Red shining silica: macroscopic pigments and nanoparticles by silylation†

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Red shining perylene fluorescent dyes were obtained by their lateral extension with imidazole attached with methoxysilanes and applied for the grafting of silica nanoparticles. The interaction of chromophores at the surface of the nanoparticles was managed by external media and controlled their optical properties.

Fluorescent nanoparticles are obtaining an increasing interest, both for basic research and applications.[1] Strongly red fluorescent materials are attractive, both because of their impressive colour and the matching of the broadly used Rhodamine 6G dye laser for excitation. We started with well-established silica materials, being very variable in size, and targeted the introduction of a fluorescent chromophore by grafting. Thus, both size and spectroscopic properties can be independently adapted to various requirements. Perylene tetracarboxylic bisimides,[2] such as **1**, are interesting chromophores for grafting[3] because of their chemical stability, light fastness and high fluorescent quantum yields. However, yellow fluorescent light is obtained, and a bathochromic shift is required to obtain red fluorescent light. The introduction of donor groups can cause bathochromic shifts.[4] However, they strongly deform the chromophore. A lateral extension of the naphthalene sub-units to anthracene units would be an attractive alternative because strong bathochromic shifts[5] are obtained, such as in aceanthrene green. However, fluorescence quantum yields decreased to some 20%. One may ask if it is possible to re-establish high fluorescence quantum yields by lateral extension with heterocyclic rings instead of carbocyclic rings.

We started our synthesis with **1**, where the two long chain secondary alkyl groups ("swallow-tail substituents") render the otherwise pigment-like perylene material soluble[6] and allowed the reaction with strongly nucleophilic sodium amide in the dipolar aprotic solvent benzonitrile (see Fig. 1). Not only the nucleophilic displacement reaction proceeded with **1**, but also a subsequent ring closure with the incorporation of benzonitrile to form **2**. The pattern of extension is not straightforward, but could be confirmed by three vicinal H–H couplings in the ^{1}H NMR spectrum. **2** was alkylated at the secondary nitrogen atom by means of allyl bromide to form strongly red fluorescent **3**, where a fluorescence quantum yield of close to unity was found in chloroform.

The regio-orientation of the nucleophilic attack was confirmed by ^{1}H NOE NMR, where no cross signal was found between the protons of the allylic CH_2 group and the perylene nucleus. The hydrosilylation of **3** with trimethoxysilane by

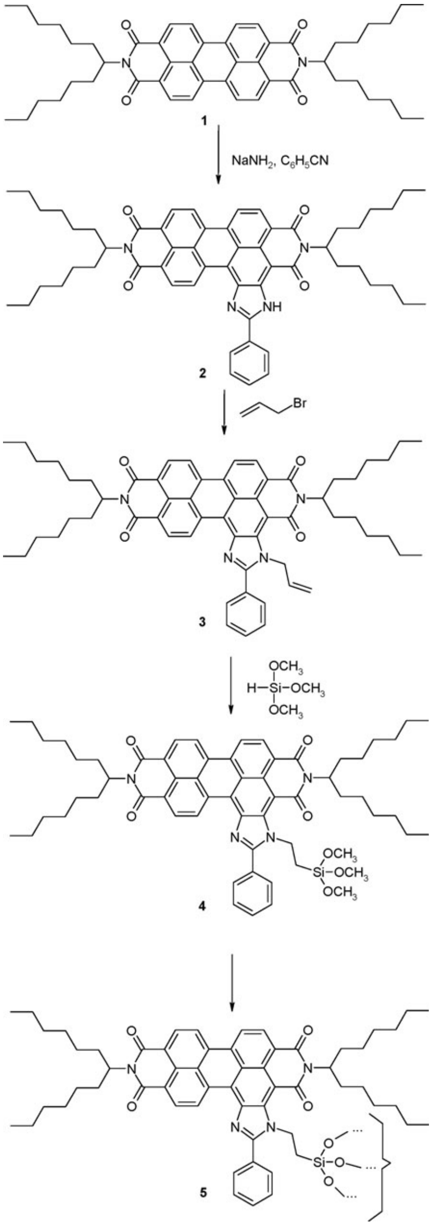

Fig. 1 Synthesis of the material for grafting.

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means of Karstedt's catalyst[7] gave silane **4** as the reagent for grafting (see also ref. 3). The exchange of the methoxy groups in **4** with the free silanol of silica was applied for a covalent linkage to the surface according to Fig. 1, where the colouration could neither be removed in refluxing DMF nor in refluxing chloroform/methanol 5 : 1 (5 h each), not even in trace amounts. The covering of the surface was 1.0×10^{-3} nm^{-2} chromophores, as calculated from the optical density. The thermal stability was high; decomposition monitored by thermogravimetry and DSC, respectively, required more than 380 °C. The material is very light-fast; direct solar radiation for more than half a year did not change its colouration.

The method of grafting can be universally applied to silica, independent of the particle size. The grafting of silica 60 gave an intensely red shining fluorescent pigment. On the other hand, even the grafting of silica nanoparticles was successful, such as with Cabosil® M-5 or the chemical bulk product pyrogenic silica,[8] for example HDK T40 and HDK CMKS13, which was indicated by the strong fluorescence. The particle size was characterised by means of DLS (see Fig. 2).

The dispersed nanoparticles were initially purified by filtration through a D5 glass filter in order to exclude macroscopic by-product particles. The grafted nanoparticles were collected by centrifugation and re-dispersed for the change of solvent. An average size of some 150 nm was obtained in ethanol, both for Cabosil® and HDK T40. The particle size could be further processed by the medium. The application of water caused an inhomogeneous distribution in size for grafted Cabosil®, with a minor component still at some 150 nm and a major component at 50 nm. The application of methanol/water to grafted HDK T40 gave a single maximum at 40 nm; the exact position of the maximum depended slightly on the entire batch. The particle size in water could be controlled by filtration, such as by passing the grafted Cabosil® particles through a Blauband® filter paper (Schleicher & Schuell), where the mean size was shifted to 70 nm. Filtration through a Millex® filter lowered the size further to 50 nm (see Fig. 3). We interpret these results in terms of solvation of the free silanol groups at the surface of the particles by polar water causing a de-aggregation, and thus shifting them to a smaller size. A further shift by filtration indicates that some particles with suitable surface structures may play the role of nuclei in aggregation. A smaller size will be obtained if such particles, having formed aggregates, are removed by filtration.

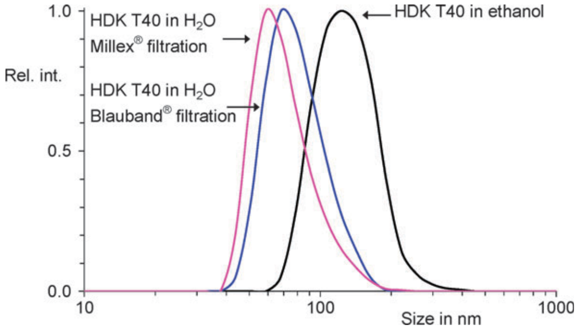

Fig. 3 The effect of nanofiltration on the particle size of grafted HDK T40 measured by DLS. Black: starting material in ethanol. Blue: particles in water after filtration through a Blauband® paper filter. Magenta: after filtration through a Millex® nanofilter.

All the grafted material was highly fluorescent, such as the silica forming a brightly red shining pigment. Fluorescence quantum yields close to unity were found both for grafted Cabosil® and HDK T40. The fluorescence excitation spectrum of the grafted Cabosil® dispersed in ethanol resembles the absorption spectrum of diluted **3** in lipophilic solvents such as chloroform (see Fig. 4). The spectrum of HDK T40 is similar. The fluorescence spectrum of grafted Cabosil® resembles the spectrum of **3** in chloroform; however, a slight amplification of the bathochromic region is found, indicating the formation of excimers to some extent. The spectrum of HDK T40 is identical. A change of the medium to water induced a proximity of aromatic structures at the surface of the particles and caused both a bathochromic shift in the fluorescence excitation and the fluorescence spectrum, and further favoured the formation of excimers, as indicated by the increased intensity of the fluorescence in the bathochromic region. This effect is still further pronounced for the grafted silica, where such spectra were obtained, even in more lipophilic chloroform (see Fig. 4).

In summary perylene fluorescent dyes could be laterally extended with an imidazole ring by a novel type of annelation to form highly bathochromically-fluorescent building blocks for grafting silica micro- and nanoparticles.

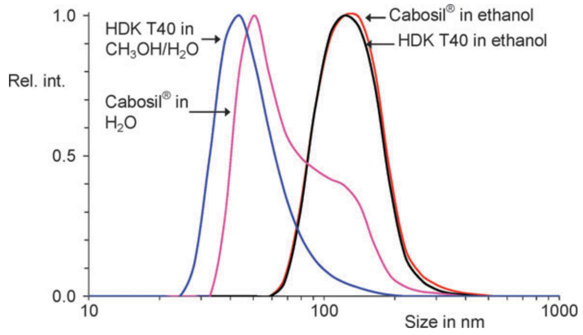

Fig. 2 Particle size of grafted nanoparticles by means of dynamic light scattering (DLS, 633 nm). In ethanol: Cabosil® in red and HDK T40 in black. In an aqueous phase: Cabosil® in magenta and HDK T40 in blue.

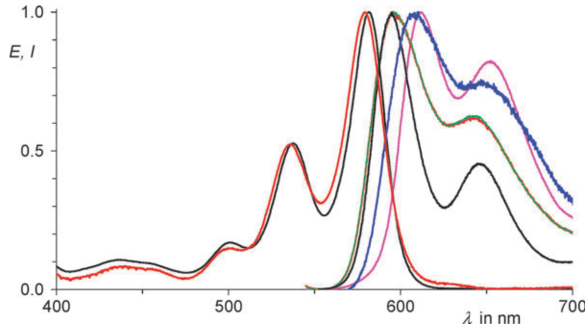

Fig. 4 UV/vis absorption (left) and fluorescence (right) spectra of the grafted material. Red: Cabosil® in ethanol. Green almost masked by red: HDK T40. Blue: Cabosil® in water. Magenta: silica T60 in chloroform. Black: **3** in chloroform.

Experimental

Instrumentation

IR spectra: Perkin-Elmer 1420 Ratio Recording Infrared Spectrometer, FT 1000. UV/vis spectra: Varian Cary 5000 and Bruins Omega 20. Fluorescence spectra: Varian Eclipse. NMR spectroscopy: Varian Mercury 200 (200 MHz), Bruker ARX300 and Varian Vnmrs 300 (300 MHz), Varian Inova 400, Varian VXR400S and Varian Vnmrs 400 (400 MHz), and Bruker AMX600 and Varian Vnmrs 600 (600 MHz). Mass spectrometry: Finnigan MAT 95.

Syntheses

2,11-Bis(1-hexylheptyl)-5-phenylimidazolo[4′,5′:3,4]anthra-[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (2). 2,9-Bis-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]-diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (**1**; 1.00 g, 1.32 mmol) and $NaNH_2$ (1.00 g, 25.6 mmol) were dispersed in benzonitrile (250 mL), heated at 165 °C for 3 h (colour change to blue), allowed to cool and shaken with a 1 : 1 mixture of 2 N HCl and chloroform (300 mL). The organic phase was dried with $MgSO_4$, evaporated *in vacuo*, dissolved in a small amount of chloroform, filtered and purified by column separation.

1st fraction: double adduct. Yield 40 mg (4%) as a black dye. m.p. > 300 °C. R_f (silica gel, chloroform) = 0.88. IR (ATR): $\tilde{\nu}$ = 3316.7 m, 2950.3 m, 2920.1 s, 2852.0 m, 1672.9 s, 1616.9 s, 1586.9 s, 1532.3 w, 1487.0 w, 1453.1 w, 1436.5 w, 1401.4 w, 1339.6 m, 1332.0 s, 1299.4 w, 1267.0 w, 1232.4 w, 1184.3 w, 1109.1 w, 1058.6 m, 1000.6 m, 955.5 w, 895.7 w, 867.9 w, 815.0 w, 779.6 w, 758.2 m, 731.6 w and 687.6 w cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 0.82–0.89 (m, 12 H, CH_3), 1.26–1.47 (m, 32 H, CH_2), 1.91–2.06 (dm, 4 H, β-CH_2), 2.28–2.43 (m, 4 H, β-CH_2), 5.22–5.36 (m, 2 H, CH–N), 7.65–7.67 (m, 3 H, CH_{aryl}), 8.33–8.38 (m, 2 H, CH_{aryl}), 8.72–8.85 (m, 6 H, $H_{perylene}$), 10.95 (d, 1 H, ^3J = 8.0 Hz) and 11.55 (s, 1H, N–H). ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ 14.1, 22.6, 27.0, 29.3, 31.8, 32.4, 54.6, 104.8, 121.2, 122.7, 123.5, 126.5, 126.6, 127.7, 128.1, 129.1, 129.4, 130.4, 130.6, 131.1, 132.2, 134.7, 134.9, 135.2, 135.2, 138.7, 39.0, 139.2, 143.9, 157.3, 163.9,164.9 and 165.7. UV/vis ($CHCl_3$): λ_{max}/nm (E_{rel}) = 388.6 (0.07), 413.0 (0.12), 452.6 (0.14), 481.0 (0.15), 514.4 (0.14), 547.2 (0.11), 589.6 (0.42) and 640.6 (1.00). Fluorescence ($CHCl_3$): λ_{max}/nm (I_{rel}): 650.8 (1.00) and 712.3 (0.32). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 472 nm, E_{472} = 0.0149 cm^{-1}, reference: **1** with Φ = 1.00): 1.00. MS (DEI$^+$/70 eV): m/z (%) = 990 (25) [M^+ + 4 H], 989 (63) [M^+ + 3 H], 988 (91) [M^+ + 2 H], 806 (19), 805 (20), 624 (21), 623 (66), 622 (100) and 55 (11). HMRS for $C_{64}H_{71}N_6O_4$: calc. m/z = 987.554, found m/z = 987.552, Δ = −0.002.

2nd fraction: 2,11-bis(1-hexylheptyl)-5-phenylimidazolo-[4′,5′:3,4]anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,10,12-(2*H*,11*H*)-tetraone (**2**). Yield 409 mg (36%) as a metallic shining violet dye. m.p. > 300 °C. R_f (silica gel, chloroform) = 0.85. IR (ATR): $\tilde{\nu}$ = 3411.7 m, 2954.8 m, 2923.5 s, 2855.2 m, 1689.1 s, 1656.0 s, 1640.3 s, 1623.0 s, 1591.7 s, 1534.8 w, 1486.6 w, 1455.4 w, 1432.6 w, 1396.1 w, 1375.6 w, 1342.4 s, 1332.0 s, 1305.6 m, 1257.4 m, 1219.9 w, 1179.1 w, 1090.9 m, 1054.9 m, 1016.0 m, 871.0 w, 807.6 m, 796.5 m, 748.1 m, 727.0 w and 684.0 w cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 0.81–0.85 (m, 12 H, CH_3), 1.23–1.40 (m, 32 H, CH_2), 1.86–1.97 (m, 4 H, β-CH_2), 2.24–2.37 (m, 4 H, β-CH_2), 5.18–5.30 (m, 2 H, CH–N), 7.67–7.69 (m, 3 H, CH_{aryl}), 8.33–8.35 (m, 2 H, CH_{aryl}), 8.56–8.77 (m, 6 H, $H_{perylene}$), 10.74 (d, 1 H, ^3J = 8.2 Hz) and 11.52 (s, 1 H, N–H). ^1H NMR COSY (600 MHz, $CDCl_3$, 25 °C, selected isolated signals): δ (7.67, 8.34) and (8.76, 10.74). ^{13}C NMR (151 MHz, $CDCl_3$, 25 °C): δ 14.1, 22.6, 27.0, 29.3, 31.8, 32.4, 54.6, 104.8, 121.2, 122.7, 123.5, 126.5, 126.6, 127.7, 128.1, 129.1, 129.4, 130.4, 130.6, 131.1, 132.2, 134.7, 134.9, 135.2, 135.2, 138.7, 39.0, 139.2, 143.9, 157.3, 163.9, 164.9 and 165.7. UV/vis ($CHCl_3$): λ_{max}/nm (E_{rel}) = 378.6 (9020), 396.9 (9210), 439.4 (13400), 463.6 (14700), 504.6 (15900), 541.9 (48100) and 586.6 (92 000). Fluorescence ($CHCl_3$): λ_{max}/nm (I_{rel}): 599.3 (1.00) and 651.5 (0.43). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 541 nm, E_{541} = 0.0322 cm^{-1}, reference: **1** with Φ = 1.00): 1.00. HMRS for $C_{57}H_{67}N_4O_4$: calc. m/z = 871.516, found m/z = 871.517, Δ = +0.001. Analysis for $C_{57}H_{66}N_4O_4$ (871.2): calc. C, 78.59; H, 7.64; N, 6.43. Found: C, 78.49; H, 7.78; N, 6.55%.

4-Allyl-2,11-bis(1-hexylheptyl)-5-phenylimidazolo[4′,5′:3,4]-anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (3). 2,11-Bis(1-hexylheptyl)-5-phenylimidazolo[4′,5′:3,4]-anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (**2**; 100 mg, 0.115 mmol), allylbromide (624 mg, 3.45 mmol) and potassium carbonate (300 mg, 2.17 mmol) were suspended in DMPU (5 mL), heated at 65 °C for 24 h, treated while still warm with aqueous HCl (2 N, 50 mL), collected by vacuum filtration, dried *in vacuo*, dissolved in a small amount of chloroform and purified by column separation (silica gel, chloroform/iso-hexane 2 : 1, removing allylbromide residues). Yield 87 mg (83%). m.p. > 250 °C. R_f (silica gel, chloroform) = 0.52. ^1H NMR (600 MHz, $CDCl_3$, 25 °C): δ 0.82 (t, ^3J = 7.0 Hz, 12 H, CH_3), 1.16–1.40 (m, 32 H, CH_2), 1.82–1.92 (m, 4 H, β-CH), 2.20–2.34 (m, 4 H, β-CH), 4.44–4.64 (br, 1 H, CH_{allyl}), 4.81–4.88 (br, 1 H, CH_{allyl}), 5.15–5.22 (m, 2 H, N–CH_2), 5.42–5.60 (br, 3 H, N–CH + CH_{allyl}), 7.64–7.68 (m, 3 H, CH_{aryl}), 7.95–8.00 (m, 2 H, CH_{aryl}), 8.60–8.79 (m, 5 H, $CH_{perylene}$) and 10.75 (d, ^3J = 8.1 Hz, 1 H, $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ 14.3, 22.8, 22.8, 27.2, 27.3, 29.5, 29.5, 32.0, 32.1, 32.7, 51.3, 54.9, 55.3, 121.5, 122.8, 123.9, 125.6, 127.0, 127.3, 129.3, 129.9, 130.4, 130.4, 131.5, 132.5, 135.0, 139.6, 144.8, 163.4, 164.1 and 165.1. UV/vis ($CHCl_3$): λ_{max}/nm (ε) = 376.0 (8067), 395.4 (8978), 500.3 (14530), 536.9 (43870) and 581.3 (82740). Fluorescence ($CHCl_3$): λ_{max}/nm (I_{rel}) = 594.6 (1.00) and 644.2 (0.32). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 537.5 nm, $E_{537.5}$ = 0.01405 cm^{-1}, reference: **1** with Φ = 1.00): 1.00. HRMS for $C_{60}H_{70}N_4O_4$: calc. m/z = 910.5397, found m/z = 910.5379, Δ = −0.0018. Analysis for $C_{60}H_{70}N_4O_4$ (911.2): calc. C, 79.09; H, 7.74; N, 6.15. Found C, 78.87; H, 7.71; N, 5.83%.

2,11-Bis(1-hexylheptyl)-4-(3-trimethoxysilylpropyl)-5-phenyl-imidazolo[4′,5′:3,4]anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (4). 4-Allyl-2,11-bis(1-hexylheptyl)-5-phenylimidazolo[4′,5′:3,4]anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]-diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (**3**, 50 mg, 54 μmol) in a Schlenk vessel, having been dried by heating *in vacuo*, was dissolved in anhydrous chloroform (7 mL) under an argon atmosphere and treated at room temperature cautiously dropwise by means of a septum with trimethoxysilane (1.2 mL, 9.84 mmol) and the platinum(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst; 40 mg, 3.75 mol% in vinyl-terminated polydimethylsilicone). The solution was stirred at room temperature for 6 h (the solution can be stored at room temperature under argon) and applied for grafting under an argon atmosphere without further purification. Contact with silica 60 causes immobilization within a few minutes. A chromatographic purification was successful by the application of a rotatory chromatograph (chromatotron) with chloroform and silica/gypsum plates. Yield 20 mg (36%) as a violet solid. m.p. 230 °C. R_f value ($CHCl_3$/EtOH) = 0.42. IR (ATR): $\tilde{\nu}$ = 2954.9 w, 2925.0 m, 2856.6 w, 1685.0 s, 1644.5 s, 1592.0 m, 1528.8 w, 1484.4 w, 1457.4 w, 1424.7 m, 1407.8 w, 1379.3 w, 1362.9 w, 1333.1 vs, 1256.4 s, 1185.5 m, 1081.4 vs, 1014.9 s, 933.9 w, 872.6 w, 808.0 vs, 799.8 vs, 772.8 s, 751.6 s, 738.6 s, 721.7 m and 701.9 cm^{-1} s. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ −0.05–0.03 (m, 2 H, Si–CH_2), 0.80–0.84 (m, 12 H, CH_3), 1.20–1.40 (m, 32 H, CH_2), 1.43–1.51 (m, 2 H, Si–CH_2–CH_2), 1.82–1.96 (m, 4 H, β-CH_2), 2.22–2.34 (m, 4 H, β-CH_2), 3.22 (s, 9 H, $Si(OCH_3)_3$), 4.95 (t, $^3J_{H,H}$ = 6.8 Hz, 2 H, N–CH_2), 5.16–5.28 (m, 2 H, N–CH), 7.67–7.69 (m, 3 H, $CH_{aromatic}$), 8.00–8.03 (m, 2 H, $CH_{aromatic}$), 8.64–8.00 (m, 5 H, $CH_{perylene}$) and 10.79–10.83 (d, J = 8.2 Hz, 1 H, $CH_{perylene}$). ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C, TMS): δ 5.4, 14.1, 22.1, 22.6, 26.9, 27.0, 29.2, 29.3, 31.8, 32.4, 50.3, 51.3, 54.6, 54.8, 121.2, 122.6, 123.6, 126.8, 127.1, 129.1, 129.9, 130.3, 131.1, 131.3, 134.9, 144.8 and 163.9. ^{29}Si NMR (80 MHz, $CDCl_3$, 22 °C): δ −43.3. UV/vis ($CHCl_3$): λ_{max}/nm (E_{rel}) = 502.4 (0.18), 539.2 (0.53) and 583.7 (1.00). Fluorescence ($CHCl_3$): λ_{max}/nm (I_{rel}) = 596.4 (1.00) and 648.9 (0.46). Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 539 nm, E_{539} = 0.0105 cm^{-1}, reference: **1** with Φ = 1.00): 1.00. MS (DEP^+/EI^+): m/z (%): 1034.6 (32) [M^+ + 2 H], 1033.6 (73) [M^+ + H], 1032.6 (100) [M^+], 851.4 (12), 850.4 (10), 507.1 (20), 506.1 (31) and 121.0 (23). HRMS for $C_{63}H_{80}N_4O_7Si$: calc. 1032.5796, found 1032.5799, Δ = +0.0003.

General procedure for grafting silica particles

The particles were dehydrated before grafting by heating them at 80 °C for 1 h in a medium vacuum. 100 mg of the silica particles (Cabosil® M-5 and HDK T 40, respectively) were dispersed in chloroform (8 mL) at room temperature for 16 h, treated dropwise with the rough solution of 2,11-bis(1-hexylheptyl)-4-(3-trimethoxysilylpropyl)-5-phenylimidazolo[4′,5′:3,4]anthra-[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,10,12(2*H*,11*H*)-tetraone (**4**; 0.5 mL), refluxed for 5 h, stirred for 16 h at room temperature, repetitively centrifugated (minimum 15 min. at 19 000 rpm) and re-dispersed in chloroform by stirring (minimum 30 min.) at room temperature until the solvent was colourless and re-dispersed in ethanol. The solvent was exchanged for further processing by water or methanol/water by centrifugation and re-dispersion, and furthermore by filtration through a Blauband® filter (porosity ≤450 nm, Schleicher and Schüll)) or a Millex® filter (porosity 220 nm).

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