Full Paper

Israel Journal of Chemistry

doi.org/10.1002/ijch.202100021

FRET in Orthogonal, Increasingly Strain-Rigidified Systems

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Dedication to Prof. Niyazi Serdar Sariciftci on the occasion of his 60th birthday

Abstract: The influence of the geometry factor κ on the efficiency of energy transfer by FRET (Förster resonance energy transfer) was studied by means of dyads of benzoperylene and perylene interlinked by a spacer of the cage bicyclo-[2.2.2]octane. The electronic transition moments were arranged orthogonally for extinguishing the energy transfer according to Förster's theory. In contrast to the theory energy transfer proceeded unrestrictedly attributed to molecular vibrations. A further rigidifying of the spacer by means of annellation with benzo groups until the very rigid triptycene as a spacer could not hinder the energy transfer so that general strongly coupled molecular framework vibrations seem to be dominant in the energy transfer whereas molecular flexibility seems to be of minor importance. Application such as molecular mirrors are discussed.

Keywords: FRET · Energy transfer · Fluorescence · Perylenes · Triptycene

1. Introduction

Electron and energy transfer[1] are fundamental processes in the function in photosynthesis.[2] Electron transfer finally mediates the conversion of light energy into chemical energy whereas energy transfer[3] is responsible for light collection to the reactive centre.[4] Förster resonance energy transfer[5] (FRET) is the generally accepted process for such light collection whereas the Dexter mechanism[6] as a well-known alternative can be excluded because of lacking the required direct contact of the orbitals of the involved chromophores. FRET[7] is generally attributed to a resonance energy transfer by dipole-dipole interaction[8] between the energy donor D and the acceptor A. The process is quantitatively described by equation (1) according to fundamental theoretical work by Perrin[9] and Förster.[8]

$$k_T = \frac{9000 \cdot (\ln 10) \cdot \kappa^2 \cdot J \cdot \Phi_D}{128 \cdot \pi^5 \cdot N_A \cdot \tau_D \cdot n^4 \cdot R^6} \quad (1)$$

The rate constant k_T in eq. (1) of such energy transfer processes depends on the fluorescence quantum yield of the donor Φ_D, the overlap integral J between the fluorescence spectrum of the donor, the absorption spectrum of the acceptor, the fluorescence lifetime τ_D of the donor and the index of refraction n of the medium and some mathematical and natural (N_A) constants; R is the distance between the dipoles of the transition moments of the donor and the acceptor; this parameter of the chemical structure is often used as a molecular ruler. The minor commonly used geometry parameter κ can be calculated from a sum of scalar products simplified to *cos* expression of eq. (2) where θ_T means the angle between the transition moments of the donor and acceptor and the angle θ_D between the donor transition moment and the interconnecting vector the angle θ_A the analogous angle of the acceptor.

$$\kappa = \cos(\theta_T) - 3\cos(\theta_D)\cos(\theta_A) \quad (2)$$

The theory-based eq. (2) is generally estimated to be valid; however, doubts came about from the investigation of real systems.[10]

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/ijch.202100021

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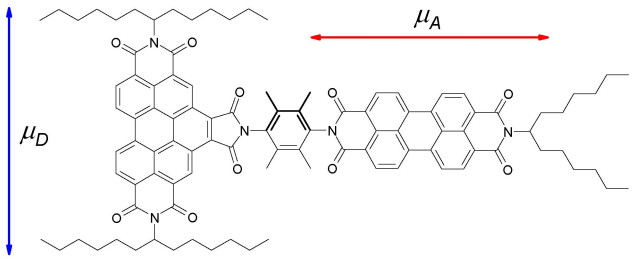

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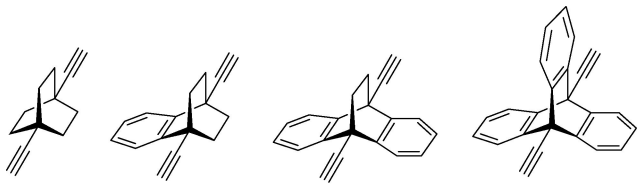
Moreover, a fast energy transfer[11] was found in **1** with a time constant of 9.4 ps from the left hypsochromically absorbing benzoperylene unit as the donor (μ_D) to the right bathochromically absorbing perylene unit as the acceptor (μ_A) was observed; in contrast to this experimental result the energy transfer should be inhibited according to the Förster theory where κ becomes zero according to eq. (2) because $\theta_T = \theta_D = 90°$. This discrepancy was attributed to an energy transfer mediated by molecular vibrations.[12] Even the application of diamantane[13] as a very rigid diamond-like spacer could not inhibit the energy transfer; on the other hand, this spacer caused a slight lateral shift of the chromophores due to its structure; compare a verifying in Ref.[14] with skew-oriented nearly orthogonal oligothiophenes. The effect of an exact orthogonal alignment of the chromophores with rigid spacers would be still of interest.

2. Results and Discussion

The bis-ethynylbicyclo[2.2.2]octane **2** fulfills the condition of a co-linear linker between chromophores for the study of FRET because the ethynyl groups are in line; however, the aliphatic cage is slightly twisted indicating its flexibility; see the x-ray crystal structure in Figure 1, left.



2 3 4 5

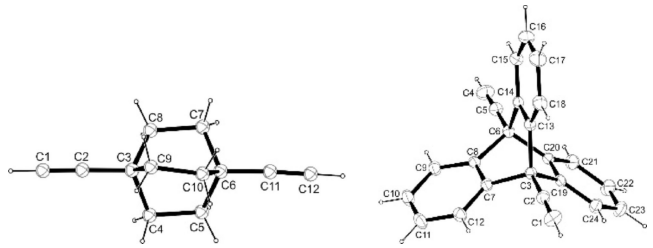
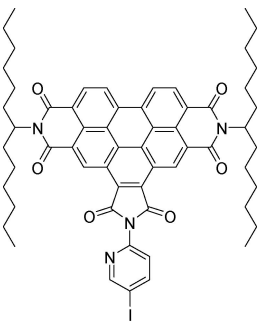


Figure 1. X-ray crystal structure analyses of **2** (left, CCDC 1844469[15]) and **5** (right, CCDC 2070379).

The spacer **2** was increasingly strain-rigidified by means of annellated benzo groups in the series from **3** until the stiff **5** as is demonstrated by the x-ray crystal structure analysis in Figure 1, right: The aliphatic carbon atoms of the ethylene bridges allowing some conformational flexibility were progressively replaced by the stiff, flat *o*-benzoic rings.

The spacers **2** until **5** were prepared according to the literature.[16] Single crystals of **5** for x-ray crystal structure analysis could be obtained from *n*-hexane/dichloromethane.



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The benzoperylenetriscarboximide **6** was applied as the energy donor D and the perylene biscarboximide **7** (see Scheme 1, below) as the energy acceptor for the study of FRET such as in the dyad **1**. Iodine atoms were introduced into **6** and **7** as the reactive positions for palladium-mediated C–C-coupling by the Sonogashira reaction. The long-chain *sec*-alkyl groups (swallow-tail substituents) in **6** and in **7**, respectively, increase the solubility of the compounds in lipophilic media necessary both for synthesis and spectroscopic investigations and furthermore diminish the tendency

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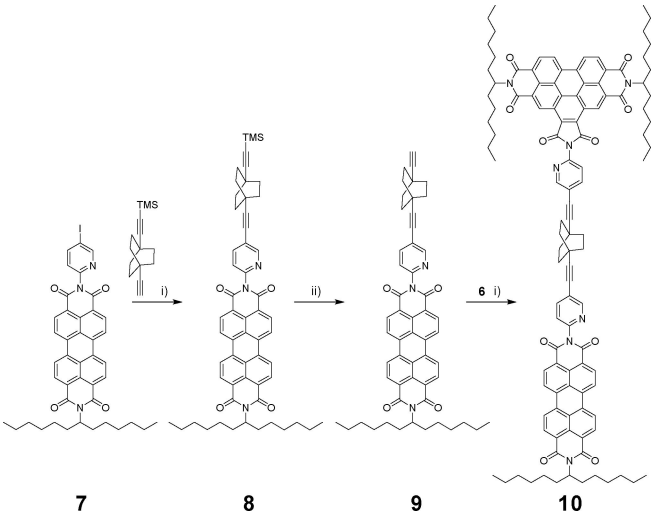
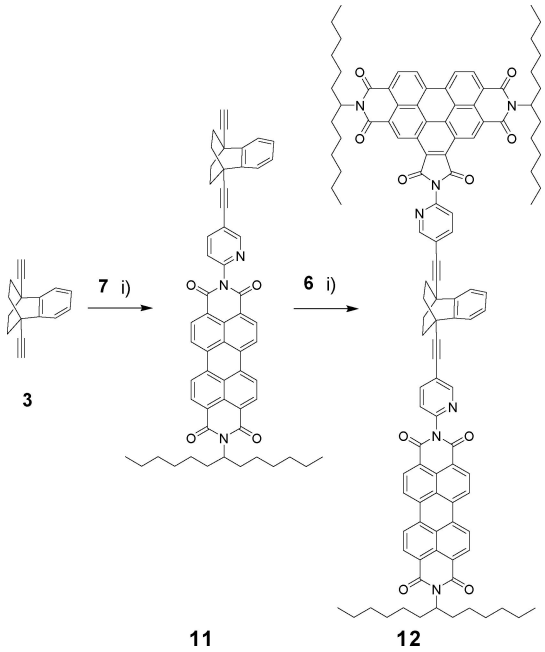


Scheme 1. Synthesis of **10**; i) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3 THF/TEA, 80 °C, ii) TBAF, THF



Scheme 2. Synthesis of 12; i) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3 THF/TEA, 80 °C.

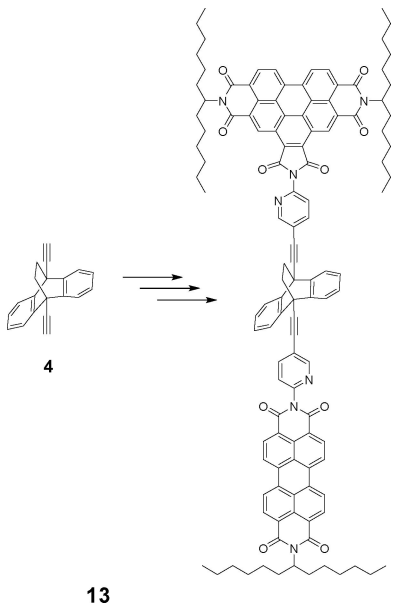
for aggregation.[17] The iodine atoms in **6** and **7** for linking were not attached to simple phenyl groups because of preventing a competting of FRET by electron transfer[11b] from the comparably electron-rich linkers in the the target compounds; pyridine groups instead cause a sufficient electron depletion because of the electronegative nitrogen atoms.

One of the ethynyl groups in the spacer **2** was protected[15,18] by means of a trimethylsilyl group (TMS) and allowed to react according to Scheme 1 by palladium and copper-mediated Sonogashira coupling with **7** as the the perylene building block to form **8**. Deprotection with TBAF (tetrabutylammoniumfluoride) to **9** and metal-mediated coupling with **6** allowed to obtain the dyad **10**.

Experiments with substituted cage compounds by two ethynyl groups indicated that the formation of by-products in Sonogashira reactions is unimportant compared to aromatic ethynyl compounds. As a consequence, the protection of **3** and the deprotection of the reaction product were exposed saving two synthetic steps. Thus, **7** was directly allowed to react with a large excess of **3** in a reduced reaction time and gave 63 % of pure **11**; the yield is similar to the yield of the reaction with semi-protected bis-ethynyl derivatives. The subsequent reaction with **6** finally gave **12**.

The spacer **4** was allowed to react analogously to **3** with an excess of **7** and further with **6** to obtain **13** in similar yield as **12**; see Scheme 3.

Finally, the reaction of the semi-protected bisethynyl triptycene[19] with **7**, deprotection and further reaction with **6** gave the dyad **14** with the stiff triptycene as the spacer between the chromophores; see Scheme 4.



Scheme 3. Synthesis of **13**; the steps are analogous to Scheme 2.

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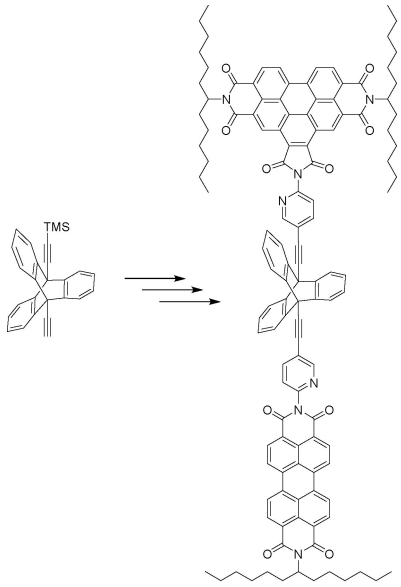

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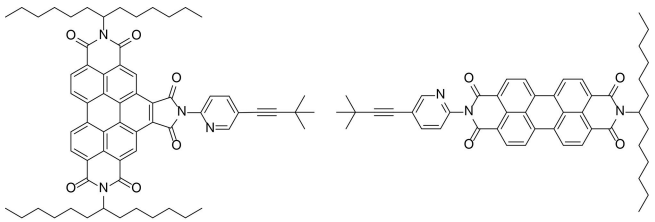
Scheme 4. Synthesis of **14**; the steps are analogous to Scheme 1.



15 16

Compound **15** was prepared representing the isolated donor (*D*) for comparison and **16** representing the isolated acceptor (*A*). **15** and **16** were obtained from **7** and **6**, respectively, and 3,3-dimethylbutyne by means of the Sonogashira reaction analogously to Scheme 2.

The UV/Vis absorption spectrum of **10** is the sum of the spectra of the donor and the acceptor, as can be seen in Figure 2, and the comparison there with **15** and **16**; the cage in **10** was simulated by simple *tert*-butyl groups, where a different electronic influence on the chromophore is unimportant. Strong fluorescence of the acceptor is observed if electronically excited in solution at 491 nm; a fluorescence quantum yield close to 100% was found in chloroform. The excitation of the donor in **10** at 437 nm indicated a fluorescence quenching of the donor (lack of emission below 500 nm). Instead, strong fluorescence of the acceptor was found (above 500 nm); a fluorescence quantum yield of 96% was found in chloroform, indicating an efficient energy transfer although the transition moments in **10** are orthogonal.

The cage of the bicyclo[2.2.2]octane in **10** is slightly twisted, as can be seen in the x-ray crystal structure analysis in Figure 1, indicating some residual flexibility. As a consequence, compound **12** with a more rigid spacer was investigated and gave the UV/Vis spectra in Figure 3. The absorption spectrum of **12** is identical to the spectrum of **10** and thus, the sum of the spectra of donor and acceptor. The fluorescence quantum yield of the acceptor remained unaltered high and close to 100% (excitation at 491 nm). The fluorescence of the donor (excitation at 437 nm) is essentially quenched, where the fluorescence quantum yield of the acceptor is found to be 93%, indicating an efficient energy transfer. The quantum yield is very slightly lower than of **10**; however, the difference is nearly in the scope of experimental error.

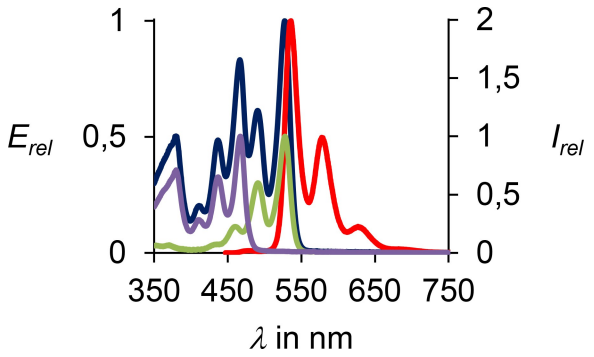


Figure 2. Normalized UV/Vis spectra of **10** in chloroform. Blue: Absorption spectrum, red: Fluorescence spectrum (optical excitation of the donor at $\lambda_{exc}=437$ nm, normalized to $I=2$), violet: Absorption spectrum of **15** for comparison (normalized to $E=0.5$ for clearness), green: absorption spectrum of **16** (normalized to $E=0.5$).

The even more rigid **13** exhibits still the same absorption spectrum as **10**; see Figure 4. The fluorescence quantum yield of the donor (excited at 491 nm) remains close to 100%. The fluorescence of the donor (excited at 437 nm) is quenched and an energy transfer to the acceptor is observed with a fluorescence quantum yield of 94%.

Finally, dyad **14** with the triptycene as a very rigid spacer was UV/Vis spectroscopically investigated; see Figure 5. Again, the absorption spectrum of **14** is identical with **10**

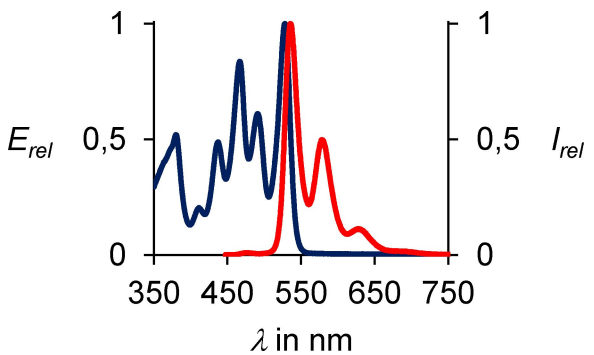


Figure 3. Normalized UV/Vis spectra of **12** in chloroform. Blue: Absorption spectrum, red: Fluorescence spectrum (optical excitation of the donor at $\lambda_{exc}=437$ nm).

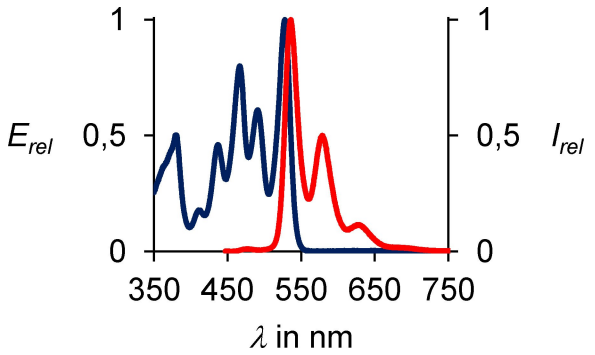


Figure 4. Normalized UV/Vis spectra of **13** in chloroform. Blue: Absorption spectrum, red: Fluorescence spectrum (optical excitation of the donor at $\lambda_{exc} = 437$ nm).

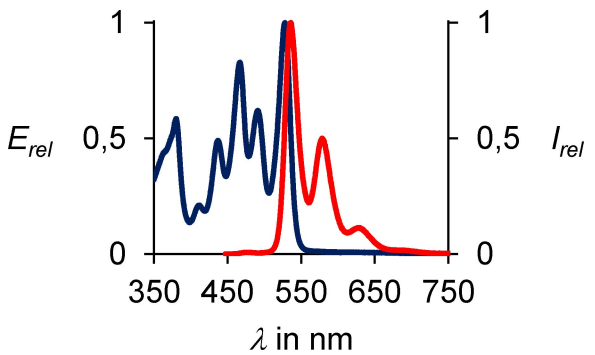


Figure 5. Normalized UV/Vis spectra of **14** in chloroform. Blue: Absorption spectrum, red: Fluorescence spectrum (optical excitation of the donor at $\lambda_{exc} = 437$ nm).

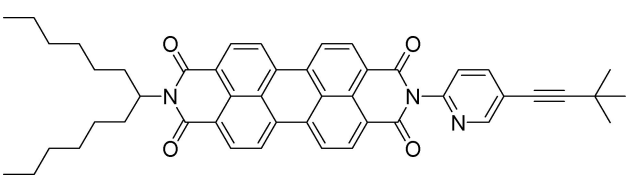
indicating the sum of donor and acceptor, and the fluorescence quantum yield of the acceptor (excitation at 491 nm) remained close to 100%. The fluorescence of the donor (excited at 437 nm) is quenched and a fluorescence quantum yield of 96% of the acceptor is found and is identical with **10**.

3. Summary

The dyad **10** of a benzoperylenecarboximide as energy donor, the aliphatic cage bicyclo[2.2.2]octane as spacer and a perylenecarboximide as the energy acceptor was synthesized by means of the Sonogashira coupling. The spacer was stepwise rigidified by means of benzo annellation to finally obtain the triptycene-derived dyad **14**. The resonance energy transfer in the dyad **10** with orthogonal electronic transition moments proceeded with an efficiency of 96% in contrast to Förster's theory (FRET) because the orientation factor κ is zero as a consequence of orthogonality. Molecular flexibility seems to be unimportant for the energy transfer because the transfer is unaltered efficient in the rigid triptycene derivative **14** and must proceed fast compared with the fluorescence lifetime of the donor of 6.8 ns[20] to be complete within a few picoseconds. The process of the energy transfer is attributed to be mediated by slow molecular vibrations. On the other hand, rigid orthogonal dyads may be applied to flip a light beam exactly by 90° because the transition moments both for absorption and fluorescence are parallel to the longitudinal axes of the chromophores (for measurements of polarization see ref.[20]) so that the incoming absorbed light is emitted in a 90° angle as the fluorescent light such as by a molecular mirror placed at 45° to the incoming light. This may be of interest such as for light-collecting devices.[21]

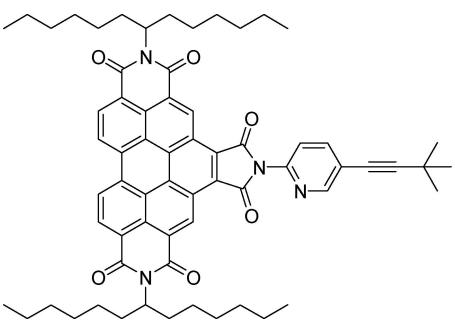
4. Experimental Section

General Information. Available standard chemicals were applied in synthesis grade without further purification. Chloroform was used in spectrophotometric grade. Yields refer to the isolated compounds estimated to be >95% pure as determined by ^{1}H NMR (25 °C); all dyes were uniform according to T.L.C. Chemical shifts are reported as δ values in ppm calibrated with the solvent peak. NMR spectra were recorded in the solution of $CDCl_3$ (residual chloroform: $\delta = 7.27$ ppm for ^{1}H NMR and $\delta = 77.0$ ppm for $^{13}C\{^1H\}$ NMR). Abbreviations for signal coupling are as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sxt, sextet; and m, multiplet. Infrared spectra were recorded from 4000–400 cm^{-1} on a Perkin 281 IR spectrometer. Samples were measured neat (ATR, Smiths Detection Dura Sample IR II Diamond ATR). The absorption bands were reported in wave numbers (cm^{-1}). Mass spectra were recorded on a Finnigan MAT 95Q or Finnigan MAT 90 instrument for electron impact ionization (EI) with direct vaporization of the sample (DEP/EI) from a platinum fiber 20 until 1600 °C at 60 °C·min^{-1}. High-resolution mass spectra (HRMS) were recorded on the same instrument. UV–Vis spectra were obtained with a Varian Cary5000 spectrometer. Fluorescence spectra were obtained with a Varian Cary Eclipse spectrometer, slit width 2.5 nm. Column chromatography was performed using SiO_2 (0.040–0.063 mm, 230–400 mesh ASTM) from Merck if not indicated. Fluorescence quantum yields were determined analogously to ref.[22] by means the standard **S-13** (CAS RN 110590-84-6) or **C-25**[20] (CAS RN 335458-21-4). The interpretation of NMR signals was verified with carbon–proton (HMBC) and proton–proton (COSY, NOESY) correlation methods. All reagents were obtained from commercial sources and used without further purification if not otherwise stated.

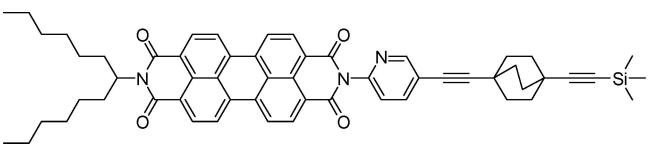


2-[5-(3,3-Dimethylbut-1-yn-1-yl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-1,3,8,10-tetraone (16): 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-

yl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-1,3,8,10-tetraone (**7**, 100 mg, 129 µmol) under argon atmosphere was dissolved in THF (5.0 mL), treated with $PdCl_2(PPh_3)_2$ (15 mg, 13 µmol), CuI (3.2 mg, 17 µmol), PPh_3 (3.4 mg, 13 µmol), then treated with 3,3-dimethyl-1-butyne (27 mg, 0.32 mmol), triethylamine (2.5 mL), stirred at 80 °C for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 800×44 mm, chloroform/ethanol 80:1). Yield 44 mg (47%) red dye, m.p. >250 °C). R_f -value (silica gel, $CHCl_3$/ethanol 80:1) = 0.30. IR (ATR): $\tilde{\nu}$ = 2952.3 (w), 2923.1 (w), 2856.0 (w), 1710.5 (m), 1696.3 (m), 1653.4 (s), 1592.6 (s), 1577.0 (m), 1557.9 (w), 1505.9 (w), 1472.1 (m), 1456.8 (w), 1431.8 (m), 1340.8 (s), 1294.6 (m), 1252.1 (s), 1200.9 (m), 1175.5 (m), 1139.6 (w), 1124.6 (w), 1106.7 (w), 1027.4 (w), 965.1 (w), 918.0 (w), 891.8 (w), 849.3 (m), 808.3 (s), 781.2 (w), 743.1 (m), 723.2 (w), 673.9 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, $^3J(H,H)$ = 6.9 Hz, 6 H, 2×CH_3), 1.18–1.27 (m, 16 H, 8×CH_2), 1.36 (s, 9 H, 3×CH_3), 1.83–1.91 (m, 2 H, β-CH_2), 2.20–2.29 (m, 2 H, β-CH_2), 5.15–5.21 (m, 1 H, N–CH), 7.35 (s, 1 H, $CH_{pyridine}$), 7.91 (d, $^3J(H,H)$ = 8.1 Hz, 1 H, $CH_{pyridine}$), 8.63–8.72 ppm (m, 9 H, 8×$CH_{perylene}$, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 28.1, 29.2, 30.8, 31.7, 32.4, 54.8, 75.4, 103.4, 123.0, 123.3, 126.2, 126.5, 129.4, 129.8, 131.6, 134.1, 135.1, 140.9, 163.2 ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 28.1, 29.2, 30.8, 31.7, 32.4, 54.8, 75.4, 103.4, 123.0, 123.3, 126.2, 126.5, 129.4, 129.8, 131.6, 134.1, 135.1, 140.9, 163.2 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 459.8 (23200), 490.6 (56800), 527.4 nm (92000). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 543.8 (1.00), 578.4 (0.50), 625.79 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0117, reference: S-13 with Φ = 1.00): 1.00. MS (FAB^+): *m/z* (%): 730.7 (96) [M^+ + H], 729.7 (20) [M^+], 714.7 (13), 548.4 (98), 532.4 (41), 373.3 (100), 345.3 (39). HRMS ($C_{48}H_{47}N_3O_4$): Calcd. 730.3639 [M^+]; found 730.3645 [M^+]; Δ = +0.0006. $C_{48}H_{47}N_3O_4$ (729.4): Calcd. C 78.98, H 6.49, N 5.76; found C 78.73, H 6.41, N 5.65.

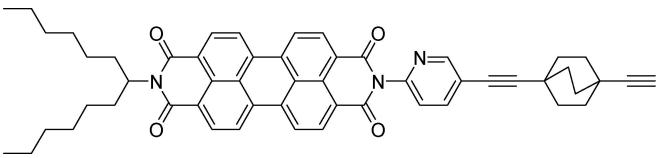


***N,N′′*-Bis-(1-hexylheptyl)-*N′*-[5-(3,3-dimethylbut-1-yn-1-yl)pyridin-2-yl]benzo[*ghi*]perylene-1′,2′:3,4:9,10-hexacarboxylic-1′,2′:3,4:9,10-tris(dicarboximide) (15)**: *N,N**-Bis(1-hexylheptyl)-*N**-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1',2':3,4:9,10-hexacarboxylic-1',2':3,4:9,10-tris (dicarboximide) (**6**, 100 mg, 95.2 µmol) under argon atmosphere was dissolved in THF (4.0 mL), treated with $PdCl_2(PPh_3)_2$ (11 mg, 10 µmol), CuI (2.2 mg, 13 µmol), PPh_3 (3.0 mg, 10 µmol), then treated with 3,3-dimethyl-1-butyne (31 mg, 0.38 mmol), triethylamine (2.0 mL), stirred at 80 °C for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 800×44 mm, chloroform). Yield 45 mg (47%) red dye, m.p. >250 °C). R_f -value (silica gel, $CHCl_3$/ethanol 80:1) = 0.30. IR (ATR): $\tilde{\nu}$ = 2954.1 (m), 2924.7 (m), 2856.2 (m), 2241.7 (w), 1776.0 (w), 1717.7 (s), 1706.4 (s), 1661.6 (s), 1625.1 (w), 1595.4 (m), 1570.3 (w), 1556.2 (w), 1522.4 (w), 1471.8 (m), 1413.5 (m), 1364.8 (s), 1317.7 (s), 1295.0 (s), 1277.3 (m), 1244.0 (m), 1203.9 (w), 1177.3 (w), 1166.8 (w), 1101.7 (w), 1026.4 (w), 964.3 (w), 940.8 (w), 918.3 (w), 885.4 (w), 845.0 (w), 810.0 (m), 764.0 (m), 746.4 (m), 725.7 (w), 660.0 (w), 698.3 (w), 676.7 (w), 660.0 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, $^3J(H,H)$ = 7.0 Hz, 12 H, 4×CH_3), 1.21–1.37 (m, 32 H, 16×CH_2), 1.39 (s, 9 H, 3×CH_3), 1.91–2.03 (m, 4 H, 2×β-CH_2), 2.26–2.43 (m, 4 H, 2×β-CH_2), 5.23–5.36 (m, 2 H, 2×N-CH), 7.72 (d, $^3J(H,H)$ = 8.1 Hz, 1 H, $CH_{pyridine}$), 8.01 (dd, $^3J(H,H)$ = 8.2 Hz, $^4J(H,H)$ = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.75 (d, $^4J(H,H)$ = 2.3 Hz, 1 H, $CH_{pyridine}$), 9.17–9.43 (m, 4 H, 4×$CH_{perylene}$), 10.42 ppm (s, 2 H, 2×$CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 28.2, 29.2, 30.8, 31.8, 32.5, 55.3, 75.4, 103.5, 121.5, 123.3, 124.0, 125.0, 127.0, 127.7, 128.1, 133.2, 140.9, 152.0, 166.3 ppm. UV/VIS ($CHCl_3$): λ_{max} (E_{rel}) = 379.40 (0.71), 411.00 (0.25), 436.80 (0.65), 467.00 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 437 nm): λ_{max} (I_{rel}) = 477.4 (1.00), 511.6 (0.63), 549.4 nm (0.17). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437\ nm/1\ cm}$ = 0.0118, reference: S-13 with Φ = 1.00): 0.16. MS (FAB^+): *m/z* (%): 1005.9 (38) [M^+ + H], 1004.9 (16) [M^+], 989.0 (5), 823.7 (25), 641.5 (45), 625.0 (25). HRMS ($C_{65}H_{72}N_4O_6$): Calcd. 1005.5525 [M^+], found 1005.5530 [M^+]; Δ = +0.0005.

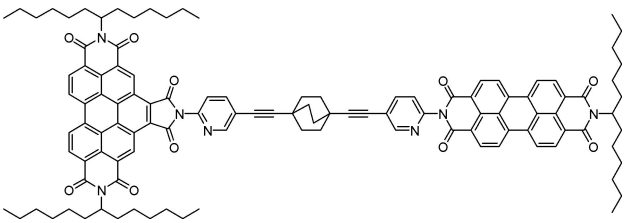


2-(1-Hexylheptyl)-9-[5-(4-trimethylsilanylethynylbicyclo[2.2.2]oct-1-ylethynyl)pyridin-2-yl]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-1,3,8,10-tetraone (8): 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-1,3,8,10-tetraone (**7**, 300 mg, 389 µmol) under argon atmosphere was dissolved in THF (10.0 mL), treated with $PdCl_2(PPh_3)_2$ (27 mg, 39 µmol), CuI (7.4 mg, 39 µmol), PPh_3 (10 mg, 39 µmol), then treated with (4-ethynylbicyclo[2.2.2]oct-1-ylethynyl)trimethylsilane (128 mg, 555 µmol), triethylamine (5.0 mL), stirred at 80 °C for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel 800×44 mm, chloroform/ethanol 100:1). Yield 219 mg

(64%) red dye, m.p. >250 °C). R_f -value (silica gel, $CHCl_3$/ethanol 100:1) = 0.25. IR (ATR): $\tilde{\nu}$ = 2921.0 (m), 2855.9 (w), 2225.9 (w), 2163 (w), 1696.8 (m), 1655.9 (s), 1592.7 (s), 1577.7 (m), 1505 (w), 1455.1 (w), 1431.5 (m), 1403.7 (m), 1338.9 (s), 1247.7 (m), 1199.4 (w), 1174.5 (w), 1124.0 (w), 1105.8 (w), 1025.2 (w), 965.2 (w), 965.2 (w), 902.3 (w), 841.6 (s), 808.6 (s), 757.9 (w), 742.8 (s), 725.1 (w), 696.1 (w), 675 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.13 (s, 9 H, $Si(CH_3)_3$), 0.83 (t, $^3J(H,H)$ = 7.0 Hz, 6 H, 2×CH_3), 1.18–1.38 (m, 16 H, 8×CH_2), 1.80–1.92 (m, 14 H, β-CH_2, 6×CH_2), 2.20–2.29 (m, 2 H, β-CH_2), 5.15–5.21 (m, 1 H, N-CH), 7.36 (d, $^3J(H,H)$ = 8.2 Hz, 1 H, $CH_{pyridine}$), 7.89 (dd, $^3J(H,H)$ = 7.9 Hz, $^4J(H,H)$ = 2.1 Hz, 1 H, $CH_{pyridine}$), 8.62–8.73 ppm (m, 9 H, 8×$CH_{perylene}$, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 0.3, 14.0, 22.6, 27.0, 29.2, 30.2, 31.6, 31.7, 31.8, 32.2, 32.4, 54.9, 83.9, 102.1, 113.6, 121.9, 123.1, 123.4, 123.6, 126.4, 126.7, 129.5, 130.0, 131.8, 134.3, 135.4, 141.1, 147.2, 152.2, 163.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 459.8 (19700), 491.0 (53800), 527.4 nm (89500). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.2 (1.00), 579.1 (0.50), 628.7 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0197, reference S-13 with Φ = 1.00): 1.00. MS (FAB^+): *m/z* (%): 878.6 (71) [M^+ + H], 696.4 (42), 373.2 (35), 307.3 (22). HRMS ($C_{57}H_{60}N_3O_4Si$): Calcd. 878.4353 [M^+ + H], found 878.4376 [M^+ + H]; Δ = +0.0023. $C_{57}H_{59}N_3O_4Si$ (877.4): Calcd. C 77.96, H 6.77, N 4.78; found C 77.62, H 6.86, N 4.73.

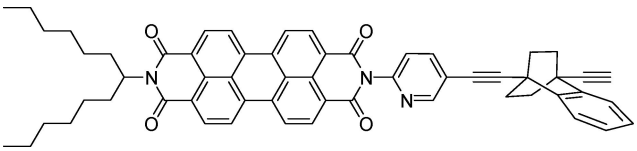


2-[5-(4-Ethynylbicyclo[2.2.2]oct-1-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*] diisoquinoline-1,3,8,10-tetraone (9): 2-(1-Hexylheptyl)-9-[5-(4-trimethylsilanylethynylbicyclo[2.2.2]oct-1-ylethynyl) pyridin-2-yl]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**8**, 206 mg, 235 µmol) was dissolved in THF (18 mL), stirred with tetrabutylammoniumfluoride (TBAF, 0.45 mL, 0.45 mmol, 1 M in THF), diluted with distilled water, extracted with chloroform (3×), dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel, chloroform/ethanol 80:1). Yield 175 mg (92%), m.p. >250 °C. R_f-value (chloroform/ethanol 80:1) = 0.40. IR (ATR): $\tilde{\nu}$ = 3305.0 (w), 2920.3 (m), 2855.4 (w), 2361.2 (w), 2339.1 (w), 2228.1 (w), 2105.8 (w), 1695.9 (m), 1653.3 (s), 1592.9 (s), 1577.4 (m), 1505.9 (w), 1474.7 (w), 1455.4 (w), 1431.1 (w), 1403.5 (m), 1339.1 (s), 1251.1 (s), 1198.0 (w), 1175.1 (m), 1124.3 (w), 1106.7 (w), 1026.6 (w), 963.6 (w), 846.0 (m), 807.6 (s), 742.0 (s), 694.4 (w), 667.6 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, $^3J(H,H)$ = 7.0 Hz, 6 H, 2×CH_3), 1.18–1.38 (m, 16 H, 8×CH_2), 1.82–1.94 (m, 14 H, β-CH_2, 6×CH_2), 2.11 (s, 1 H, CH_{alkyne}), 2.20–2.28 (m, 2 H, β-CH_2), 5.14–5.21 (m, 1 H, N-CH), 7.36 (d, 8.0 Hz, 1 H, $CH_{pyridine}$), 7.89 (dd, $^3J(H,H)$ = 8.1 Hz, $^4J(H,H)$ = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.59–8.72 ppm (m, 9 H, 8×$CH_{perylene}$, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 26.9, 29.2, 31.6, 31.7, 32.4, 54.8, 68.2, 91.0, 101.1 121.8, 123.0, 123.4, 123.5, 126.4, 126.7, 129.5, 129.9, 131.8, 134.2, 135.3, 140.9, 147.4, 152.4, 163.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 460.0 (21000), 491.0 (59000), 527.6 nm (98900). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.4 (1.00), 578.4 (0.50), 627.4 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0136, reference S-13 with Φ = 1.00): 1.00. MS (FAB^+): *m/z* (%): 806.4 (22) [M^+ + H], 624.3 (8), 391.2 (5), 373.2 (7), 345.1 (4). HRMS ($C_{54}H_{52}N_3O_4$): Calcd. 806.3958 [M^+ + H], found 806.3971 [M^+ + H]; Δ = +0.0013. $C_{54}H_{51}N_3O_4$ (805.4): Calcd. C 80.47, H 6.38, N 5.21; found C 80.30, H 6.36, N 5.16.

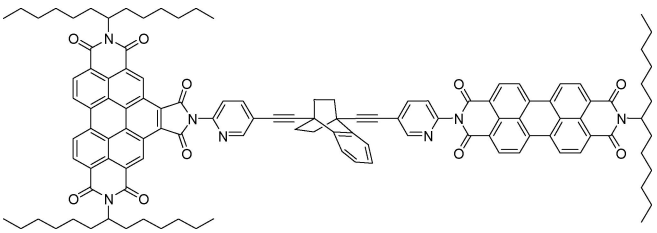


2,10-Bis(1-hexylheptyl)-6-{4'-[3,8,9,10-tetrahydro-9-(1-hexylheptyl)-1,3,8,10-tetraoxo]anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinolin-2(1*H*)-yl}-[5-(5-pyridin-2-yl-1-ethynyl-bicyclo[2.2.2]octan-4-ylethynyl)pyridin-2-yl]-1*H*-pyrrolo [3',4':4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (10): 2-[5-(4-Ethynylbicyclo [2.2.2]oct-1-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra [2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**9**, 147 mg, 183 µmol) under argon atmosphere, *N,N''*-bis(1-hexylheptyl)-*N'*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1',2':3,4:9,10-hexacarboxylic-1',2':3,4:9,10-tris (dicarboximide) (**6**, 181 mg, 172 µmol), $PdCl_2(PPh_3)_2$ (13 mg, 18 µmol), CuI (3.4 mg, 18 µmol) and PPh_3 (4.7 mg, 18 µmol), dissolved in THF (16 mL) and triethylamine (8.0 mL) were stirred at 80 °C for 16 h, evaporated in vacuo stirred in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (fine silica gel, 600×44 mm), chloroform/ethanol 70:1). Yield 178 mg (60%) orange solid, m.p. >250 °C. R_f-value (chloroform/ethanol 60:1) = 0.35. IR (ATR): $\tilde{\nu}$ = 2950.1 (w), 2923.1 (m), 2855.2 (w), 2229.1 (w), 1775.1 (w), 1718.5 (w), 1701.9 (m), 1660.3 (s), 1625.9 (w), 1593.7 (m), 1522.1 (w), 1506.0 (w), 1467.5 (w), 1455.4 (w), 1431.3 (w), 1413.4 (w), 1404.3 (w), 1364.5 (m), 1339.5 (s), 1317.5 (s), 1277.9 (w), 1247.6 (m), 1200.4 (w), 1168.0 (w), 1124.2 (w), 1105.6 (w), 1025.0 (w), 964.5 (w), 941.8 (w), 885.9 (w), 874.0 (w), 850.2 (w), 810.0 (s), 765.2 (w), 745.6 (m), 723.4 (w), 697.7 (w), 659.7 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.82-0.86 (m, 18 H, 6×CH_3), 1.20–1.48 (m, 48 H, 24×CH_2), 1.85–1.93 (m, 2 H, β-CH_2), 1.95–2.05 (m, 4 H, 2×β-CH_2), 2.03 (s, 12 H, 6×CH_2), 2.20–2.29 (m, 2 H, β-CH_2), 2.30–2.41 (m, 4 H, 2×β-CH_2), 5.15–5.21 (m, 1 H, N-CH), 5.26–5.35 (m, 2 H, 2×N-CH), 7.36 (d, $^3J(H,H)$ = 8.0 Hz, 1 H, $CH_{pyridine}$), 7.76 (d, $^3J(H,H)$ = 8.0 Hz,

1 H, $CH_{pyridine}$), 7.92 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.02 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.41–8.61 (m, 8 H, 8 × $CH_{perylene}$), 8.73 (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.76 (d, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 9.06–9.23 (m, 4 H, 4 × $CH_{perylene}$), 10.31 ppm (s, 2 H, 2 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.1, 22.6, 27.0, 27.1, 29.3, 29.7, 31.7, 31.8, 32.4, 54.9, 55.3, 101.0, 101.2, 121.2, 121.6, 121.7, 122.8, 123.0, 123.5, 123.9, 124.7, 126.1, 126.4, 126.8, 127.5, 127.8, 129.3, 129.7, 131.6, 132.9, 133.9, 134.9, 141.0, 143.9, 147.4, 152.0, 152.3, 163.1, 166.1 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 411.2 (12500), 437.2 (40600), 466.9 (77000), 491.0 (59000), 527.2 nm (93600). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 536.1 (1.00), 578.8 (0.50), 627.8 nm (0.12). ($CHCl_3$, λ_{exc} = 437 nm): λ_{max} (I_{rel}) = 535.8 (1.00), 578.8 (0.50), 627.2 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491nm\ /1\ cm}$ = 0.0130, reference: C-25 with Φ = 1.00): 1.00. ($CHCl_3$, λ_{exc} = 437 nm, $E_{437nm\ /1\ cm}$ = 0.0103, reference: C-25 with Φ = 1.00): 0.96. MS (FAB$^+$): *m/z* (%): 1730.0 (2) [M^+ + H], 1548.1 (1), 1365.6 (1), 1182.5 (1). HRMS ($C_{113}H_{114}N_7O_{10}$): Calcd. 1729.8661 [M^+ + H], found 1729.8633 [M^+ + H]; Δ = −0.0028. $C_{113}H_{113}N_7O_{10}$ (1727.9): Calcd. C 78.49, H 6.59, N 5.67; found C 78.79, H 6.55, N 5.45.

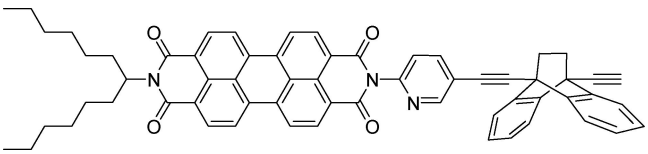


2-[5-(4-Ethynylbenzobicyclo[2.2.2]oct-1-ylethynyl) pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*] diisoquinoline-1,3,8,10-tetraone: 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-1,3,8,10-tetraone (**7**, 88 mg, 85 µmol) under argon atmosphere was dissolved in THF (5.0 mL), treated with $PdCl_2(PPh_3)_2$ (13 mg, 19 µmol), CuI (3.6 mg, 19 µmol), PPh_3 (5.0 mg, 19 µmol), then treated with 1,4-diethynylbenzobicyclo[2.2.2] octane (88 mg, 0.43 mmol), triethylamine (2.5 mL), stirred at 80 °C for 2 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel 400 × 44 mm, chloroform/ethanol 60 : 1). Yield 49 mg (68 %) red dye, m.p. > 250 °C). R_f -value (silica gel, $CHCl_3$/ethanol 60 : 1) = 0.30. IR (ATR): $\tilde{\nu}$ = 3305.0 (w), 2923.0 (m), 2854.7 (w), 1696.5 (m), 1656.2 (s), 1592.6 (s), 1577.5 (w), 1505.9 (w), 1480.5 (w), 1454.9 (w), 1431.3 (w), 1403.7 (m), 1338.4 (s), 1251.3 (m), 1198.9 (w), 1174.5 (m), 1138.5 (w), 1124.0 (w), 1174.5 (w), 1047.8 (w), 1025.6 (w), 964.6 (w), 926.9 (w), 850.4 (m), 808.7 (s), 775.3 (w), 742.9 (s) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.82 (t, ^3J(H,H) = 7.1 Hz, 6 H, 2 × CH_3), 1.18–1.37 (m, 16 H, 8 × CH_2), 1.67–1.80 (m, 4 H, 4 × CH), 1.83–1.91 (m, 2 H, β-CH_2), 2.14–2.28 (m, 6 H, 4 × CH, β-CH_2), 2.54 (s, 1 H, CH_{alkyne}), 5.15–5.21 (m, 1 H, N-CH), 7.34–7.39 (m, 2 H, 2 × $CH_{aromat.}$), 7.43 (d, ^3J(H,H) = 8.2 Hz, 1 H, $CH_{pyridine}$), 7.65–7.68 (m, 2 H, 2 × $CH_{aromat.}$), 8.05 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.61–8.72 (m, 8 H, 8 × $CH_{perylene}$), 8.85 (d, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 26.9, 29.2, 29.7, 31.7, 32.4, 33.1, 33.2, 35.0, 35.8, 54.8, 72.9, 81.4, 86.3, 96.6, 121.4, 122.5, 122.7, 123.0, 123.4, 123.6, 126.4, 126.7, 126.9, 127.0, 129.5, 130.0, 131.8, 134.2, 135.4, 139.9, 139.9, 141.1, 147.8, 147.8, 152.6, 163.3 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 459.8 (0.21), 491.2 (0.60), 527.8 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.4 (1.00), 579.3 (0.51), 626.8 nm (0.12). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0153, reference: S-13 with Φ = 1.00): 1.00. MS (FAB$^+$): *m/z* (%): 854.3 (38) [M^+], 672.2 (29), 642.2 (13), 373.1 (100), 345.2 (63). HRMS ($C_{58}H_{51}N_3O_4$): Calcd. 854.3958 [M^+], found 854.3948 [M^+]; Δ = −0.0010.

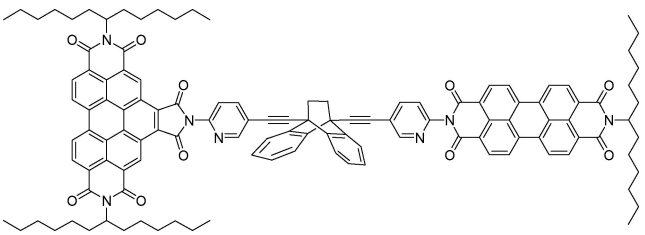


2,10-Bis(1-hexylheptyl)-6-{4′-[3,8,9,10-tetrahydro-9-(1-hexylheptyl)-1,3,8,10-tetraoxo]anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinolin-2(1*H*)-yl}-[5-(5-pyridin-2-yl-1-ethynyl-benzobicyclo[2.2.2]octan-4-ylethynyl)pyridin-2-yl]-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (12): 2-[5-(4-Ethynylbenzobicyclo[2.2.2]octan-1-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra [2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (39 mg, 46 µmol) under argon atmosphere, *N,N′*-bis(1-hexylheptyl)-*N′*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1′,2′:3,4 : 9,10-hexacarboxylic-1′,2′:3,4 : 9,10-tris (dicaroximide) (**6**, 58 mg, 55 µmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 5.0 µmol), CuI (1.0 mg, 5.0 µmol) and PPh_3 (1.3 mg, 5.0 µmol), dissolved in THF (5 mL) and triethylamine (2.5 mL) were stirred at 80 °C for 16 h, evaporated in vacuo stirred in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (fine silica gel, 400 × 44 mm), chloroform/ethanol 65 : 1). Yield 32 mg (39 %) orange solid, m.p. > 250 °C. R_f-value (chloroform/ethanol 60 : 1) = 0.40. IR (ATR): $\tilde{\nu}$ = 2924.0 (m), 2853.7 (w), 1776.2 (w), 1701.1 (m), 1659.0 (s), 1626.1 (w), 1593.4 (m), 1521.2 (w), 1466.9 (w), 1431.8 (w), 1404.3 (w), 1364.0 (m), 1338.0 (s), 1316.9 (s), 1246.6 (m), 1199.2 (w), 1167.5 (w), 1123.2 (w), 1105.1 (w), 1024.2 (w), 964.6 (w), 940.2 (w), 850.7 (w), 809.9 (s), 775.5 (w), 764.9 (w), 746.3 (m), 724.1 (w), 697.6 (w), 659.5 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.80-0.88 (m, 18 H, 6 × CH_3), 1.19–1.49 (m, 48 H, 24 × CH_2), 1.76–1.93 (m, 6 H, 4 × CH, β-CH_2), 1.95–2.02 (m, 4 H, 2 × β-CH_2), 2.22–2.41 (m, 10 H, 4 × CH, 3 × β-CH_2), 5.15–5.21 (m, 1 H, N-CH), 5.27–5.36 (m, 2 H, 2 × N-CH), 7.40 (d, ^3J(H,H) = 8.1 Hz, 1 H, $CH_{pyridine}$), 7.41–7.46 (m, 2 H, 2 × $CH_{aromat.}$), 7.72–7.77 (m, 2 H, 2 × $CH_{aromat.}$), 7.79 (d, ^3J(H,H) = 8.1 Hz, 1 H, $CH_{pyridine}$), 8.07

(dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.17 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.38–8.66 (m, 8 H, 8 × $CH_{perylene}$), 8.88 (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 8.92 (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 9.07–9.28 (m, 4 H, 4 × $CH_{perylene}$), 10.37 ppm (s, 2 H, 2 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 22.7, 27.0, 27.1, 29.2, 29.7, 31.8, 32.4, 33.1, 33.2, 35.8, 54.8, 55.3, 81.5, 96.4, 96.6, 122.8, 123.0, 123.2, 123.7, 124.0, 126.9, 127.2, 131.7, 135.0, 140.0, 141.2, 152.2, 152.6, 163.1, 166.2 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 380.0 (35400), 437.0 (35500), 466.6 (69100), 491.0 (49300), 527.8 nm (86400). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.5 (1.00), 578.4 (0.51), 627.5 nm (0.12). ($CHCl_3$, λ_{exc} = 437 nm): λ_{max} (I_{rel}) = 535.2 (1.00), 578.4 (0.50), 627.8 nm (0.11). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491nm\ /1\ cm}$ = 0.0141, reference: C-25 with Φ = 1.00): 1.00. ($CHCl_3$, λ_{exc} = 437 nm, $E_{437nm\ /1\ cm}$ = 0.0113, reference: C-25 with Φ = 1.00): 0.93. MS (FAB$^+$): *m/z* (%): 1777.7 (1) [M^+ + H], 1594.5 (0.7), 1412.3 (0.4), 1231.3 (0.5). HRMS ($C_{117}H_{113}N_7O_{10}$): Calcd. 1776.8627 [M^+], found 1776.8607 [M^+]; Δ = −0.0020. $C_{117}H_{113}N_7O_{10}$ (1777.2): Calcd. C 79.07, H 6.41, N 5.52; found C 78.76, H 6.56, N 5.33.

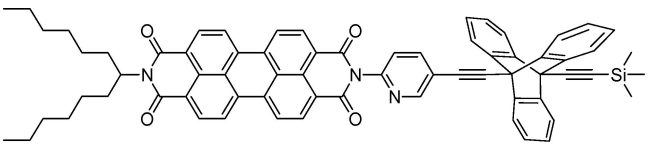


2-[5-(8-Ethynyldibenzobicyclo[2.2.2]oct-1-ylethynyl) pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*] diisoquinoline-1,3,8,10-tetraone: 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (**7**, 0.152 g, 0.197 mmol) under argon atmosphere was dissolved in THF (10.0 mL), treated with $PdCl_2(PPh_3)_2$ (0.028 g, 0.039 mmol), CuI (3.2 mg, 17 µmol), PPh_3 (0.010 g, 0.039 mmol), then treated with bis(ethynyl)-9,10-ethanoanthracene (0.250 g, 0.983 mmol), triethylamine (5.0 mL), stirred at 80 °C for 90 min, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$ evaporated in vacuo and purified by column separation (silica gel 500 × 44 mm, chloroform/ethanol 30 : 1). Yield 115 mg (65 %) bright orange dye, m.p. > 250 °C). R_f -value (silica gel, $CHCl_3$/ethanol 50 : 1) = 0.16. IR (ATR): $\tilde{\nu}$ = IR (ATR): $\tilde{\nu}$ = 3306.9 (w), 3063.8 (w), 2951.8 (w), 2924.5 (m), 2852.4 (w), 1693.3 (m), 1656.2 (s), 1592.9 (m), 1578.2 (m), 1506.5 (w), 1470.0 (w), 1455.4 (m), 1431.5 (m), 1405.2 (m), 1372.4 (m), 1341.7 (s), 1285.0 (w), 1253.4 (m), 1203.5 (m), 1175.3 (m), 1140.7 (w), 1123.8 (w), 1107.0 (w), 1032.7 (w), 1021.2 (w), 965.5 (m), 935.1 (w), 886.8 (w), 873.9 (w), 856.8 (m), 810.9 (s), 801.4 (m), 779.8 (w), 767.4 (m), 758.2 (m), 747.7 (m), 726.7 (m), 696.1 (w), 677.1 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.82 (t, ^3J(H,H) = 7.0 Hz, 6 H, 2 × CH_3), 1.12–1.34 (m, 16 H, 8 × CH_2), 1.76–1.86 (m, 2 H, β-CH_2), 1.98–2.10 (m, 4 H, 2 × CH_2), 2.12–2.24 (m, 2 H, β-CH_2), 2.92 (s, 1 H, 1 × CH_{alkyne}), 5.09–5.16 (m, 1 H, N-CH), 7.19–7.24 (m, 4 H, 4 × $CH_{aromat.}$), 7.47 (d, ^3J(H,H) = 8.0 Hz, 1 H, $CH_{pyridine}$), 7.66–7.72 (m, 4 H, 4 × $CH_{aromat.}$), 8.18 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.56–8.70 (m, 8 H, 8 × $CH_{perylene}$), 8.96 ppm (d, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 26.9, 29.2, 29.7, 31.7, 32.4, 35.0, 35.0, 43.7, 44.4, 54.8, 76.8, 81.9, 92.4, 122.1, 122.3, 123.0, 123.4, 126.3, 126.5, 126.6, 126.7, 129.5, 130.0, 131.1, 131.8, 134.1, 135.3, 140.6, 163.3 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 460.0 (15800), 491.0 (44000), 527.8 nm (73300). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 536.1 (1.00), 579.1 nm (0.48). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{490\ nm/1\ cm}$ = 0.0262, reference: S-13 with Φ = 1.00): 1.00. MS (FAB$^+$): *m/z* (%): 902.5 (6) [M^+ + H], 874 (2), 692 (2). HRMS ($C_{62}H_{52}O_4N_3$): Calcd. 902.3958 [M^+ + H], found 902.3963 [M^+ + H]; Δ = −0.0005. $C_{62}H_{51}O_4N_3$ (902.1): Calcd. C 82.55, H 5.70, N 4.66; found C 82.32, H 5.73, N 4.57.

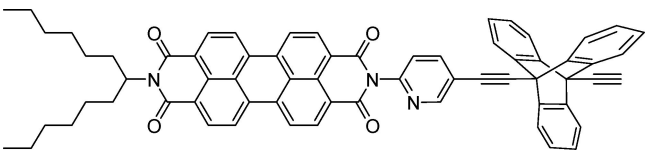


2,10-Bis(1-hexylheptyl)-6-{4′-[3,8,9,10-tetrahydro-9-(1-hexylheptyl)-1,3,8,10-tetraoxo]anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinolin-2(1*H*)-yl}-[5-(5-pyridin-2-yl-1-ethynyl-dibenzobicyclo[2.2.2]octan-4-ylethynyl)pyridin-2-yl]-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*] diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (13): 2-[5-(8-Ethynyldibenzobicyclo[2.2.2]oct-1-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra-[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (0.094 g, 0.10 mmol) under argon atmosphere, *N,N‴*-bis(1-hexylheptyl)-*N′*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1′,2′:3,4 : 9,10-hexacarboxylic-1′,2′:3,4 : 9,10-tris(dicarboximide) (**6**, 0.121 g, 0.115 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.01 mmol), CuI (0.002 g, 0.01 mmol) and PPh_3 (0.003 g, 0.01 mmol), dissolved in THF (15 mL) and triethylamine (7.5 mL) were stirred at 80 °C for 16 h, evaporated in vacuo stirred with chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel, 500 × 44 mm), chloroform/ethanol 50 : 1). Yield 48 mg (25 %) orange solid, m.p. > 250 °C. R_f-value (chloroform/ethanol 40 : 1) = 0.18. IR (ATR): $\tilde{\nu}$ = 2923.8 (w), 2853.0 (w), 1776.8 (w), 1701.9 (m), 1660.2 (s), 1593.5 (m), 1578.3 (w), 1456.4 (w), 1404.1 (w), 1364.2 (m), 1339.5 (s), 1317.6 (s), 1247.5 (m), 1167.2 (w), 1123.3 (w), 1105.2 (w), 1023.3 (w), 964.2 (w), 850.7 (w), 809.9 (s), 779.5 (w), 764.6 (m), 746.5 (m), 725.1 (w), 659.4 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.77-0.90 (m, 18 H, 6 × CH_3), 1.16–1.51 (m, 48 H, 24 × CH_2), 1.87–1.95 (m, 2 H, β-CH_2), 1.97–2.07 (m, 6 H, 2 x β-CH_2, 2 × CH), 2.12–2.18 (m, 2 H, 2 × CH), 2.22–2.29 (m, 2 H, β-CH_2), 2.32–2.42 (m, 4 H, 2 × β-CH_2), 5.15–5.22 (m, 1 H, N-CH), 5.27–5.38 (m, 2 H, 2 × N-CH), 7.28–7.36 (m, 4 H, 4 × $CH_{aromat.}$), 7.49 (d, ^3J(H,H) = 7.8 Hz, 1 H, $CH_{pyridine}$), 7.77–7.86 (m, 4 H, 4 ×

$CH_{aromat.}$), 7.90 (d, ^3J(H,H) = 7.9 Hz, 1 H, $CH_{pyridine}$), 8.24 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.35 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.37–8.71 (m, 8 H, 8 × $CH_{perylene}$), 9.05 (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 9.08–9.32 (m, 5 H, 4 × $CH_{perylene}$, $CH_{pyridine}$), 10.35 ppm (s, 2 H, 2 × $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.6, 27.0, 27.1, 29.2, 29.3, 29.7, 31.8, 32.4, 34.9, 35.2, 44.4, 44.5, 54.9, 55.3, 85.5, 92.2, 92.4, 121.0, 121.8, 122.3, 122.4, 122.8, 123.0, 123.1, 123.9, 124.8, 126.0, 126.3, 126.7, 126.8, 127.5, 127.9, 129.2, 129.8, 130.8, 131.6, 133.0, 133.8, 134.9, 140.6, 141.4, 141.4, 144.7, 148.3, 152.3, 152.7, 163.1, 166.1 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 380.0 (47400), 411.2 (17500), 437.2 (42600), 466.6 (73100), 491.0 (55900), 527.8 nm (91100). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.2 (1.00), 578.5 (0.41), 628.0 nm (0.10). ($CHCl_3$, λ_{exc} = 437 nm): λ_{max} (I_{rel}) = 536.0 (1.00), 578.4 nm (0.50). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0094, reference: C-25 with Φ = 1.00): 1.00. ($CHCl_3$, λ_{exc} = 437 nm, $E_{43\ nm/1\ cm}$ = 0.0071, reference: C-25 with Φ = 1.00): 0.94. MS (FAB$^+$): *m/z* (%): 1825.6 (5) [M^+ + H], 1797.7 (5), 1615.4 (3), 1432.3 (3), 1250.2 (3), 1222.2 (2), 1031.2 (1), 810.2 (2), 741.2 (1), 668.2 (2), 596.2 (2), 561.2 (2), 484.2 (2), 413.2 (5), 391.2 (6), 373.2 (16), 345.2 (12), 275.2 (6), 55 (15), 41 (16). $C_{121}H_{113}N_7O_{10}$ (1825.2): Calcd. C 79.62, H 6.24, N 5.37; found C 79.41, H 6.29, N 5.27.

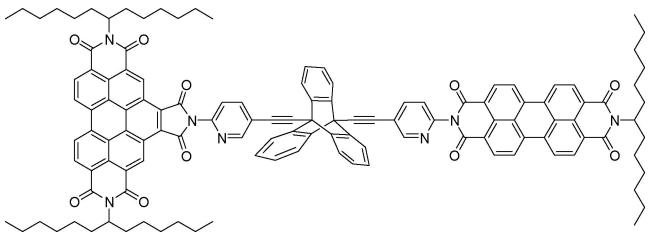


2-(1-Hexylheptyl)-9-{5-[10-(trimethylsilylethynyl) triptycen-9-ylethynyl]pyridin-2-yl}anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone: 2-(1-Hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*] diisoquinoline-1,3,8,10-tetraone (**7**, 178 mg, 230 µmol) under argon atmosphere was dissolved in THF (5.0 mL), treated with $PdCl_2(PPh_3)_2$ (18 mg, 25 µmol), CuI (4.8 mg, 25 µmol), PPh_3 (6.6 mg, 25 µmol), then treated with [(10-ethynyltriptycen-9-yl)ethynyl]trimethylsilane (46 mg, 0.21 mmol), triethylamine (2.5 mL), stirred at 80 °C for 16 h, evaporated in vacuo, dispersed in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel 800 × 44 mm, chloroform/ethanol 80 : 1). Yield 92 mg (39 %) bright orange dye, m.p. > 250 °C). R_f -value (silica gel, $CHCl_3$/ethanol 80 : 1) = 0.15. IR (ATR): $\tilde{\nu}$ = IR (ATR): $\tilde{\nu}$ = 3063.4 (w), 2952.3 (w), 2926.8 (w), 2857.5 (w), 2361.9 (w), 2334.2 (w), 2178.8 (w), 1710.8 (m), 1697.3 (s), 1657.5 (s), 1593.8 (m), 1578.3 (m), 1505.8 (w), 1452.8 (m), 1431.9 (m), 1404.6 (m), 1340.9 (s), 1250.6 (s), 1201.1 (m), 1174.2 (m), 1124.6 (m), 1106.6 (w), 1072.2 (w), 1030.4 (w), 966.7 (m), 851.6 (s), 810.1 (s), 783.9 cm^{-1} (w). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.48 (s, 9 H, 3 × CH_3), 0.83 (t, ^3J(H,H) = 6.9 Hz, 6 H, 2 × CH_3), 1.19–1.42 (m, 16 H, 8 × CH_2), 1.82–1.94 (m, 2 H, β-CH_2), 2.20–2.33 (m, 2 H, β-CH_2), 5.14–5.25 (m, 1 H, N-CH), 7.12–7.18 (m, 6 H, 6 × $CH_{aromat.}$), 7.58 (d, ^3J(H,H) = 8.1 Hz, 1 H, $CH_{pyridine}$), 7.73–7.84 (m, 6 H, 6 × $CH_{aromat.}$), 8.37 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.4 Hz, 1 H, $CH_{pyridine}$), 8.64–8.80 (m, 8 H, 8 × $CH_{perylene}$), 9.18 ppm (d, ^4J(H,H) = 2.4 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 0.3, 14.0, 22.6, 26.9, 29.2, 31.8, 32.4, 52.8, 53.1, 54.9, 88.5, 89.0, 98.3, 99.4, 120.7, 122.1, 122.4, 122.5, 123.0, 123.1, 123.5, 124.0, 125.8, 125.9, 126.2, 126.5, 126.8, 129.5, 130.1, 131.9, 134.2, 135.5, 141.6, 143.1, 143.3, 148.7, 152.9, 163.4 ppm. UV/VIS ($CHCl_3$): λ_{exc} (E_{rel}) = 460.0 (0.23), 491.4 (0.60), 528.0 nm (1.00). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 536.4 (1.00), 578.4 (0.40), 624.6 nm (0.07). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm/1\ cm}$ = 0.0146, reference: S-13 with Φ = 1.00): 1.00. MS (FAB$^+$): *m/z* (%): 1023.1 (9) [M^+ + H], 1022.1 (3) [M^+], 951.1 (2), 840.9 (4), 768.8 (1). HRMS ($C_{69}H_{59}N_3O_4Si$): Calcd. 1022.4348 [M^+ + H], found 1022.4353 [M^+ + H]; Δ = + 0.0005.



2-[5-(10-Ethynyl-9,10-triptycen-9-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*] diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone: 2-(1-Hexylheptyl)-9-{5-[10-(trimethylsilylethynyl)triptycen-9-ylethynyl]pyridin-2-yl}anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (80 mg, 78 µmol) was dissolved in THF (6 mL), stirred with tetrabutylammoniumfluoride (TBAF, 0.15 mmol, 0.15 mL, 1 M in THF), diluted with distilled water, extracted with chloroform (3 ×), dried with $MgSO_4$, evaporated in vacuo and purified by column separation (silica gel, chloroform/ethanol 80 : 1). Yield 59 mg (80 %) bright red solid, m.p. > 250 °C. R_f -value ($CHCl_3$/EtOH 80 : 1) = 0.30. IR (ATR): $\tilde{\nu}$ = 3297.6 (w), 3063.4 (w), 2923.7 (m), 2855.3 (w), 1696.9 (s), 1657.1 (s), 1593.2 (s), 1578.5 (s), 1453.2 (m), 1431.0 (m), 1405.2 (m), 1369.6 (w), 1339.9 (s), 1250.7 (s), 1197.1 (m), 1173.2 (m), 1124.6 (w), 1105.9 (w), 1031.1 (w), 964.7 (w), 852.5 (m), 809.9 (m), 800.6 (m), 781.9 (w), 745.9 cm^{-1} (s). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, ^3J(H,H) = 6.9 Hz, 6 H, 2 × CH_3), 1.15–1.40 (m, 16 H, 8 × CH_2), 1.81–1.95 (m, 2 H, β-CH_2), 2.17–2.35 (m, 2 H, 2 H, β-CH_2), 3.33 (s, 1 H, CH_{alkyne}) 5.11–5.27 (m, 1 H, N-CH), 7.11–7.19 (m, 6 H, 6 × $CH_{aromat.}$), 7.60 (d, ^3J(H,H) = 8.0 Hz, 1 H, $CH_{pyridine}$), 7.77–7.84 (m, 6 H, 6 × $CH_{aromat.}$), 8.38 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.64–8.80 (m, 8 H, 8 × $CH_{perylene}$), 9.18 ppm (d, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 26.9, 29.2, 31.7, 32.4, 52.3, 52.9, 64.8, 77.9, 81.0, 88.3, 89.0, 120.7, 122.2, 122.4, 123.0, 123.1, 124.0, 125.9, 126.0, 126.8, 129.5, 130.1, 131.9, 134.3, 135.5, 141.6, 143.0, 148.8, 152.9, 163.4 ppm. UV/VIS ($CHCl_3$): λ_{max} (ε) = 460.4 (18500), 491.0 (47200), 527.8 nm (80300). Fluorescence ($CHCl_3$, λ_{exc} = 491 nm): λ_{max} (I_{rel}) = 535.5 (1.00), 578.5 (0.50), 628.3 nm (0.12). Fluorescence

quantum yield ($CHCl_3$, $\lambda_{exc}=491$ nm, $E_{491\ nm/1\ cm}=0.0157$, reference: S-13 with $\Phi=1.00$): 1.00. MS (FAB^+): *m/z* (%): 951.0 (7) [$M^+ + H$], 874.0 (1), 768.7 (2), 692 (1), 3910 (1), 373.3 (4), 345 (2). HRMS ($C_{66}H_{51}N_3O_4$): Calcd. 950.3952 [$M^+ + H$], found 950.3958 [$M^+ + H$]; $\Delta = +0.0006$. $C_{66}H_{51}N_3O_4$ (949.4): Calcd. C 83.43, H 5.41, N 4.42; found C 83.28, H 5.46, N 4.25.



2,10-Bis(1-hexylheptyl)-6-{4'-[3,8,9,10-tetrahydro-9-(1-hexylheptyl)-1,3,8,10-tetraoxo]anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinolin-2(1*H*)-yl}-[5-(5-pyridin-2-yl-9-ethynyl-triptycen-10-ylethynyl)pyridin-2-yl]-1*H*-pyrrolo[3',4':4,5]pyreno[2,1,10-*def*:7,8,9-*d'e'f'*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (14): 2-[5-(10-Ethynyl-9,10-triptycen-9-ylethynyl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d'e'f'*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (49 mg, 52 µmol) under argon atmosphere, *N,N''*-bis(1-hexylheptyl)-*N'*-(5-iodopyridin-2-yl)benzo[*ghi*]perylene-1',2':3,4:9,10-hexacarboxylic-1',2':3,4:9,10-tris(dicarboximide) (**6**, 40 mg, 38 µmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 10 µmol), CuI (1.9 mg, 10 µmol) and PPh_3 (2.6 mg, 10 µmol), dissolved in THF (2.5 mL) and triethylamine (1.25 mL) were stirred at 80 °C for 15 h, evaporated in vacuo stirred in chloroform, washed with 2 M aqueous HCl and distilled water, dried with $MgSO_4$, evaporated in vacuo and purified by column separation (fine silica gel, 300×44 mm, chloroform). Yield 46 mg (40%) bright red solid, m.p. >250 °C. R_f-value (chloroform/ethanol 80:1) = 0.30. IR (ATR): $\tilde{\nu}=3063.4$ (w), 2952.3 (w), 2932.9 (m), 2854.2 (m), 1777.9 (w), 1722.2 (m), 1704.1 (s), 1659.2 (s), 1628.9 (m), 1593.6 (s), 1551.1 (w), 1529.8 (w), 1512.3 (w), 1500.4 (w), 1479.6 (m), 1468.0 (m), 1452.2 (m), 1431.0 (m), 1404.2 (m), 1363.6 (m), 1338.6 (s), 1316.5 (s), 1276.4 (m), 1247.8 (s), 1197.1 (m), 1167.4 (m), 1123.7 (m), 1103.9 (m), 1032.5 (w), 1020.7 (w), 964.3 (w), 887.8 (w), 849.8 (w), 809.6 (s), 782.8 (w), 746.0 (s), 699.0 (w), 659.7 cm^{-1} (w). ^1H NMR (600 MHz, $CDCl_3$, 25 °C): $\delta=$ 0.76-0.92 (m, 18 H, 6×CH_3), 1.18–1.51 (m, 48 H, 24×CH_2), 1.84–1.94 (m, 2 H, β-CH_2), 1.94–2.06 (m, 4 H, 2×β-CH_2), 2.21–2.31 (m, 2 H, β-CH_2), 2.33–2.46 (m, 4 H, 2×β-CH_2), 5.14–5.24 (m, 1 H, N-CH), 5.30–5.38 (m, 2 H, 2×N-CH), 7.18–7.24 (m, 6 H, 6×$CH_{aromat.}$), 7.63 (d, ^3J(H,H) = 7.8 Hz, 1 H, $CH_{pyridine}$), 7.83–7.93 (m, 6 H, 6×$CH_{aromat.}$), 8.00 (d, ^3J(H,H) = 7.9 Hz, 1 H, $CH_{pyridine}$), 8.41 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.51 (dd, ^3J(H,H) = 7.9 Hz, ^4J(H,H) = 2.3 Hz, 1 H, $CH_{pyridine}$), 8.56- 8.74 (m, 8 H, 8×$CH_{perylene}$), 9.14–9.34 (m, 4 H, 4×$CH_{perylene}$), 9.22 (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 9.25 (d, ^4J(H,H) = 2.2 Hz, 1 H, $CH_{pyridine}$), 10.43 ppm (s, 2 H, 2×$CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): $\delta=$ 14.1, 22.6, 27.0, 27.1, 29.3, 29.7, 31.8, 32.4, 53.0, 54.9, 55.4, 89.2, 90.96, 96.45 122.0, 122.4, 123.0, 123.2, 123.4, 124.0, 124.9, 126.1, 126.9, 130.0, 131.8, 135.3, 141.6, 143.1, 152.6, 153.0, 163.3, 166.2 ppm. UV/VIS ($CHCl_3$): λ_{exc} (ε) = 380.6 (38800), 411.2 (13000), 437.2 (40600), 466.9 (77000), 491.0 (59000), 527.2 nm (93600). Fluorescence ($CHCl_3$, $\lambda_{exc}=491$ nm): λ_{max} (I_{rel}) = 536.1 (1.00), 578.8 (0.50), 627.8 nm (0.12). ($CHCl_3$, $\lambda_{exc}=$ 437 nm): λ_{max} (I_{rel}) = 537.1 (1.00), 578.4 (0.50), 627.4 nm (0.11). Fluorescence quantum yield ($CHCl_3$, $\lambda_{exc}=491$ nm, $E_{491\ nm/1\ cm}=0.0133$, reference: C-25 with $\Phi=1.00$): 1.00. ($CHCl_3$, $\lambda_{exc}=437$ nm, $E_{437\ nm/1\ cm}=0.0105$, reference: C-25 with $\Phi=1.00$): 0.96. MS (FAB^+): *m/z* (%): 1874.5 (1.0) [M^+], 1693.2 (0.5), 1692.3 (0.4), 1510.6 (0.3), 1509.8 (0.3), 1328.5 (0.5), 1327.3 (0.5), 1251.3 (0.2), 1072.2 (0.3), 1027.2 (0.3), 373.4 (75). $C_{125}H_{113}N_7O_{10}$ (1871.9): Calcd. C 80.15, H 6.08, N 5.23; found C 79.90, H 6.08, N 5.02.

Acknowledgements

We thank the Fonds der Chemischen Industrie and the CIPSM cluster for protein research for financial support. Open access funding enabled and organized by Projekt DEAL.

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Manuscript received: March 17, 2021
Revised manuscript received: June 19, 2021
Version of record online: ■■, ■■

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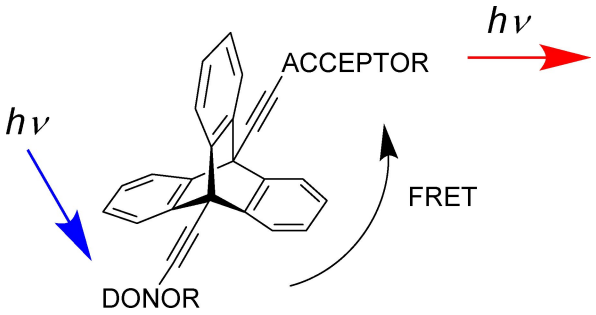

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