-d'ef']diisoquinoline-1,3,5,7,9,11 (2H,10H)-hexone (2) (42.5 mg, 50.0 \( \mu \)mol) and quinoline (2 mL) were stirred at 220°C and 100 W microwave radiation for 4 h (dark yellow mixture), allowed to cool, still warm dropped with vigorous stirring into 2 M aqueous HCl (300 mL), stirred for 2 h, allowed to stand for 16 h, collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl (300 mL) and hot distilled water (300 mL), dried at 110°C for 16 h and purified by column separation (silica gel, CHCl₃/methanol 60:1). Yield 39 mg (78 %) yellowish green solid, m.p. > 300°C. \( R_f \) value (CHCl₃/methanol 60:1): 0.7. IR (ATR): \( \tilde{\nu} = 3486 \) (w), 3404 (w), 3081 (w), 2953 (m), 2922 (m), 2854 (m), 2358 (w), 1771 (w), 1711 (s), 1660 (s), 1625 (m), 1594 (m), 1522 (w), 1495 (m), 1415 (m), 1395 (m), 1375 (m), 1365 (m), 1345 (w), 1309 (s), 1276 (w), 1250 (w), 1234 (w), 1206 (w), 1176 (w), 1113 (m), 945 (w), 875 (w), 848 (w), 813 (m), 797 (w), 780 (w), 767 (m), 750 (m), 725 (w), 699 (w), 661 (w), 647 cm⁻¹ (w). \(^1\)H NMR (600 MHz, CDCl₃, 27.0°C, TMS): \( \delta = 10.58 \) (s, 1 H, CH\text{arom. benzoperylene}), 10.54 (s, 1 H, CH\text{arom. benzoperylene}).
9.45 (d, $^{3}J(H,H) = 8.4$ Hz, 2 H, CH$_{arom.}$ benzoperylene), 9.26-9.14 (m, 2 H, CH$_{arom.}$ benzoperylene), 5.36-5.25 (m, 2 H, 2×CH), 3.90 (br, 2 H, NH$_2$), 2.39-2.28 (m, 4 H, 2×β-CH$_2$), 2.22 (s, 6 H, 2×CH$_3$), 2.20 (s, 6 H, 2×CH$_3$), 1.97-1.91 (m, 4 H, 2×β-CH$_2$), 1.45-1.16 (m, 32 H, 16×CH$_2$), 0.82 ppm (t, $^{3}J(H,H) = 7.0$ Hz, 12 H, 4×CH$_3$).

13C NMR (150 MHz, CDCl$_3$, 27.0°C, TMS): δ = 167.5, 133.4, 132.5, 130.1, 128.3, 127.8, 127.5, 125.3, 124.1, 123.6, 55.3, 32.4, 31.8, 29.2, 27.0, 22.6, 15.5, 14.0 ppm. UV/VIS (CHCl$_3$): λ$_{max}$ ($\varepsilon$) = 273.4 (35000), 371.8 (37400), 411.2 (14900), 436.0 (39100), 465.8 nm (60300). Fluorescence quantum yield (CHCl$_3$, $\lambda_{exc}$ = 436 nm, $E_{436nm,1cm} = 0.0131$, reference: C25 with $\Phi = 1.00$): << 0.01. MS (DEP/EI) m/z (%): 995 (100) [M$^{+}$+H], 813 (28) [M$^{+}$+H – C$_{13}$H$_{26}$], 631 (19) [M$^{+}$+H – 2 · C$_{13}$H$_{26}$]. HRMS (C$_{64}$H$_{75}$N$_{4}$O$_{6}$) m/z: Calcd. 995.5608, found 995.5656; Δ = 0.0048. C$_{64}$H$_{74}$N$_{4}$O$_{6}$ (994.6): Calcd. C 77.23, H 7.49, N 5.63; found C 77.08, H 7.46, N 5.53.

2,10-Bis(1-hexylheptyl)-[6-(4'-benzo[5,10]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione)]-2,3,5,6-tetramethylphenyl-1H-pyrrolo[3'4':5,4]pyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-1,3,5,7,9,11 (2H,6H,10H)-hexone (4): 6-(4-Amino-2,3,5,6-tetramethylphenyl)-2,10-bis(1-hexylheptyl)-1H-pyrrolo[3'4':4,5]pyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-1,3,5,7,9,11(2H,6H,10H)-hexone (3) (150 mg, 151 µmol), benzo[5,10]anthra[2,1,9-def]isochromen-1,3-dione$^4$ (40 mg, 0.12 mmol), zincacetate (5 mg, 27 µmol) and quinoline (3 mL) were stirred at 210°C for 8.5 h (orange mixture), allowed to cool, still warm dropped with vigorous stirring into 2 M aqueous HCl (400 mL), stirred for 2 h, allowed to stand for 16 h, collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl (500 mL), hot distilled water (500 mL) and a mixture of methanol and distilled water (500 mL, 1:1), dried at 110°C for 2 d and purified by column separation (neutral alumina, CHCl$_3$/methanol 80:1 and then silica gel, CHCl$_3$/methanol 60:1). Yield 35 mg (21 %) red solid, m.p. >300°C. $R_v$ value (CHCl$_3$/MeOH = 60:1): 0.8. IR (ATR): $\tilde{\nu}$ = 3853 (w), 3744 (w), 3649 (w), 3322 (w), 2922 (m), 2856 (m), 2361 (w), 2339 (w), 1973 (w), 1925 (w), 1772 (w), 1718 (m), 1704 (s), 1666 (s), 1625 (w), 1593.0 (m), 1578 (w), 1521 (w), 1500 (w), 1457 (m), 1413 (m), 1393 (w), 1352 (s), 1317 (s), 1255 (w), 1186 (w), 1171 (w), 1133 (w), 1096 (w), 1055 (w), 1030 (w), 978 (m), 949 (w), 844 (w), 806 (m), 778 (m), 730 (w), 695 (w), 649 (w), 570 (w), 532 (w), 490 (w).
1273 (w), 1246 (m), 1198 (w), 1112 (w), 1021 (w), 971 (w), 945 (w), 918 (w), 885 (w), 854 (w), 845 (w), 810 (s), 795 (w), 761 (m), 753 (m), 747 (s), 726 (w), 698 (w), 659 (w), 644 (w), 630 (w), 621 (w), 613 cm$^{-1}$ (w).

$^1$H NMR (600 MHz, CDCl$_3$, 27.0°C, TMS): $\delta = 10.61$ (s, 1 H, CH$_{arom}$. benzoperylene), 10.56 (s, 1 H, CH$_{arom}$. benzoperylene), 9.47 (d, $^3$J(H,H) = 8.5 Hz, 2 H, CH$_{arom}$. perylene), 9.23 (d, $^3$J(H,H) = 8.4 Hz, 2 H, CH$_{arom}$. perylene), 8.72 (d, $^3$J(H,H) = 7.8 Hz, 2 H, CH$_{arom}$. perylene), 8.50 (d, $^3$J(H,H) = 7.8 Hz, 2 H, CH$_{arom}$. perylene), 7.96 (d, $^3$J(H,H) = 7.8 Hz, 2 H, CH$_{arom}$. perylene), 7.66 (dd, $^3$J(H,H) = 8.4 Hz, $^3$J(H,H) = 8.4 Hz, 2 H, CH$_{arom}$. perylene), 5.38-5.26 (m, 2 H, 2 $\times$CH), 2.42-2.30 (m, 4 H, 2 $\times$CH$_2$), 2.28 (s, 6 H, 2×CH$_3$), 2.20 (s, 6 H, 2×CH$_3$), 1.99-1.90 (m, 4 H, 2×$\beta$-CH$_2$), 1.46-1.17 (m, 32 H, 16 $\times$CH$_2$), 0.82 ppm (t, $^3$J(H,H) = 7.0 Hz, 12 H, 4×CH$_3$).

$^{13}$C NMR (150 MHz, CDCl$_3$, 27.0°C, TMS): $\delta = 167.1$, 163.3, 133.9, 133.5, 133.0, 132.1, 131.1, 129.2, 128.4, 127.6, 127.1, 125.3, 124.1, 124.0, 123.6, 120.9, 120.3, 55.3, 32.4, 31.8, 29.7, 29.2, 27.0, 22.6, 15.9, 15.4, 14.0 ppm. UV/VIS (CHCl$_3$): $\lambda_{\text{max}}$ ($E_{\text{rel}}$) = 264.6 (0.69), 374.6 (0.46), 410.6 (0.21), 436.8 (0.57), 466.6 (1.00), 511.2 nm (0.56).

Fluorescence (CHCl$_3$): $\lambda_{\text{max}}$ ($I_{\text{rel}}$) = 544.9 (1.00), 582.9 nm (0.80). Fluorescence quantum yield (CHCl$_3$, $\lambda_{\text{exc}}$ = 436 nm, $E_{436}$ nm, 1 cm = 0.0214, reference: 3,4,9,10-Perylenetetramethylester with $\Phi$ = 1.00): 0.68. MS (FAB) m/z: 1299 [M$^+$+H], 935 [M$^+$+H – 2·C$_{13}$H$_{26}$]. C$_{76}$H$_{78}$N$_4$O$_8$ (1298.6): Calcd. C 79.48, H 6.36, N 4.31; found C 78.65, H 6.14, N 4.36.

![Chemical structure](image)

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2-(4-Amino-2,3,5,6-tetramethylphenyl)-11-(1-nonyldecyl)-benzo[13,14]pentapheno[3,4,5-def:10,9,8-d'e'f']diisoquinoline-1,3,10,12(2H,11H)-tetraone (9): 2,3,5,6-Tetramethylbenzene-1,4-diamine (RN 3102-87-2) (66 mg, 0.40 mmol), 11-(nonyldecyl)-1H-benzo[13,14]isochromeno[6',5',4':8,9,10]pentapheno[3,4,5-def]diisoquinoline-1,3,10,12(11H)-tetraone (8) (78 mg, 0.10 mmol), zincacetate (11 mg, 60 $\mu$mol) and quinoline (1.8 mL) under argon atmosphere were stirred at 210°C for 4 h (deep blue mixture), allowed to cool, still warm dropped with vigorous stirring into 2 m aqueous HCl (300 mL), stirred for 2 h, allowed to stand for 16 h, collected by vacuum filtration (D4
glass filter), washed with 2 M aqueous HCl (300 mL), hot distilled water (300 mL) and a mixture of methanol and distilled water (300 mL, 1:1), dried in vacuo at 110°C for 2 d and purified by column separation (neutral alumina, CHCl₃/methanol 80:1 and then silica gel, CHCl₃/methanol 40:1). Yield 71 mg (76 %) deep blue solid, m.p. >300°C, Rₜ value (silica gel, CHCl₃/methanol 40:1):0.4. IR (ATR): ν = 3482 (w), 3398 (w), 2920 (m), 2850 (m), 1693 (s), 1653 (s), 1632 (s), 1584 (s), 1506 (w), 1467 (m), 1437 (m), 1418 (w), 1379 (m), 1351 (s), 1322 (s), 1302 (s), 1250 (m), 1206 (m), 1182 (w), 1139 (w), 1119 (m), 1053 (w), 1009 (w), 854 (w), 841 (m), 806 (s), 790 (m), 750 (m), 721 (m), 694 (w), 680 (w), 668 cm⁻¹ (w). ¹H NMR (600 MHz, CDCl₃, 27.0°C, TMS): δ = 8.70 (d, 3J(H,H) = 8.0 Hz, 2 H, CH₉arom. terrylene), 8.63-8.38 (m, 10 H, CH₉arom. terrylene), 5.25-5.19 (m, 1 H, CH), 3.73 (br, 2 H, NH₂), 2.32-2.24 (m, 2 H, β-CH₂), 2.17 (s, 6 H, 2×CH₃), 2.10 (s, 6 H, 2×CH₃), 1.93-1.86 (m, 2 H, β-CH₂), 1.42-1.13 (m, 28 H, 14×CH₂), 0.83 ppm (t, 3J(H,H) = 7.1 Hz, 6 H, 2×CH₃). ¹³C NMR (150 MHz, CDCl₃, 27.0°C): δ = 163.7, 135.9, 135.3, 131.9, 131.0, 130.9, 130.8, 129.7, 128.5, 126.2, 125.8, 124.2, 124.1, 121.9, 121.3, 118.9, 54.6, 32.4, 31.9, 29.7, 29.6, 29.3, 27.0, 22.6, 15.1, 14.1, 13.9 ppm.

UV/VIS (CHCl₃): λₘₐₓ (ε) = 555.3 (22300), 600.4 (66300), 653.8 nm (130400).

Fluorescence (CHCl₃): λₘₐₓ (Iₐₜ): 673.9 (1.00), 731.3 nm (0.43). Fluorescence quantum yield (CHCl₃, λₑₓᶜₑₓ = 600 nm, E₆₀₀ nm, 1 cm = 0.0322, reference: S-19Terylene with Φ = 0.94): 0.04. MS (DEP/EI) m/z (%): 928 (89) [M⁺], 661 (66) [M⁺ – C₁₉H₃₉], 514 (55) [M⁺ – C₁₀H₂₉ – C₁₀H₁₅]. HRMS (C₆₃H₆₅N₃O₄) m/z: Calcd. 927.4975, found 927.4984; Δ = 0.0009. C₆₃H₆₅N₃O₄ (927.5): Calcd. C 81.52, H 7.06, N 4.53; found C 80.70, H 7.09, N 4.33.

2,10-Bis(1-hexylheptyl)-6[4’-(3,8,9,10-tetrahydro-11-(1-nonyldecyl)benzo[13,14]pentapheno1,3,8,10-tetraoxoanthra[3,4,5-def:10,9,8-d’e’f’]diisoquinoline-1,3,10,12(2H,11H)-yl-2,3,5,6-tetramethylphenyl)-1H-pyrrolo[3’4’:4,5]pyrreno[2,1,10-def:7,8,9-d’e’f’]diisoquinoline-1,3,5,7,9,11(2H,6H,10H)-hexone (10): 2-(4-Amino-2,3,5,6-tetramethyl-phenyl)-11-(1-nonyldecyl)-benzo[13,14]pentapheno[3,4,5-def:10,9,8-d’e’f’]diisoquinoline-1,3,10,12(2H,11H)-tetrone (9) (28 mg, 30 μmol), 2,10-bis(1-
hexylheptyl)furo[3',4':4,5]pyreno[2,1,10-def:7,8,9-d'e'f']diisoquinoline-1,3,5,7,9,11(2H,10H)-hexaone (2) (51 mg, 60 µmol) and quinoline (2 mL) were heated at 230°C and 200 W microwave radiation for 9 h (greenish blue mixture), allowed to cool, still warm dropped with vigorous stirring into 2 M aqueous HCl (300 mL), stirred for 2 h, allowed to stand for 16 h, collected by vacuum filtration (D4 glass filter), washed with 2 M aqueous HCl (300 mL), hot distilled water (300 mL) and a mixture of methanol and distilled water (300 mL, 1:1), dried in vacuo at 110°C for 18 h and purified by column separation (basic alumina, CHCl₃/methanol 80:1; silica gel, CHCl₃/methanol 80:1; neutral alumina, dichloromethane; weakly acid alumina, CHCl₃/methanol 100:1). Yield 34 mg (64 %) dark green solid, m.p. >300°C. Rᵣ value (CHCl₃/methanol 60:1): 0.8. IR (ATR): ν = 2957 (m) 2924 (m), 2855 (m), 1774 (w), 1721 (m), 1707 (s), 1662 (s), ~1587 (s), 1522 (w), 1506 (w), 1460 (m), 1415 (m), 1395 (w), 1379 (m), 1354 (s), 1319 (s), 1260 (m), 1204 (w), 1176 (w), 1095 (m), 1017 (w), 946 (w), 869 (w), 842 (w), 809 (s), 767 (w), 749 (m), 723 (w), 696 (w), 684 (w), 665 (w), 645 cm⁻¹ (w).¹H NMR (600 MHz, CDCl₃, 27.0°C, TMS): δ = 10.66-10.58 (m, 2 H, CH arom. benzoperylene), 9.51 (d, J(H,H) = 8.5 Hz, 2 H, CH arom. benzoperylene ), 9.29-9.19 (m, 2 H, CH arom. benzoperylene), 8.84-8.58 (m, 10 H, CH arom. terrylene), 5.39-5.28 (m, 2 H, CH benzoperylene), 5.26-5.19 (m, 1 H, CHTerrylen), 2.43-2.32 (m, 4 H, β-CH₂), 2.32-2.25 (m, 2 H, β-CH₂), 2.30 (s, 6 H, 2×CH₃), 2.22 (s, 6 H, 2×CH₃), 2.00-1.92 (m, 4 H, β-CH₂), 1.92-1.84 (m, 2 H, β-CH₂), 1.46-1.17 (m, 60 H, 30×CH₂), 0.85-0.80 ppm (m, 18 H, 6×CH₃).¹³C NMR (150 MHz, CDCl₃, 27.0°C): δ = 167.0, 163.1, 134.0, 133.0, 130.9, 128.4, 127.6, 123.7, 121.7, 121.6, 55.7, 55.3, 32.4, 31.9, 31.8, 29.6, 29.3, 27.0, 22.6, 22.6, 15.9, 15.4, 14.1, 14.0 ppm. UV/VIS (CHCl₃): λmax (ε): 377.1 (44400), 410.2 (18400), 436.5 (40000), 466.5 (62300), 557.6 (23600), 601.1 (73000), 654.5 nm (143000). Fluorescence (CHCl₃): λmax (Irel): 669.9 (1.00), 734.7 nm (0.50). Fluorescence quantum yield (CHCl₃, λexc = 437 nm, E₂₄₃ nm, 1 cm = 0.0169, reference: C25 with Φ = 1.00): 0.63. Fluorescence quantum yield (CHCl₃, λexc = 437 nm, E₂₄₃ nm, 1 cm = 0.0169, reference: 3,4,9,10-Perlenetetramethylster with Φ = 1.00): 0.62. Fluorescence quantum yield (CHCl₃, λexc = 601 nm, E₆₀₁ nm, 1 cm = 0.0306, Reference: perylene-terrylene -dyad with Φ = 0.89): 0.91. MS (MALDI): (Matrix: Anthracene) m/z : 1758 [M⁺]. MS (FAB+) m/z: 1758 [M⁺], 1576 [M⁺ – C₁₃H₂₆], 1492 [M⁺ – C₁₉H₃₈]. HRMS (C₁₁₇H₁₂₃N₅O₁₀) m/z: Calcd. 1758.9304, found 1758.9266; Δ = -0.0038. C₁₁₇H₁₂₃N₅O₁₀ (1757.9): Calcd. C 79.88, H 7.05, N 3.98; found C 79.53, H 7.02, N 3.95.
2-(4-2,1,3-Benzoxazophenyl)-11-(1-nonyldecyl)-benzo[13,14]pentapheno[3,4,5-def:10,9,8-d’e’f’]diisoquinoline-1,3,10,12(2H,11H)-tetaone (12): 4-
Benzo[1,2,5]oxadiazol-4-yl-phenylamine\(^9\) (11) (37 mg, 0.17 mmol), 11-(nonadecan-10-yl)-1H-benzo[13,14]isochromeno[6’5’,4’:8,9,10]pentapheno[3,4,5-def]isoquinoline-1,3,10,12(11H)-tetraone (8) (68 mg, 87 \(\mu\)mol), zincacetate (3.2 mg, 17 \(\mu\)mol) and quinoline (2.0 mL) under argon atmosphere were stirred at 200°C for 6 h (deep blue mixture), allowed to cool, still warm dropped with vigorous stirring into 2 \(M\) aqueous HCl (300 mL), stirred for 2 h, allowed to stand for 16 h, collected by vacuum filtration (D4 glass filter), washed with 2 \(M\) aqueous HCl (300 mL), hot distilled water (300 mL) and a mixture of methanol and distilled water (300 mL, 1:1), dried in vacuo at 90°C for 1 d and purified by column separation (neutral alumina, CHCl\(_3\)/methanol 80:1 and then silica gel, CHCl\(_3\)/methanol 80:1). Yield 31 mg (37 %) blue solid, m.p. >300°C. \(R_f\) value (CHCl\(_3\)/methanol 60:1): 0.6. IR (ATR): \(\tilde{\nu}\) = 2955 (w), 2921 (m), 2852 (m), 1691 (s), \(\tilde{\nu}\) ~ 1652 (s), 1586 (s), 1506 (m), 1465 (w), 1421 (w), 1379 (m), 1355 (s), 1329 (m), 1305 (m), 1255 (m), 1208 (m), 1184 (m), 1144 (w), 1114 (w), 1071 (w), 1015 (m), 965 (w), 888 (w), 856 (w), 846 (m), 823 (m), 808 (s), 798 (s), 762 (w), 746 (s), 720 (w), 694 (w), 678 (m), 648 (w), 616 (w), 608 cm\(^{-1}\) (w). 1\(H\) NMR (400 MHz, C\(_2\)D\(_2\)Cl\(_4\), 105°C, TMS): \(\delta\) = 8.79-8.59 (m, 12 H, CH\(_{arom.\ terrylene}\)), 8.26 (d, \(^3\)J(H,H) = 8.3 Hz, 2 H, CH\(_{arom.}\)), 7.91 (d, \(^3\)J(H,H) = 9.0 Hz, 1 H, CH\(_{arom.}\)), 7.74 (d, \(^3\)J(H,H) = 6.8 Hz, 1 H, CH\(_{arom.}\)), 7.63-7.58 (m, 3 H, CH\(_{arom.}\)), 5.27-5.19 (m, 1 H, CH), 2.35-2.25 (m, 2 H, \(\beta\)-CH\(_2\)), 2.02-1.92 (m, 2 H, \(\beta\)-CH\(_2\)), 1.47-1.24 (m, 28 H, 14 \(\times\) CH\(_3\)), 0.91 ppm (t, \(^3\)J(H,H) = 6.8 Hz, 6 H, 2\(\times\)CH\(_3\)). UV/VIS (CHCl\(_3\)): \(\lambda_{max}\) (\(\varepsilon\)) = 314.8 (17400), 341.2 (15900), 558.3 (23000), 601.1 (70300), 655.3 nm (139500). Fluorescence (CHCl\(_3\)): \(\lambda_{max}\) (\(I_{rel}\)) = 671.8 (1.00), 738.0 nm (0.50). Fluorescence quantum yield (CHCl\(_3\), \(\lambda_{exc}\) = 602 nm, \(E_{602nm,1cm}\) = 0.0128, reference: S-19Terrylene with \(\Phi\) = 0.94): 0.90. Fluorescence quantum yield (CHCl\(_3\), \(\lambda_{exc}\) = 350 nm, \(E_{350nm,1cm}\) = 0.0050, reference: C25 with \(\Phi\) = 1.00): 0.67. Fluorescence lifetime (CHCl\(_3\), \(\lambda_{exc}\) = 633 nm): 3.98 ns. Fluorescence lifetime (CHCl\(_3\), \(\lambda_{exc}\) = 341 nm): 2.74 ns. MS (DEP/EI) \(m/z\) (%): 975 (31) \([M^{+}+H]\), 708 (94) \([M^{+} - C_{19}H_{38}]\). HRMS (C\(_{65}\)H\(_{59}\)N\(_4\)O\(_5\)) \(m/z\):
Calcd. 975.4441, found 975.4490; Δ = 0.0049. C_{65}H_{58}N_{4}O_{5} (974.4): Calcd. C 80.06, H 5.99, N 5.75; found C 79.62, H 5.96, N 5.61.

1.2 Methods
All reagents were used as received from commercial suppliers. The solvents used in the reactions were dried with standard drying agents and freshly distilled prior to use. Reaction progress was monitored by thin-layer chromatography (TLC) on E. Merck Kieselgel 60 F254. Column chromatography was performed using silica gel (60 Å, 40–63 μm, ROCC). IR spectra were recorded as ATR with a Perkin Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000 (4000–450 cm⁻¹). UV/Vis/NIR spectra: Varian Cary 5000; fluorescence spectra: Varian Carry (totally corrected). All ¹H and ¹³C NMR spectra were recorded with a Varian Vnmrs 600 (600 MHz) in CDCl₃. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. Mass spectra were performed using a Finnigan MAT 95. Elemental analyses (C, H, N) were conducted using the Elemental Analyser Elementar Vario EL from Elementar Analysensysteme GmbH. Fluorescence lifetimes τ were obtained with a PicoQuant 300 lifetime spectrometer and a PicoQuant, P-C-405 as a light source. Overlap spectra and overlap integrals were exactly calculated as was described in ref.¹⁰ (page 122) where the higher resolution of the spectra of 0.2 nm was considered. Transient spectra were exactly recorded as is described in ref.¹¹

2. References