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Axially Extended Perylene Dyes

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Dedicated to Prof. Rolf Huisgen on the occasion of his 90th birthday

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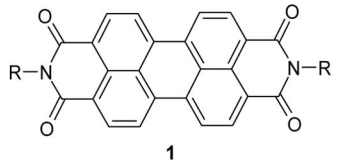
Perylenecarboxylic anhydride imides were condensed with semicarbazide and thiosemicarbazide to form perylene dyes extended by triazoline rings and bathochromically shifted UV/Vis absorption and fluorescence. The thiocarbonyl derivative reacts with diazo compounds to cause a further extension with spiro-arranged thiirane rings. Applications in analytics are discussed.

Introduction

Perylene dyes[1] are of special interest because of their remarkable properties such as unusually high lightfastness and strong fluorescence and are increasingly interesting for light conversion and collection, such as organic photovoltaic cells,[2] photoelectrochemical cells (DSSC)[3] and artificial photosynthesis.[4]

Many attempts[5] were made for the adoption of their absorption to various spectral regions. This turned out to be difficult with the variation of R, because there are orbital nodes[6] in the HOMO and LUMO of **1** at the nitrogen atoms. An exchange of a carbonyl group in **1** by the related imino group[7] caused a bathochromic shift of the absorption. We intended to extend this group to heterocyclic structures with the application of nucleophiles with the α-effect.[8]



1

1	R
a	$CH(C_6H_{13})_2$

Results and Discussion

The anhydride[9] **2** [with the solubility increased by the long-chain secondary 1-hexylheptyl group (swallow-tail substituent)] was condensed with semicarbazide to afford the axially extended compound **3** in 35% yield after 2 h reaction time. The structure of **3** was confirmed by the facts that hydrazine derivatives leave the carbonyl groups of **2** unaffected and form carboxylic imides[1] and that a condensation of urea with **2** was not successful. Thus, it was concluded that an initiation with the carboxylic imide forming step and a subsequent ring closure with the carbonyl group had occurred. Moreover, standard carbonyl absorption was found for **3** in the IR spectrum, whereas the parallel carbonyl groups in the isomer should induce a band splitting by coupling. Thiosemicarbazide proved to be more reactive in this condensation so that a quantitative conversion of **2** proceeded already in 30 min to form the thiocarbonyl analogue **5**; however, purification caused losses so that yields of pure materials are similar for **3** and **5**.

Analogous reactions were tried with carbohydrazide where the targeted dark violet compound **4a** (X = O) was formed in a fast reaction and could spectroscopically be identified; however, the stability was so low that it could not be obtained as a pure material. The dark violet thiocarbonyl analogue **4b** was also formed in a fast reaction of thiocarbohydrazide with **2**; however, its chemical stability was even lower than that of **4a** (Scheme 1).

The thiocarbonyl compound **5** is of special interest for fluorescent labelling because of two anchor groups with orthogonal reactivity: The triazoline ring is suitable for nucleophilic displacement reactions as was shown by the alkylation with 1-bromohexane to form **6**, and the thiocarbonyl group allows 1,3-dipolar cycloadditions.[10] We studied the 1,3-dipolar cycloaddition[11] of **4** with diazoacetic ester where a competition between the Schönberg reaction[12] to a dithiolane and the cyclization of the intermediate 1,3-dipole to a thiirane[13] is expected according to Scheme 2. The Schönberg reaction would be an efficient pathway for the preparation of a bichromophoric dye (dyad) with fixed geometry. Only the thiirane **7a** could be detected as the reaction product in 30% yield and no trace of a dithiolane. The thiirane **7a** is of interest for labelling because of the introduction of the electrophilic carboxylic ester. The reaction

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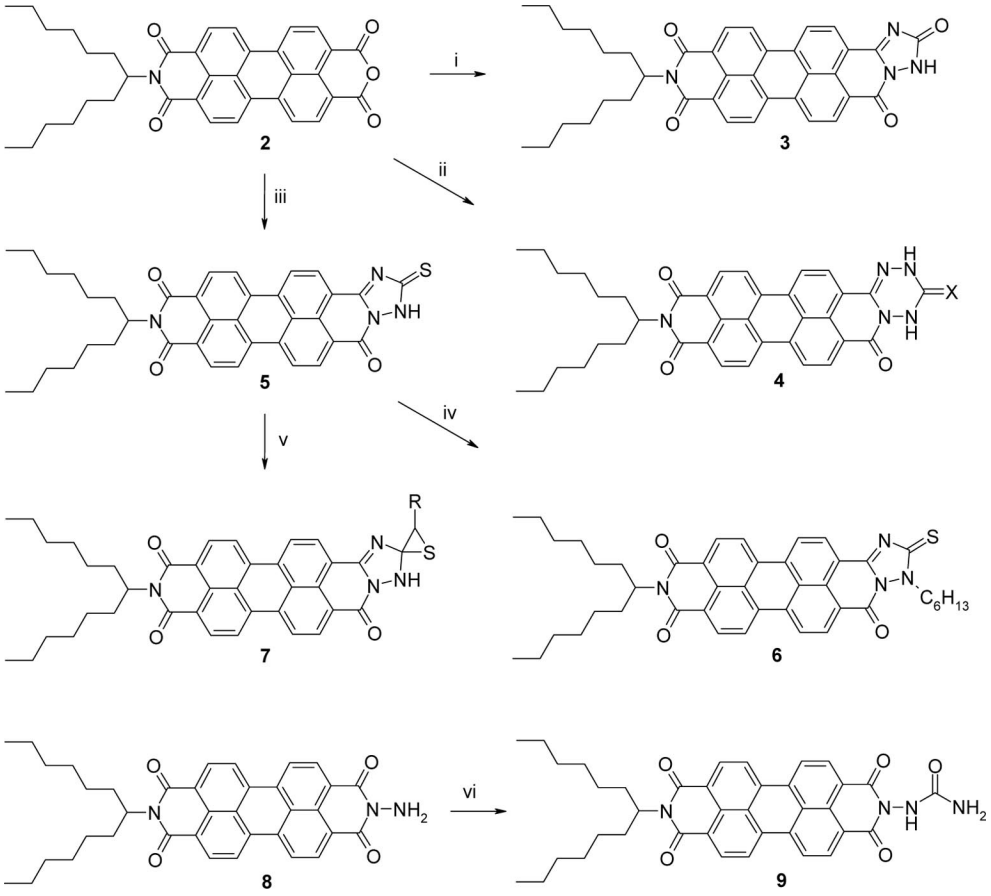
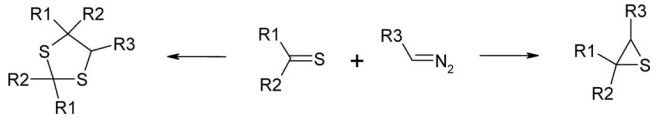


Scheme 1. Synthesis of axially extended perylene dyes. (i) $NH_2CONHNH_2$; (ii) $OC(NHNH_2)_2$ for **4a** (X = O) and $SC(NHNH_2)_2$ for **4b** (X = S); (iii) $NH_2CSNHNH_2$; (iv) *n*-$C_6H_{13}Br$; (v) $N_2CHCO_2C_2H_5$ for **7a** ($R = CO_2C_2H_5$) and $N_2CHSi(CH_3)_3$ for **7b** [$R = Si(CH_3)_3$]; (vi) KOCN.

of **5** with trimethylsilyl-substituted diazomethane was even more efficient[14] so that **7b** could be isolated in 60% yield, and no dithiolane could be detected as a by-product in analogy to the synthesis of **7a**. The trimethylsilyl group in **7b** is useful for transition-metal-mediated C–C coupling.



Scheme 2. Competition between the Schönberg reaction (left) and the 1,3-dipolar cyclization (right).

The axial extension of the chromophore from **1** to **3** causes a bathochromic shift in the UV/Vis absorption and fluorescence to form bluish solutions with an intense red fluorescence (see Figure 1 and Table 1, and compare with compound **9** where the ring is not closed). The vibronic structure of **1** is still preserved in **3**, and the fluorescent quantum yield remains higher than 90%. A variation of the carbonyl group in **3** influences the UV/Vis spectra only slightly, and the absorption and fluorescence spectra of **3** and **5** are identical and differ only slightly from the very similar spectra of **6** and **7**.

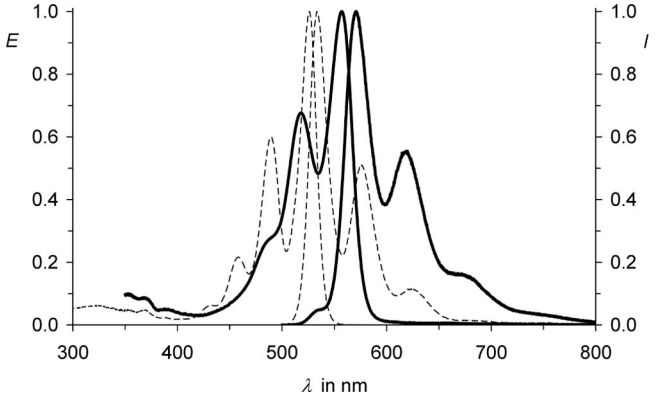


Figure 1. UV/Vis absorption (left) and fluorescence spectra (right) of **3** (thick lines) compared to **1a** (thin dashed lines).

The most bathochromic electronic transition is dominated by the orbitals HOMO and LUMO (see Figure 2). The reported central, axially oriented nodal plane[6] in **1** is essentially preserved in **3** and extends into the triazolinone ring with small atomic coefficients at the carbonyl carbon atom in both frontier orbitals and at the oxygen atom in the LUMO. This may be responsible for the insignificant influence on the UV/Vis spectra by means of alterations at

Table 1. UV/Vis absorption and fluorescence spectra in chloroform.

Compound	Absorption λ_{max} [nm]	ε[a] [L mol cm^{-1}]	Fluorescence λ_{max} [nm]	Φ[b]
1a	525	85700	534	ca. 1.0
3	557	n.d.	571	0.95
5	557	67000	572	0.93
6	554	59000	571	0.65
7a	554	n.d.	571	0.80
7b	553	n.d.	572	0.90
9	525	74000	536	ca. 1.0

[a] Molar absorptivity. [b] Fluorescence quantum yield.

this position. Even the formation of the thiirane ring in **7a** and **7b** leaves the fluorescence quantum yields essentially unaffected.

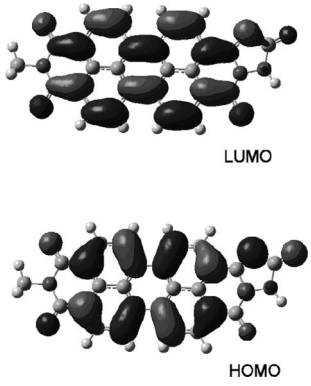


Figure 2. Calculated orbitals of the π-system of **3** (DFT B3-LYP). Top: LUMO; bottom: HOMO.

An alkylation of the nitrogen atom of **5** to form **6** remarkably decreases the fluorescence quantum yield to 65%. Quantum chemical calculation of the *N*-methyl analogues indicate a complete extension of the central nodal plane in **6** to the sulfur atom for π-HOMO-2 in contrast to **5** and in contrast to the HOMO of the analogous oxygen atom in **3** where relevant atomic coefficients were found (compare Figures 3 and 2). Two *n* orbitals of the sulfur atom in **5** are higher in energy than the highest occupied π-orbital (LUMO, *n*-HOMO, *n*-HOMO-1, π-HOMO-2: –0.145, –0.210, –0.213, –0.238 a.u.) so that an intramolecular SET process in the excited state according to Figure 4 may cause fluorescence quenching due to competition with spontaneous emission. However, this seems to be less important for **5** than for **6** where the relative energy of the *n*-orbitals at the sulfur atom is further slightly increased (LUMO, *n*-HOMO, *n*-HOMO-1, π-HOMO-2: –0.143, –0.207, –0.209, –0.235 a.u.). This seems to allow a competition between spontaneous fluorescence and an intramolecular electron transfer (SET) with filling the optically induced vacancy in the π-HOMO-2 of the excited state of **6** (see Figures 3 and 4, and compare with Figure 2). As a consequence, fluorescence will be partially quenched because of inhibition of the electronic π–π transition in the excited state (compare ref.[15]). The found diminished fluorescence quantum yield from 93% of **5** to 65% of **6** indicates this competition between spontaneous emission and SET process.

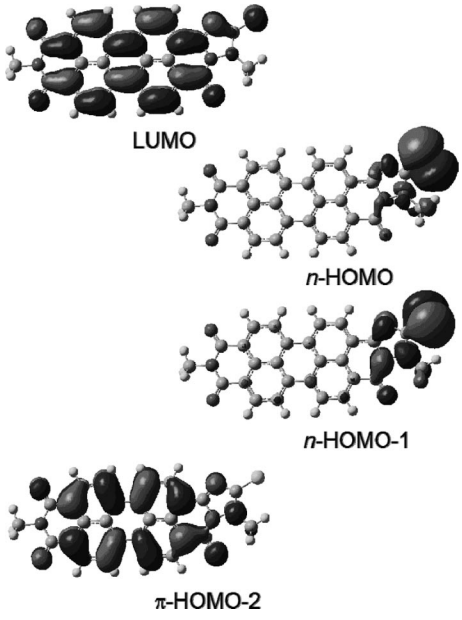


Figure 3. Calculated orbitals of the π-system of the *N*-methyl analogue of **6** (DFT B3-LYP). From top to bottom: LUMO, HOMO, HOMO-1 and HOMO-2.

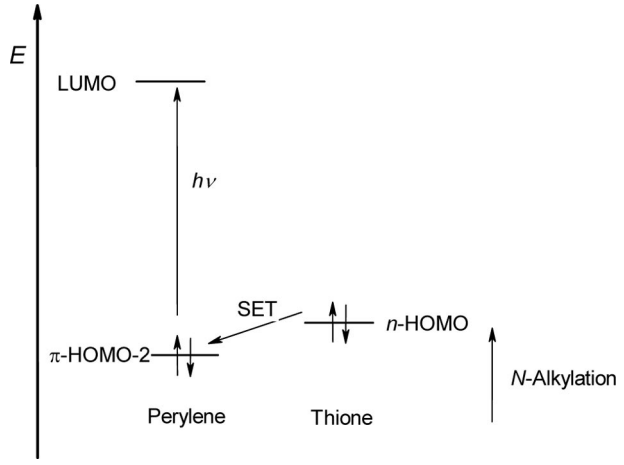


Figure 4. Optical excitation (*hν*) of the π-system of **6** and subsequent electron transfer (SET) from the lone pairs of the sulfur atom.

Conclusions

The extension of the chromophore of perylene dyes with the triazolinone ring caused an appreciable bathochromic shift in the UV/Vis absorption and fluorescence compared with **1**. The analogous extension to the six-membered heterocyclic rings were also successful, but resulted in less stable materials. The high fluorescence quantum yields of perylenes were preserved in the triazoline derivatives **3** and **5**–**7** so that intensely red-shining materials were obtained. The UV/Vis spectroscopic properties remain essentially unaltered by the exchange of the carbonyl group in the triazolinone ring by a thiocarbonyl group, however allows the 1,3-dipolar cycloaddition with diazoalkanes such as diazoacetic

ester to form spirothiiranes. The latter are useful as electrophiles for fluorescence labelling, whereas the triazoline ring is suitable for nucleophilic labelling.

Experimental Section

General: IR: Perkin–Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000. UV/Vis: Varian Cary 5000 and Bruins Omega 20. Fluorescence: Varian Eclipse. NMR: Varian Vnmrs 600 (600 MHz). MS: Finnigan MAT 95.

9-(1-Hexylheptyl)-1,2,4-triazolo[1,5-*b*]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]-diisoquinoline-2,8,10,15(1*H*)-tetraone (3): Semicarbazide hydrochloride (196 mg, 1.75 mmol), **2** (500 mg, 872 μmol) and imidazole (5 g) were heated at 110 °C with the exclusion of moisture and air (argon) for 2 h, allowed to cool, still warm diluted with ethanol for dissolving the solidifying imidazole, precipitated with 2 M aqueous HCl, collected by vacuum filtration (D4 glass filter), washed with 2 M HCl and distilled water, dried in air at 110 °C for 16 h and purified by column separation (silica gel; chloroform/ethanol, 40:1; second fraction). Yield 187 mg (35%) of a violet solid; m.p. > 300 °C. R_f (silica gel; chloroform/ethanol, 20:1) = 0.24. IR (ATR): $\tilde{\nu}$ = 3262 (w), 2954 (s), 2920 (s), 2851 (s), 1763 (s), 1696 (s), 1655 (s), 1529 (s), 1505 (w), 1455 (w), 1397 (w), 1376 (w), 1353 (m), 1336 (m), 1319 (s), 1295 (w), 1259 (m), 1210 (w), 1176 (w), 1095 (m), 970 (w), 849 (w), 806 (s), 749 (m), 625.3 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, 2 CH_3), 1.14–1.36 (m, 16 H, 8 CH_2), 1.67–1.82 (m, 2 H, β-CH_2), 2.03–2.21 (m, 2 H, β-CH_2), 5.02–5.11 (m, 1 H, α-CH), 8.34–8.66 (m, 8 H, CH_{arom}), 9.06 (s, 1 H, NH) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.3, 22.8, 27.1, 29.4, 31.9, 32.5, 55.1, 123.1, 123.3, 123.7, 126.7, 127.1, 129.8, 131.4, 132.4, 133.2, 135.8, 157.9, 163.2, 163.8 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 490 (0.29), 518 (0.68), 557 (1.00) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 535 (0.05), 571 (1.00), 618 (0.55), 680 (0.15) nm. Fluorescence quantum yield ($CHCl_3$; λ_{ex} = 490 nm; $E_{490\ nm/1\ cm}$ = 0.0068; reference:[16] **1a** with Φ = 1.00): 0.95. HRMS: calcd. for $C_{38}H_{37}N_4O_4$ 613.2809; found 613.2833 (Δ = 2.4 mmu).

9-(1-Hexylheptyl)-2-thioxo-1,2,4-triazolo[1,5-*b*]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-8,10,15(1*H*)-trione (5): Thiosemicarbazide hydrochloride (470 mg, 3.68 mmol), **2** (1.50 g, 2.61 mmol) and imidazole (4 g) were allowed to react analogously to **3** at 115 °C for 30 min and purified by column separation (silica gel; chloroform/ethanol, 50:1, and then chloroform/ethanol, 25:1; second fraction). Yield 434 mg (29%) of a violet dye; m.p. > 300 °C. R_f (silica gel; chloroform/ethanol, 40:1) = 0.12. IR (ATR): $\tilde{\nu}$ = 3067 (w), 2954 (s), 2924 (s), 2854 (s), 1695 (s), 1658 (s), 1591 (s), 1575 (m), 1556 (w), 1502 (w), 1450 (w), 1393 (m), 1376 (w), 1353 (m), 1334 (s), 1316 (s), 1294 (s), 1241 (m), 1220 (s), 1176 (w), 1150 (w), 1129 (w), 1096 (m), 1038 (w), 970 (m), 855 (m), 807 (s), 742 (s), 724 (w), 626 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.82 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, 2 CH_3), 1.14–1.39 (m, 16 H, 8 CH_2), 1.81–1.92 (m, 2 H, β-CH_2), 2.18–2.29 (m, 2 H, β-CH_2), 5.14–5.21 (m, 1 H, α-CH), 8.60–8.87 (m, 8 H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.1, 22.8, 27.0, 29.3, 31.9, 32.5, 55.3, 123.3, 123.8, 127.0, 127.1, 129.9, 131.2, 132.4, 133.2, 135.8, 160.2, 163.2, 169.8, 188.9 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 485 (17610), 518 (46500), 557 (66760) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 535 (0.10), 572 (1.00), 619 (0.55), 682 (0.15) nm. Fluorescence quantum yield ($CHCl_3$; λ_{ex} = 490 nm; $E_{490\ nm/1\ cm}$ = 0.0095; reference:[16] **1a** with Φ = 1.00): 0.93. HRMS: calcd. for $C_{38}H_{36}N_4O_3S$ 628.2508; found 628.2557 (Δ = 4.9 mmu). $C_{38}H_{36}N_4O_3S$ (628.8): calcd. C 72.59, H 5.77, N 8.91, S 5.10; found C 72.71, H 5.67, N 8.52, S 5.11.

9-(1-Hexylheptyl)-1,2,4,5-tetrazino[1,6-*b*]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-2,9,11,16(1*H*,3*H*)-tetraone (4a): Carbohydrazide hydrochloride (160 mg, 1.75 mmol), **2** (500 mg, 870 μmol) and imidazole (5 g) were allowed to react as was described for **3** and purified by column separation (silica gel; dichloromethane/methanol, 50:1). A TLC control of the main fraction indicated a permanent slow decomposition. MS (DEI^+/70 eV): *m*/*z* (%) = 629.3 (5) [MH_2^+], 628.3 (15) [MH^+], 627.3 (33) [M^+], 613.2 (6), 612.3 (16), 588.3 (16), 587.3 (40), 572.3 (12), 570.3 (7), 447.1 (10), 446.1 (27), 445.1 (30), 432.1 (9), 431.1 (31), 430.1 (81), 407.1 (20), 406.1 (63), 405.1 (100), 404.1 (7), 392.1 (7), 391.1 (34), 390.1 (58), 388.1 (7), 377.1 (11), 376.1 (26), 374.1 (6), 373.1 (8), 362.1 (6), 361.1 (8), 360.1 (6), 346.1 (7), 345.1 (8), 83.1 (6), 69.1 (11), 57.1 (9), 55.1 (16), 44.0 (10), 43.0 (9), 41.0 (11). HRMS: calcd. for $C_{38}H_{37}N_5O_4$ 627.2846; found 627.2829 (Δ = 1.7 mmu).

9-(1-Hexylheptyl)-2-thioxo-1,2,4,5-tetrazino[1,6-*b*]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-9,11,16(1*H*,3*H*)-trione (4b): Thiocarbohydrazide hydrochloride (111 mg, 1.05 mmol), **2** (300 mg, 523 μmol) and imidazole (5 g) were allowed to react as was described for **5** and purified by column separation (silica gel; chloroform/ethanol, 60:1). A TLC control of the main fraction indicated a permanent slow decomposition. MS (DEI^+/70 eV): *m*/*z* (%) = 643.3 (1) [M^+], 642.3 (2) [M^+ – H], 597.3 (4), 596.3 (11), 573.3 (8), 572.3 (22), 468.1 (4), 460.1 (4), 446.0 (6), 429.1 (3), 417.1 (4), 416.1 (10), 415.1 (21), 414.1 (37), 406.1 (4), 405.1 (4), 404.1 (4), 403.1 (6), 392.1 (13), 391.1 (49), 390.1 (100), 389.1 (9), 386.1 (4), 379.0 (5), 377.1 (4), 376.1 (14), 375.1 (8), 374.1 (5), 373.1 (10), 346.1 (7), 345.1 (7), 281.0 (12), 207.0 (12), 83.1 (3), 69.1 (7), 57.1 (5), 57.1 (6), 55.0 (11), 44.0 (6), 43.1 (6), 41.1 (9). HRMS: calcd. for $C_{38}H_{37}N_5O_3S$ 643.2617; found 643.2618 (Δ = 0.1 mmu).

1-Hexyl-9-(1-hexylheptyl)-2-thioxo-1,2,4-triazolo[1,5-*b*]anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-8,10,15-trione (6): Compound **5** (200 mg, 319 μmol), 1-bromohexane (209 mg, 1.27 mmol) and *N*,*N*-dimethylformamide (15 mL) were stirred at 90 °C for 1 h, treated with triethylamine (128 mg, 1.27 mmol), stirred at 110 °C for further 2 h, concentrated in medium vacuum, dissolved in chloroform, shaken with 2 M aqueous HCl (100 mL) and distilled water (100 mL), dried with magnesium sulfate and purified by column separation (silica gel; chloroform/ethanol, 40:1; first fraction). Yield 64 mg (28%) of a violet solid; m.p. > 250 °C. R_f (silica gel; chloroform/ethanol, 40:1) = 0.21. IR (ATR): $\tilde{\nu}$ = 2955 (m), 2922 (s), 2854 (m), 1694 (s), 1658 (s), 1614 (w), 1593 (s), 1574 (m), 1556 (w), 1502 (w), 1451 (w), 1432 (w), 1412 (w), 1396 (m), 1378 (w), 1354 (m), 1337 (s), 1320 (m), 1297 (w), 1246 (m), 1230 (s), 1198 (w), 1176 (w), 1149 (w), 1128 (w), 1106 (w), 1037 (w), 972 (m), 904 (w), 871 (w), 846 (w), 827 (w), 807 (s), 793 (w), 752 (w), 749 (s), 627 (w) cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.80–0.94 (m, 9 H, 3 CH_3), 1.16–1.47 (m, 22 H, 11 CH_2), 1.58–1.93 (m, 4 H, 2 CH_2), 2.20–2.40 (m, 2 H, β-CH_2), 4.24–4.37 (m, 2 H, NCH_2), 5.15–5.30 (m, 1 H, α-CH), 8.63–8.97 (m, 8 H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 10.92, 14.0, 16.38, 19.16, 22.9, 23.8, 24.5, 27.4, 29.7, 32.7, 38.7, 54.8, 58.4, 113.1, 123.2, 126.2, 127.7, 128.7, 130.9, 132.3, 136.9, 141.6, 144.8, 155.7, 167.7, 173.5 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 484 (21000), 517 (44500), 554 (59480) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 535 (0.15), 571 (1.00), 618 (0.67), 678 (0.25) nm. Fluorescence quantum yield ($CHCl_3$; λ_{ex} = 490 nm; $E_{490\ nm/1\ cm}$ = 0.0125; reference:[16] **1a** with Φ = 1.00): 0.65. MS (DEI^+/70 eV): *m*/*z* (%) = 714.3 (13), 713.3 (43) [MH^+], 712.3 (93) [M^+], 666.3 (19), 665.3 (40), 652.3 (10), 629.3 (19) [$MH^+ – C_6H_{13}$], 628.3 (37) [$M^+ – C_6H_{13}$], 624.3 (8), 623.3 (14),

532.1 (19), 531.1 (39), 530.1 (30), 484.1 (8), 483.1 (25), 460.1 (7), 448.1 (16), 447.1 (53), 446.1 (100), 441.1 (14), 418.0 (7), 415.1 (12), 373.1 (14), 345.1 (7), 55.1 (12). HRMS: calcd. for $C_{44}H_{48}N_4O_3S$ 712.3447; found 712.3445 (Δ = 0.2 mmu). $C_{44}H_{48}N_4O_3S$ (712.9): calcd. C 74.13, H 6.79, N 7.86, S 4.50; found C 73.87, H 6.72, N 7.83, S 4.35.

Thiirane 7a: Compound **5** (70.0 mg, 0.11 mmol) was dissolved in dichloromethane (10 mL), treated with the exclusion of moisture and air (argon) at 0 °C by means of a syringe system dropwise with ethyl diazoacetate (125 mg, 1.10 mmol), stirred at room temperature for 5 h, treated again with ethyl diazoacetate (125 mg, 1.10 mmol) stirred at 40 °C for 2 h, concentrated in medium vacuum, dissolved in chloroform, shaken with 2 M aqueous HCl and with distilled water (100 mL), dried with magnesium sulfate and purified by column separation (silica gel; chloroform/ethanol, 40:1; first fraction). Yield 20 mg (29%) of a violet solid; m.p. > 250 °C. R_f (silica gel; chloroform/ethanol, 30:1) = 0.42. IR (ATR): $\tilde{\nu}$ = 3100 (w), 2956 (s), 2920 (s), 2851 (s), 1716 (s), 1695 (s), 1654 (s), 1594 (s), 1575 (m), 1550 (w), 1502 (w), 1443 (w), 1397 (m), 1355 (m), 1337 (s), 1297 (m), 1255 (m), 1246 (m), 1173 (m), 1176 (w), 1131 (w), 1095 (m), 1022 (w), 975 (m), 848 (m), 807 (s), 741 (s), 726 (w), 628 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.82 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 CH_3), 1.17–1.38 (m, 16 H, 8 CH_2), 1.34 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, OCH_2CH_3), 1.83–1.91 (m, 2 H, β-CH_2), 2.20–2.29 (m, 2 H, β-CH_2), 4.21 (s, 1 H, $CH_{thiirane}$), 4.29 (q, $^3J_{H,H}$ = 7.1 Hz, OCH_2CH_3), 5.15–5.22 (m, 1 H, α-CH), 8.66–9.07 (m, 8 H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 14.2 22.6, 26.9, 29.2, 29.7, 31.7, 32.4, 34.0, 54.8, 62.0, 122.9, 123.2, 123.6, 124.1 125.9, 127.1, 127.4, 128.7, 133.9, 154.8, 155.7, 165.4, 168.5 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 484 (0.32), 517 (072), 554 (1.00) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 571 (1.00), 618 (0.62), 680 (0.15) nm. Fluorescence quantum yield ($CHCl_3$; λ_{ex} = 490 nm; $E_{490\ nm/1\ cm}$ = 0.048; reference:[16] **1a** with Φ = 1.00): 0.80. MS (DEI$^+$/70 eV): *m/z* (%) = 716.3 (11), 715.3 (28) [MH^+], 714.3 (64) [M^+], 697.3 (10), 657.3 (7), 656.3 (15), 535.1 (10), 534.1 (32), 533.1 (75), 532.1 (100) [$MH^+ - C_{13}H_{27}$], 486.0 (10), 475.1 (14), 474.1 (19), 460.1 (19), 459.0 (32), 458.0 (15), 447.0 (11), 446.0 (26), 432.0 (13), 418.0 (10), 415.1 (11) [$MH^+ - C_{17}H_{33}O_2S$], 373.1 (19), 346.1 (7), 345.1 (11), 55.0 (12). HRMS: calcd. for $C_{42}H_{42}N_4O_5S$ 714.2876; found 714.2868 (Δ = 0.8 mmu).

Thiirane 7b: Compound **5** (300 mg, 0.48 mmol) in dichloromethane (6 mL) and (diazomethyl)trimethylsilane (2 × 219 mg, 2 × 1.92 mmol) were allowed to react as was described for **7a** (room temperature, 2 h each). Yield 216 mg (63%) of a violet dye; m.p. > 300 °C. R_f (silica gel; chloroform/ethanol, 30:1) = 0.58. IR (ATR): $\tilde{\nu}$ = 3088 (w), 2957 (s), 2922 (s), 2853 (s), 1694 (s), 1659 (s), 1593 (s), 1576 (m), 1503 (w), 1453 (w), 1432 (w), 1396 (m), 1378 (m), 1354 (m), 1336 (s), 1318 (w), 1297 (w), 1257 (s), 1231 (m), 1175 (m), 1127 (w), 1092 (m), 1017 (w), 972 (m), 849 (m), 807 (s), 740 (s), 700 (m), 661 (w), 626 (w) cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 0.83 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 CH_3), 1.16 –1.40 (m, 16 H, 8 CH_2), 1.83–1.92 (m, 2 H, β-CH_2), 2.20–2.30 (m, 2 H, β-CH_2), 2.68 (s, 1 H, $CH_{thiirane}$), 5.14–5.22 (m, 1 H, α-CH), 8.64–9.08 (m, 8 H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = –1.77, 14.0, 16.8 22.6, 26.9, 29.2, 31.7, 32.4, 54.8, 118.9, 122.9, 123.3, 123.5, 124.0 126.0, 127.1, 127.5, 128.5, 129.4, 133.7, 154.7, 155.9, 169.5 ppm. UV/Vis ($CHCl_3$): λ_{max} (E_{rel}) = 480 (0.38), 518 (0.78), 553 (1.00) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 535 (0.14), 572 (1.00), 615 (0.67), 680 (0.22) nm. Fluorescence quantum yield ($CHCl_3$; λ_{ex} = 472 nm; $E_{472\ nm/1\ cm}$ = 0.01876; reference:[16] **1a** with Φ = 1.00): 0.90. MS (DEI$^+$/70 eV): *m/z* (%) = 716.3 (20), 715.3 (52) [MH^+], 714.3 (92) [M^+], 713.3 (21), 701.3 (22), 700.3 (47), 699.3 (93), 670.3 (10), 669.3 (28), 534.1 (9) [$MH^+ - C_{13}H_{27}$], 533.1 (17) [$M^+ - C_{13}H_{27}$], 532.1 (14), 530.8 (17), 518.0 (23), 517.0 (40), 487.4 (16), 472.5 (7), 471.5 (8), 461.6 (13), 460.6 (8), 373.7 (22), 346.7 (9), 111.0 (8), 99.0 (8), 97.0 (12), 95.0 (7), 85.0 (14), 83.0 (16), 75.0 (7), 73.0 (24), 71.0 (17), 70.0 (10), 69.0 (21), 57.1 (23), 55.0 (18), 44.0 (100), 43.1 (15), 41.0 (13). HRMS: calcd. for $C_{42}H_{46}N_4O_3SSi$ 714.3060; found 714.3060 (Δ = 0.0 mmu).

[9-(1-Hexylheptyl)-1,3,8,10-tetraoxo-3,6,8,9,10,14c-hexahydro-1*H*-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinolin-2-yl]urea (9): A solution of **8**[15] (100 mg, 170 μmol) in chloroform (15 mL) was cooled to 0 °C with the exclusion of moisture and air (argon) and treated while stirring with potassium cyanate (28.0 mg, 340 μmol), acetic acid (20.0 mg, 340 μmol) and tetraethylammonium bromide (ca. 50 mg), stirred at 0 °C for 2 h, warmed at room temperature, stirred for 72 h, concentrated in vacuo, treated with a small amount of chloroform, precipitated with methanol, allowed to stand for 1 h, collected by vacuum filtration, washed with 2 M aqueous HCl and then with distilled water, dried in air at 110 °C and purified by column separation (silica gel; chloroform/ethanol, 40:1, and then chloroform/ethanol, 10:1; fourth fraction). Yield 670 mg (59%) of a bright-red solid; m.p. > 300 °C. R_f (silica gel; chloroform/ethanol, 20:1) = 0.20. IR (ATR): $\tilde{\nu}$ = 3450 (m), 3342 (m), 2924 (s), 2855 (s), 1699.6 (s), 1652 (s), 1592 (s), 1576 (s), 1506.0 (m), 1456 (m), 1433 (w), 1403 (m), 1377 (m), 1341 (s), 1303 (m), 1248 (s), 1198 (m), 1172 (s), 1105 (m), 1050 (w), 964 (w), 851.5 (w), 808 (m), 741 (w), 658 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.82 (t, $^3J_{H,H}$ = 6.6 Hz, 6 H, 2 CH_3), 1.18–1.37 (m, 16 H, 8 CH_2), 1.83–1.91 (m, 2 H, β-CH_2), 2.19–2.27 (m, 2 H, β-CH_2), 3.88 (s, 2 H, NH_2), 5.14–5.20 (m, 1 H, α-CH), 5.30 (s, 1 H, NH), 8.61–8.71 (m, 8 H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 14.0, 22.7, 27.0, 29.3, 31.9, 32.5, 55.1, 122.7, 122.9, 123.4, 123.8, 123.9, 126.5, 126.8, 126.9, 129.6, 131.4, 132.1, 132.3, 132.4, 134.4, 135.6, 135.8, 154.4, 155.7, 162.1, 162.7 ppm. UV/Vis ($CHCl_3$): λ_{max} (ε) = 458 (17040), 489 (45140), 525 (73530) nm. Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 536 (1.00), 578 (0.54), 627 (0.15) nm. Fluorescence quantum yield ($CHCl_3$; λ_{ex} = 488 nm; $E_{488\ nm/1cm}$ = 0.0268; reference:[16] **1a** with Φ = 1.00): 1.00. HRMS: calcd. for $C_{38}H_{39}N_4O_5$ 631.2915; found 631.2937 (Δ = 2.2 mmu). $C_{38}H_{38}N_4O_5$ (630.3): calcd. C 72.36, H 6.07, N 8.88; found C 71.87, H 6.07, N 8.65.

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