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SUPPORTING INFORMATION

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Title: Synthesis of Photochromic Compounds for Aqueous Solutions and Focusable Light
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Experimental Procedures

2-(5-Methylthiophen-3-yl)ethanol (4)[1]: To a solution of 4-bromo-2-methylthiophene (**3**)[2,3] (8.86 g, 50.0 mmol) in anhydrous THF (30 mL) and toluene (300 mL), 2.5 M solution of *n*BuLi in hexane (24 mL, 60.0 mmol) was added dropwise at –78 °C under inert atmosphere. The mixture was stirred for 30 min at this temperature, then liquid ethylene oxide (8.8 mL; **CAUTION upon addition and working-up! HIGHLY POISONOUS SUBSTANCE with b. p. 10 °C**) was added followed by $BF_3 \times Et_2O$ (8.8 mL), which was added after 3 min. The mixture was stirred at –78 °C for 1 h, then MeOH (20 mL) was added at 0 °C, and the reaction mixture was washed with sat. aq. NH_4Cl (100 mL), and dried over Na_2SO_4. The solvents were evaporated under reduced pressure, and the residue was distilled in vacuo to obtain 5.32 g (75%) of colorless oil, b.p. 60 °C (0.7 mbar). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 2.80 (t, J = 6.3 Hz, 2 H, CH_2), 3.81 (dt, J = 6.0, 6.3 Hz, 2 H, CH_2O), 6.64 (s, 1 H, CH), 6.78 ppm (s, 1 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.1 (CH_3), 33.7 (CH_2), 62.8 (CH_2O), 119.5 (CH), 126.6 (CH), 138.7 (C), 140.5 ppm (C). $C_7H_{10}OS$ (142), EI-MS, positive mode, *m/z* (rel. int., %): 142.0 [$M^{+\cdot}$] (40), 111.0 [M–CH_2OH](100).

4-[2-(*tert*-Butyldiphenylsilyloxy)ethyl]-2-methylthiophene (5): To a solution of compound **4** (3.15 g, 22.2 mmol) and imidazole (3.02 g, 44.4 mmol) in anhydrous DMF (2 mL), *tert*-butyl diphenylsilyl chloride (7.32 g, 26.6 mmol) was added at 0 °C under nitrogen, and the mixture was stirred at room temperature for 24 h. Then the reaction mixture was diluted with Et_2O (100 mL), washed with 0.5 M aqueous citric acid (until pH-value of the aqueous layer reached 5.0), water (50 mL), 5% aq. Na_2CO_3, water (3×50 mL), brine, and dried over $MgSO_4$. After evaporation of the solvents under reduced pressure, the title compound was isolated by chromatography (100 g SiO_2) eluting with hexane/EtOAc (30:1) to yield 7.49 g (89%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, *t*BuSi), 2.44 (s, 3 H, CH_3), 2.80 (t, J = 6.9 Hz, 2 H, CH_2), 3.83 (t, J = 6.9 Hz, 2 H, CH_2O), 6.56 (s, 1 H, CH), 6.70 (s, 1 H, CH), 7.31–7.48 (m, 6 H, CH), 7.59–7.68 ppm (m, 4 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.1 (CH_3), 19.0 (C-Si), 26.7 (3×CH_3), 33.7 (CH_2), 64.4 (CH_2O), 119.1 (CH), 127.3 (CH), 127.7 (4×CH), 129.6 (2×CH), 133.9 (2×C-Si), 135.7 (4×CH), 139.3 (C), 139.4 ppm (C). ESI-MS, positive mode, *m/z* (rel. int., %): 403 (16) [M+Na]$^+$, 381 (100) [M+H]$^+$. Elemental analysis: found: C 72.61, H 7.15; calcd. for $C_{23}H_{28}OSSi$ (380.6): C 72.58, H 7.41.

3-[2-(*tert*-Butyldiphenylsilyloxy)ethyl]-2,4-dibromo-5-methyl-thiophene (6): A solution of bromine (2.1 mL, 41.3 mmol) in AcOH (10 mL) was added dropwise to a stirring mixture of compound **5** (7.49 g, 19.7 mmol) and KOAc (4.87 g, 49.6 mmol) in AcOH (25 mL) at 0 °C, and stirring was continued at room temperature for 20 min. Then the reaction mixture was poured into the crushed ice which contained Na_2CO_3, neutralized with aq. Na_2CO_3, and extracted with $CHCl_3$ (200 mL). The organic phase was washed with water (3×100 mL), brine, and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, the title compound was isolated by chromatography (150 g SiO_2) eluting with hexane/EtOAc (70:1) to give 7.06 g (67%) of colorless powder; m. p. 60–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (s, 9 H, *t*BuSi), 2.31 (s, 3 H, CH_3), 2.93 (t, J = 7.2 Hz, 2 H, CH_2), 3.77 (t, J = 7.2 Hz, 2 H, CH_2O),

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7.33–7.42 (m, 6 H, CH), 7.61–7.66 ppm (m, 4 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.2 (CH_3), 19.0 (C-Si), 26.6 (3×CH_3), 33.1 (CH_2), 61.7 (CH_2O), 106.7 (CBr), 111.3 (CBr), 127.7 (4×CH), 129.6 (2×CH), 133.8 (2×CSi), 134.2 (C), 135.7 (4×CH), 136.9 ppm (C). ESI-MS, positive mode, *m/z* (rel. int., %): 539.0 (100) $[M+H]^+$, 282.9 (92) $[M+H+Na]^{2+}$. Elemental analysis: found: C 51.57, H 4.63; calcd. for $C_{23}H_{26}Br_2OSSi$ (538.4): C 51.31, H 4.87.

4-Bromo-3-[2-(*tert*-butyldiphenylsilyloxy)ethy]-5-methyl-thiophene-2-boronic acid (7): To a solution of compound **6** (0.81 g, 1.5 mmol) in anhydrous Et_2O (6 mL), 2.5 M solution of *n*BuLi in hexane (0.63 mL, 1.58 mmol) was added dropwise at –78 °C under argon, and the mixture was stirred for 1 h at this temperature. Then $B(OiPr)_3$ (0.42 g, 2.25 mmol) was added dropwise, and the mixture was stirred for 10 min at –78 °C and 2 h at room temperature. Then water (1 mL) was added at 0 °C, the organic layer was extracted with 1 M NaOH (3×20 mL), and the aqueous solution was acidified with citric acid at 0 °C. The precipitate was filtered, and dried to give 0.55 g (74%) of the title compound as colorless powder. ^{1}H NMR (300 MHz, [D_6]DMSO, mixture with anhydride): δ = 0.92/0.96 (s, 18 H, *t*BuSi), 2.25/2.35 (s, 6 H, CH_3), 3.19 (t, *J* = 7.1 Hz, 2 H, part of CH_2), 3.32 (t, *J* = 7.4 Hz, 2 H, part of CH_2), 3.73 (t, *J* = 7.1 Hz, 2 H, part of CH_2), 3.80 (t, *J* = 7.3 Hz, 2 H, part of CH_2), 7.25–7.47 (m, 6 H, CH), 7.51–7.59 (m, 4 H, CH), 7.92 ppm (s, 2 H, OH). ^{13}C NMR (75.5 MHz, [D_6]DMSO, mixture with anhydride): δ = 15.1 (CH_3), 18.6 (C-Si), 26.5 (3×CH_3), 32.7 (CH_2), 63.6 (CH_2O), 113.7 (CBr), 127.5/127.7 (4×CH), 129.5/129.6 (2×CH), 132.9 (2×CSi), 133.1 (C), 134.9/135.0 (4×CH), 138.0 (C), 144.1 ppm (C). Monomer ($C_{23}H_{28}BBrO_3SSi$), M_1=502/504; anhydride (dimer, $C_{46}H_{54}B_2Br_2O_5S_2Si_2$), M_2=986/988/990; ESI-MS, positive mode, m/z (rel. int., %): 987/989/991 (100) $[M_2+H]^+$, 527/525 (59) $[M_1+Na]^+$.

4-[4'-Bromo-3'-[2-(*tert*-butyldiphenylsilyloxy)ethyl]-5'-methyl-[2,2']bithiophen-5-yl]pyridine (9): Into a Schlenk-flask filled with argon, 4-(5-iodothiophen-2-yl)pyridine (**8**) (0.51 g, 1.77 mmol), PPh_3 (0.19 g, 0.71 mmol), $Pd(dba)_2$ (0.10 g, 0.18 mmol), and anhydrous THF (20 mL) were added, and the mixture was stirred at room temperature for 10 min. In the second Schlenk-flask, to a solution of compound **6** (1.91 g, 3.54 mmol) in anhydrous THF (10 mL), 2.5 M solution of *n*BuLi in hexane (1.42 mL, 3.54 mmol) was added dropwise at –78 °C under argon, and the mixture was stirred for 1 h at this temperature. Then 1 M $ZnCl_2$ in Et_2O (3.9 mL) was added into the second Schlenk-flask, the mixture was left for warming-up to room temperature, and this solution was added to the solution in the first Schlenk-flask. The yellow reaction mixture was stirred at 40 °C for 18 h. Then the reaction was quenched with sat. aq. NH_4Cl (5 mL); organic layer was separated, washed with water, brine, and dried over Na_2SO_4. After evaporation of the solvents under reduced pressure, the title compound was isolated by chromatography (50 g SiO_2) eluting with CH_2Cl_2/MeOH (100:1) to give 0.83 g (76%) of yellow powder; m. p. 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (s, 9 H, *t*BuSi), 2.40 (s, 3 H, CH_3), 3.15 (t, *J* = 7.1 Hz, 2 H, CH_2), 3.89 (t, *J* = 7.1 Hz, 2 H, CH_2O), 7.16 (d, *J* = 3.8 Hz, 1 H, CH), 7.28 (d, *J* = 3.8 Hz, 1 H, CH), 7.31–7.44 (m, 8 H, CH and CH_{py}), 7.59–7.63 (m, 4 H, CH), 8.57–8.62 ppm (m, 2 H, CH_{py}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.2 (CH_3), 19.2 (CSi), 26.8 (3×CH_3), 32.7 (CH_2), 62.7 (CH_2O), 113.9 (CBr), 119.5 (2×CH), 125.7 (CH), 127.4 (CH), 127.6 (4×CH), 129.0 (2×CH), 129.5 (C), 133.6 (2×CSi), 134.4 (C), 135.6 (4×CH), 137.5 (C), 140.3 (C), 140.7 (C), 141.0 (C), 150.4 ppm (2×CH). ESI-MS, positive mode, m/z (rel. int., %): 618.1 and 620.1 $[M+H]^+$ (100). HR-MS (ESI, positive mode): found: 618.0949; calcd. for $C_{32}H_{32}BrNOS_2Si$: 618.0951 $[M+H]^+$.

3-Bromo-4-[2-(*tert*-butyldiphenylsilyloxy)ethyl]-2-methyl-thiophene (10): The title compound was isolated from the reaction mixtures of the synthesis of compound **9**. It was formed in the course of the protonation of the intermediate Zn-

derivative obtained from the starting material **6**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, *t*BuSi), 2.40 (s, 3 H, CH_3), 2.87 (t, *J* = 6.8 Hz, 2 H, CH_2), 3.87 (t, *J* = 6.8 Hz, 2H, CH_2O), 6.88 (s, 1 H, CH), 7.45–7.34 (m, 6 H, CH), 7.67–7.62 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 15.2 (CH_3), 19.1 (CSi), 26.8 (3×CH_3), 33.8 (CH_2), 62.9 (CH_2O), 112.2 (CBr), 118.8 (CH), 127.6 (4×CH), 129.5 (2×CH), 133.7 (2×CSi), 135.6 (4×CH), 137.7 ppm (2×C). $C_{23}H_{27}BrOSSi$ (458/460), CI-MS (NH_3), positive mode, *m/z* (rel. int., %): 476.2 and 478.2 $[M+NH_4]^+$ (100).

***tert*-Butyl *N*-(2-phenoxyethyl)-*N*-prop-2-enyl carbamate (13):** To a stirred 35% suspension of KH in mineral oil (5.29 g, 45.0 mmol KH) in anhydrous THF (75 mL), a solution of compound **12**[3] (7.11 g, 30.0 mmol) in anhydrous THF (30 mL) was added under argon, and the mixture was stirred at room temperature for 10 min. Then allyl bromide (5.45 g, 45.0 mmol) was added at 0 °C, and the mixture was stirred for 3 h at this temperature followed by quenching with sat. aq. NH_4Cl (18 mL). The reaction mixture was diluted with Et_2O (100 mL), washed with water, brine, and dried. After evaporation of the solvents under reduced pressure, the title compound was isolated by chromatography (150 g SiO_2) eluting with hexane/EtOAc (16:1) to give 7.40 g (89%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 9 H, *t*Bu), 3.50–3.65 (m, 2 H, CH_2N), 3.88–4.02 (m, 2 H, NCH_2CH), 4.02–4.16 (m, 2 H, CH_2O), 5.04–5.23 (m, 2 H, CH_2=), 5.71–5.89 (m, 1 H, CH=), 6.85–7.00 (m, 3 H, CH), 7.23–7.34 ppm (m, 2 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 28.4 (3×CH_3), 45.7/46.3 (CH_2N), 50.3/51.3 (CH_2N), 66.0/66.6 (CH_2O), 79.8 (C), 114.4 (2×CH), 116.0/116.7 (CH_2=), 120.8 (CH), 129.4 (2×CH), 134.1 (CH=), 155.5 (CO), 158.6 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 300.0 $[M+Na]^+$ (100). Elemental analysis: found: C 69.06, H 8.33, N 5.29; calcd. for $C_{16}H_{23}NO_3$ (277.4): C 69.29, H 8.36, N 5.05.

***tert*-Butyl *N*-(3-hydroxypropyl)-*N*-(2-phenoxyethyl) carbamate (14):** To a solution of compound **13** (7.20 g, 26.0 mmol) in anhydrous THF (12 mL), 0.5 M solution of 9-BBN in THF (72.8 mL, 36.4 mmol) was added at 0 °C under argon, the mixture was stirred at 0 °C for 3 h and at room temperature for 18 h. Then 3 M aq. NaOH (12 mL) was added followed by the slow addition of 30% aq. H_2O_2 (12 mL), and the mixture was stirred at 50 °C for 2 h. The reaction mixture was saturated with Na_2CO_3, the aqueous phase was extracted with Et_2O (2×50 mL), and combined organic solutions were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The title compound was isolated by chromatography (150 g SiO_2) eluting with hexane/EtOAc (2:1) to obtain 7.28 g (95%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.46 (s, 9 H, *t*Bu), 1.67–1.80 (m, 2 H, CH_2), 3.39–3.70 (m, 6 H, 2×CH_2N and C*H*$_2$OH), 3.76 (t, *J* = 6.9 Hz, 1 H, OH), 4.03–4.14 (m, 2 H, CH_2O), 6.84–6.92 (m, 2 H, CH), 6.96 (t, *J* = 7.3 Hz, 1 H, CH), 7.27–7.34 ppm (m, 2 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.2 (3×CH_3), 30.5 (CH_2), 43.7 (CH_2N), 46.6 (CH_2N), 58.2 (CH_2OH), 65.9 (CH_2O), 80.5 (C), 114.4 (2×CH), 121.2 (CH), 129.6 (2×CH), 157.1 (CO), 158.6 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 318.2 $[M+Na]^+$ (100). Elemental analysis: found: C 64.84, H 8.21, N 4.58; calcd. for $C_{16}H_{25}NO_4$ (295.4): C 65.06, H 8.53, N 4.74.

***tert*-Butyl *N*-[3-(*tert*-butyldiphenylsilyloxy)propyl]-*N*-(2-phenoxyethyl) carbamate (15):** To a mixture of compound **14** (6.55 g, 22.2 mmol) and imidazole (3.02 g, 44.4 mmol) in anhydrous DMF (10 mL), *tert*-butyl diphenylsilyl chloride (7.33 g, 26.6 mmol) was added at 0 °C under argon, and the mixture was stirred at room temperature for 18 h. Then 0.5 M aq. citric acid was added until pH-value reached 5.0. The reaction mixture was diluted with Et_2O (100 mL), washed with water (50 mL), 5% aq. Na_2CO_3, water (3×50 mL), brine, and dried over $MgSO_4$. After evaporation of the

solvents under reduced pressure, the title compound was isolated by chromatography (150 g SiO_2) eluting with CH_2Cl_2 to give 11.7 g (99%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 9 H, *t*BuSi), 1.42 (s, 9 H, *t*Bu), 1.75–1.89 (m, 2 H, CH_2), 3.45 (t, J = 7.0 Hz, 2 H, NCH_2CH$_2$CH$_2$O), 3.51–3.63 (m, 2 H, OCH$_2$CH_2N), 3.65–3.75 (m, 2 H, NCH$_2$CH$_2$CH_2O), 4.00–4.14 (m, 2 H, OCH_2CH$_2$N), 6.86–7.00 (m, 3 H, CH), 7.26–7.33 (m, 2 H, CH), 7.33–7.47 (m, 6 H, CH), 7.63–7.70 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 19.2 (CSi), 26.8 (3×CH_3), 28.4 (3×CH_3), 31.2/31.8 (CH_2), 45.4/46.2 (CH_2N), 46.9/47.2 (CH_2N), 61.6 (CH_2OSi), 66.1/66.6 (CH_2O), 79.5 (C), 114.4 (2×CH), 120.7 (CH), 127.6 (4×CH), 129.4 (2×CH), 129.6 (2×CH), 133.7 (2×C), 135.5 (4×CH), 155.6 (CO), 158.7 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 556.3 $[M+Na]^+$ (100). Elemental analysis: found: C 72.22, H 7.82, N 2.80; calcd. for $C_{32}H_{43}NO_4Si$ (533.8): C 72.00, H 8.12, N 2.62.

***tert*-Butyl *N*-[3-(*tert*-butyldiphenylsilyloxy)propyl]-*N*-[2-(4-iodophenoxy)ethyl] carbamate (16):** To a solution of compound **15** (11.7 g, 22.0 mmol) and iodine (3.07 g, 12.1 mmol) in $CHCl_3$ (200 mL), bis(trifluoroacetoxy)iodobenzene (5.20 g, 12.1 mmol) was added in small portions at 0 °C, and the mixture was stirred overnight at room temperature. The solution was washed with 5% aq. Na_2SO_3 (200 ml), water, brine, dried and evaporated under reduced pressure. The product was isolated as yellow oil (13.6 g; 89% yield) after filtration through SiO_2 (300 mL) and eluting with CH_2Cl_2 (it contained ca. 5% of the starting material). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, *t*BuSi), 1.41 (s, 9 H, *t*Bu), 1.73–1.89 (m, 2 H, CH_2), 3.36–3.48 (m, 2 H, NCH_2CH$_2$CH$_2$O), 3.48–3.62 (m, 2 H, OCH$_2$CH_2N), 3.62–3.74 (m, 2 H, NCH$_2$CH$_2$CH_2O), 3.95–4.13 (m, 2 H, OCH_2CH$_2$N), 6.61–6.69 (m, 2 H, CH), 7.32–7.46 (m, 6 H, CH), 7.49–7.57 (m, 2 H, CH), 7.62–7.73 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 19.2 (CSi), 26.9 (3×CH_3), 28.4 (3×CH_3), 31.2/31.8 (CH_2), 45.5/46.2 (CH_2N), 46.8/47.1 (CH_2N), 61.6 (CH_2OSi), 66.6/66.8 (CH_2N), 79.6 (C), 82.8 (CI), 116.8 (2×CH), 127.6 (4×CH), 129.6 (2×CH), 133.7 (2×C), 135.5 (4×CH), 138.2 (2×CH), 155.6 (CO), 158.6 ppm (CO). ESI-MS, positive mode, m/z (rel. int., %): 682.2 (100) $[M+Na]^+$. HR-MS (ESI, positive mode): found: 682.1819; calcd. for $C_{32}H_{42}INO_4Si$: 682.1820 $[M+Na]^+$.

***tert*-Butyl *N*-[3-(*tert*-butyldiphenylsilyloxy)propyl]-*N*-[2-[4-(thiophen-2-yl)phenoxy]ethyl] carbamate (18):** Iodide **16** (12.9 g, 19.5 mmol), thiophen-2-boronic acid (**17**, 3.00 g, 23.4 mmol), $Pd(dba)_2$ (0.2 g, 0.4 mmol) and PPh_3 (0.4 g, 1.6 mmol) were loaded into the Schlenk-flask with a reflux condenser and a bubble-counter. The flask was evacuated and flushed with argon several times. Then THF (100 mL) and 20% aq. Na_2CO_3 (100 mL) were added, and the mixture was refluxed (bath temp. 78 °C) for 12 h. After dilution with EtOAc (100 mL), the organic layer was separated, washed with brine, dried, and evaporated under reduced pressure. The title product was isolated as yellow oil (10.6 g, 88%) by chromatography on SiO_2 (200 g) with hexane/EtOAc mixture (8:1) as an eluent. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, *t*BuSi), 1.42 (s, 9 H, *t*Bu), 1.74–1.90 (m, 2 H, CH_2), 3.39–3.51 (m, 2 H, NCH_2CH$_2$CH$_2$O), 3.52–3.64 (m, 2 H, OCH$_2$CH_2N), 3.64–3.76 (m, 2 H, NCH$_2$CH$_2$CH_2O), 4.02–4.16 (m, 2 H, OCH_2CH$_2$N), 6.86–6.93 (m, 2 H, CH), 7.05 (dd, J = 3.6, 5.0 Hz, 1 H, CH), 7.18–7.24 (m, 2 H, CH), 7.33–7.47 (m, 6 H, CH), 7.48–7.55 (m, 2 H, CH), 7.64–7.70 ppm (m, 4 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$, 2 rotamers): δ = 19.1 (CSi), 26.7 (3×CH_3), 28.3 (3×CH_3), 31.1/31.7 (CH_2), 44.2–47.1 (2×CH_2N), 61.6 (CH_2OSi), 66.4/66.8 (CH_2O), 79.6 (C), 114.8 (2×CH), 122.2 (CH), 123.9 (CH), 127.3 (2×CH), 127.8 (4×CH), 128.0 (CH), 129.7 (2×CH), 133.9 (2×C-Si), 135.7 (4×CH), 143.5 (C), 144.4 (C), 155.8 (CO), 158.5 ppm

(CO). ESI-MS, positive mode, m/z (rel. int., %): 616.3 $[M+H]^+$ (100). Elemental analysis: found: C 70.48, H 7.08, N 2.33; calcd. for $C_{36}H_{45}NO_4SSi$ (615.9): C 70.20, H 7.36, N 2.27.

***tert*-Butyl *N*-[3-(*tert*-butyldiphenylsilyloxy)propyl]-*N*-[2-[4-(5-iodothiophen-2-yl)phenoxy]ethyl] carbamate (19):** To a mixture of compound **18** (10.4 g, 16.9 mmol) and KOAc (1.8 g, 18.6 mmol) in AcOH (100 mL), 0.5 M solution of ICl in AcOH (37 mL, 18.6 mmol ICl) was added at 0 °C, and the mixture was stirred at 50 °C for 12 h. After cooling, AcOH was evaporated under reduced pressure, and the semi-solid residue was triturated with cold 5% aq. Na_2SO_3 and CH_2Cl_2 (250 mL each). The organic layer was separated, washed with water, brine, dried and evaporated under reduced pressure. The title product was isolated as yellow oil (9.5 g; 78% yield) by chromatography (200 g SiO_2) eluting with hexane/EtOAc (30:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, *t*BuSi), 1.42 (s, 9 H, *t*Bu), 1.75–1.89 (m, 2 H, CH_2), 3.37–3.50 (m, 2 H, $NCH_2CH_2CH_2O$), 3.52–3.64 (m, 2 H, OCH_2CH_2N), 3.64–3.75 (m, 2 H, $NCH_2CH_2CH_2O$), 4.01–4.17 (m, 2 H, OCH_2CH_2N), 6.84–6.92 (m, 2 H, CH), 7.18 (d, *J* = 3.8 Hz, 1 H, CH), 7.33–7.46 (m, 8 H, CH), 7.63–7.69 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.2 (CSi), 26.8 (3×CH_3), 28.4 (3×CH_3), 31.3/31.8 (CH_2), 45.4/46.21 (CH_2N), 46.8/47.1 (CH_2N), 61.6 (CH_2OSi), 66.4/66.8 (CH_2O), 71.0 (CI), 79.6 (C), 114.8 (2×CH), 123.5 (CH), 126.5 (C), 127.1 (2×CH), 127.6 (4×CH), 129.6 (2×CH), 133.7 (2×CSi), 135.5 (4×CH), 137.8 (CH), 150.3 (C), 155.6 (CO), 158.7 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 1505.4 $[2M+Na]^+$ (35), 764.1 $[M+Na]^+$ (100), 741.8 $[M+H]^+$ (22). HR-MS (ESI, positive mode): found: 764.1691; calcd. for $C_{36}H_{44}INO_4SSi$: 764.1697 $[M+Na]^+$.

***tert*-Butyl *N*-(3-hydroxypropyl)-*N*-[2-[4-(5-iodothiophen-2-yl)phenoxy]ethyl] carbamate (20):** To a solution of iodide **19** (9.23 g, 12.5 mmol) in THF (40 mL), 1 M solution of Bu_4NF in THF (18.8 mL) was added, and the mixture was stirred at room temperature for 2 h. Then it was diluted with Et_2O (100 mL), washed with water, brine, and dried over Na_2SO_4. After evaporation of the solvents under reduced pressure, the title compound was isolated by chromatography (200 g SiO_2) eluting with CH_2Cl_2/MeOH (10:1) to give 6.0 g (95%) of colorless powder; m. p. 88–89 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 9 H, *t*Bu), 1.63–1.87 (m, 2 H, CH_2), 3.39–3.79 (m, 6 H, CH_2), 4.03–4.17 (m, 2 H, OCH_2CH_2N), 6.86 (d, *J* = 3.8 Hz, 1H, CH), 6.84–6.92 (m, 2 H, CH), 7.18 (d, *J* = 3.8 Hz, 1 H, CH), 7.40–7.47 ppm (m, 2 H, CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.3 (3×CH_3), 30.5 (CH_2), 43.8 (CH_2N), 46.6 (CH_2N), 58.2 (CH_2OH), 66.2 (CH_2O), 71.1 (CI), 80.7 (C), 114.9 (2×CH), 123.7 (CH), 126.9 (C), 127.2 (2×CH), 137.9 (CH), 150.3 (C), 157.0 (CO), 158.5 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 1029.1 $[2M+Na]^+$ (100), 526.1 $[M+Na]^+$ (99). Elemental analysis: found: C 47.73, H 5.05, N 3.00; calcd. for $C_{20}H_{26}INO_4S$ (503.4): C 47.72, H 5.21, N 2.78.

***tert*-Butyl *N*-[2-[4-(5-iodothiophen-2-yl)phenoxy]ethyl]-*N*-[3-(4-methoxybenzyloxy)propyl] carbamate (21):** To a 35% suspension of KH in mineral oil (1.63 g, 14.0 mmol KH) in anhydrous THF (40 mL), compound **20** (3.52 g, 7.0 mmol) was added at 0 °C, and the mixture was stirred for 20 min at this temperature. Then 4-methoxybenzyl bromide (2.11 g, 10.5 mmol) was added at 0 °C followed by Bu_4NI (0.52 g, 1.4 mmol), and stirring was continued for 12 h at room temperature. An excess of KH was carefully destroyed with sat. aq. NH_4Cl, and the reaction mixture was diluted with EtOAc (80 mL). The organic layer was separated, washed with water, brine, and dried over Na_2SO_4. After evaporation of the solvents under reduced pressure, the title compound was isolated by chromatography (100 g SiO_2) eluting with hexane/EtOAc (4:1) to yield 4.0 g (92%) of yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 9 H,

*t*Bu), 1.80–1.93 (m, 2 H, CH_2), 3.34–3.43 (m, 2 H, $NCH_2CH_2CH_2O$), 3.43–3.51 (m, 2 H, OCH_2CH_2N), 3.52–3.62 (m, 2 H, $NCH_2CH_2CH_2O$), 3.79 (s, 3 H, OCH_3), 4.01–4.15 (m, 2 H, OCH_2CH_2N), 4.42 (s, 2 H, OCH_2), 6.83–6.92 (m, 5 H, CH), 7.18 (d, J = 3.7 Hz, 1 H, CH), 7.22–7.28 (m, 2 H, CH), 7.38–7.45 ppm (m, 2 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 28.4 (3×CH_3), 29.2 (CH_2), 45.6/46.2 (CH_2N), 46.8/47.2 (CH_2N), 55.2 (OCH_3), 66.3/66.6 (CH_2O), 67.5 (CH_2OPh), 71.0 (CI), 72.6 ($PhCH_2O$), 79.7 (C), 113.7 (2×CH), 114.8 (2×CH), 123.5 (CH), 126.5 (C), 127.0 (2×CH), 129.2 (2×CH), 130.4 (C), 137.8 (CH), 150.3 (C), 155.2/155.6 (CO), 158.6 (CO), 159.1 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 1269.2 (55) $[2M+Na]^+$, 662.1 (27) $[M+K]^+$, 646.1 (52) $[M+Na]^+$, 624.1 (100) $[M+H]^+$. HR-MS (ESI, positive mode): found: 624.1274; calcd. for $C_{28}H_{34}INO_5S$: 624.1275 $[M+H]^+$.

***tert*-Butyl *N*-[2-[4-[4'-bromo-3'-(2-*tert*-butyldiphenylsilyloxy)ethyl-5'-methyl-[2,2']bithio-phen-5-yl]phenoxy]ethyl] -*N*-[3-(4-methoxybenzyloxy)propyl] carbamate (22):** Iodide **21** (3.86 g, 6.2 mmol), PPh_3 (0.65 g, 2.5 mmol) and $Pd(dba)_2$ (0.36 g, 0.6 mmol) were placed into a Schlenk-flask. Then anhydrous THF (37.5 mL) was added, and the mixture was stirred at room temperature for 10 min. In the second Schlenk-flask, 2.5 M solution of *n*BuLi in hexane (3.7 mL, 9.3 mmol) was added dropwise at –78 °C to a solution of compound **6** (5.0 g, 9.3 mmol) in anhydrous THF (37.5 mL) under argon. The mixture was stirred for 1 h at –78 °C, and then 1 M $ZnCl_2$ in Et_2O (10.2 mL) was added dropwise. After that, this solution was warmed up to room temperature and added to the first Schlenk-flask. The resulted yellow mixture was stirred at 40 °C for 18 h, quenched with sat. aq. NH_4Cl (5 mL), washed with water, brine, and dried over Na_2SO_4. After evaporation of the solvents under reduced pressure, the title compound was isolated by chromatography (100 g SiO_2) eluting with hexane/EtOAc (8:1) to yield 4.9 g (84%) of yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (s, 9 H, *t*BuSi), 1.47 (s, 9 H, *t*Bu), 1.83–1.97 (m, 2 H, CH_2), 2.38 (s, 3 H, CH_3), 3.15 (t, J = 7.3 Hz, 2 H, CH_2CH_2OSi), 3.37–3.53 (m, 4 H, $NCH_2CH_2CH_2O$ and OCH_2CH_2N), 3.54–3.66 (m, 2 H, $NCH_2CH_2CH_2O$), 3.79 (s, 3 H, OCH_3), 3.88 (t, J = 7.3 Hz, 2 H, CH_2CH_2OSi), 4.04–4.18 (m, 2 H, OCH_2CH_2N), 4.44 (s, 2 H, OCH_2), 6.84–6.94 (m, 4 H, CH), 7.06 (d, J = 3.8 Hz, 1 H, CH), 7.09 (d, J = 3.8 Hz, 1 H, CH), 7.24–7.29 (m, 2 H, CH), 7.30–7.40 (m, 6 H, CH), 7.46–7.52 (m, 2 H, CH), 7.61–7.67 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 15.2 (CH_3), 19.1 (CSi), 26.8 (3×CH_3), 28.4 (3×CH_3), 29.2 (CH_2), 32.6 (CH_2C), 45.6/46.3 (CH_2N), 46.8/47.2 (CH_2N), 55.2 (OCH_3), 62.7 (CH_2OSi), 66.3/66.7 (CH_2O), 67.5 (CH_2OPh), 72.6 ($PhCH_2O$), 79.7 (C), 113.5 (CBr), 113.7 (2×CH), 114.8 (2×CH), 122.4 (CH), 127.0 (2×CH), 127.1 (CH), 127.6 (4×CH), 129.2 (2×CH), 129.5 (2×CH), 130.5 (C), 132.6 (2×C), 133.4 (2×C), 133.7 (2×CSi), 133.8 (C), 135.6 (4×CH), 144.3 (C), 155.7 (CO), 158.5 (CO), 159.1 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 976.2 and 978.2 $[M+Na]^+$ (100). Elemental analysis: found: C 64.16, H 6.07, N 1.53; calcd. for $C_{51}H_{60}BrNO_6S_2Si$ (955.1): C 64.13, H 6.33, N 1.47.

***tert*-Butyl *N*-[2-[4-[3'-[2-(*tert*-butyldiphenylsilyloxy)ethyl]-5'-methyl-4'-(heptafluoro-cyclopent-1-enyl)-[2,2']bithiophen-5-yl]phenoxy]ethyl]-*N*-[3-(4-methoxybenzyloxy)propyl] carbamate (23):** To a vigorously stirred solution of bromide **22** (1.9 g, 2.0 mmol) in anhydrous THF (25 mL), *n*BuLi (2.5 M in hexane, 2.0 mL, 3.0 mmol) was added dropwise at –78 °C, and the mixture was stirred for 1 h at –78 °C. Then cooled C_5F_8 (1 mL, 6.0 mmol) was quickly added, the mixture was stirred for 1 h at –78 °C, and then quenched with brine. The reaction mixture was allowed to warm up to room temperature and diluted with EtOAc (15 mL), washed with brine, dried, and evaporated under reduced pressure. The title compound (1.7 g; 78%; contains ca. 20% of the debrominated derivative **24** formed

from bromide **22** (^{1}H NMR)) was isolated as a grey oil by chromatography (100 g SiO_2) eluting with EtOAc. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (s, 9 H, *t*BuSi), 1.46 (s, 9 H, *t*Bu), 1.81–1.85 (m, 2 H, CH_2), 2.32 (s, 3H, CH_3), 3.00 (t, J = 7.7 Hz, 2H, CH_2CH$_2$OSi), 3.36–3.53 (m, 4 H, NCH_2CH$_2$CH$_2$O and OCH$_2$CH_2N), 3.53–3.63 (m, 2 H, NCH$_2$CH$_2$CH_2O), 3.66 (t, J = 7.7 Hz, 2 H, CH$_2$CH_2OSi), 3.78 (s, 3 H, OCH_3), 4.03–4.20 (m, 2 H, OCH_2CH$_2$N), 4.43 (s, 2 H, OCH_2), 6.83–6.95 (m, 4 H, CH), 7.00 (d, J = 3.7 Hz, 1 H, CH), 7.08 (d, J = 3.7 Hz, 1 H, CH), 7.23–7.41 (m, 8 H, CH), 7.44–7.52 (m, 2 H, CH), 7.55–7.65 ppm (m, 4 H, CH). ESI-MS, positive mode, *m/z* (rel. int., %): 1090.3 $[M+Na]^+$ (100). HR-MS (ESI, positive mode): found: 1068.3586; calcd. for $C_{56}H_{60}F_7NO_6S_2Si$: 1068.3592 $[M+H]^+$.

Photochromic compound 25: To a stirred solution of compound **9** (0.10 g, 0.17 mmol) in anhydrous THF (8 mL), 1.5 M solution of *t*BuLi (0.11 mL) was added dropwise at –78 °C, and the mixture was stirred for 30 min at –78 °C. Then a solution of compound **23** (0.15 g, 0.14 mmol) in THF (2 mL) was added, the reaction mixture was kept at –78 °C for 1 h, and at room temperature overnight. After dilution with EtOAc (20 mL), washing with brine, drying and evaporation under reduced pressure, the residue was filtered through SiO_2 (50 g) eluting with EtOAc giving 22 mg (10%) of the title compound as green foam. HPLC: 100% ACN, t_R (OF) = 7.5 min. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of rotamers): δ = 0.90–1.20 (m, 18 H, *t*BuSi), 1.30–1.55 (m, 9 H, *t*Bu), 1.71–1.85 (m, 2 H, CH_2), 2.23–2.51 (m, 6 H, CH_3), 2.92–3.05 (m, 2 H, CH_2CH$_2$OSi), 3.12–3.27 (m, 2 H, CH_2CH$_2$OSi), 3.28–3.60 (m, 6 H, NCH_2CH$_2$CH$_2$O, NCH$_2$CH$_2$CH_2O and OCH$_2$CH_2N), 3.60–3.68 (m, 2 H, CH$_2$OSi), 3.78 (s, 3 H, OCH_3), 3.85–3.92 (m, 2 H, CH$_2$OSi), 4.01–4.20 (m, 2 H, OCH_2CH$_2$N), 4.40 (s, 2 H, OCH_2), 6.80–6.93 (m, 4 H, CH), 7.00–7.80 (m, 30 H, CH), 8.42–8.58 ppm (m, 2 H, CH_{py}). $C_{88}H_{92}F_6N_2O_7S_4Si_2$ (1586.5), ESI-MS, positive mode, *m/z* (rel. int., %): 1609.4 $[M+Na]^+$ (100).

*Deprotection of compound **23***: To a solution of compound **23** (0.21 g, 0.2 mmol) in THF (1 mL), 1 M solution of Bu_4NF in THF (0.3 mL, 0.3 mmol) was added, and the mixture was stirred overnight at room temperature. Then it was diluted with EtOAc, washed with water, brine, dried and evaporated under reduced pressure. The residue was filtered through SiO_2 eluting with hexane/EtOAc (2:1) to afford compounds **27**, **28** and **29**.

Compound 27. Yield: 50 mg (30%) of yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, *t*Bu), 1.78–1.93 (m, 2 H, CH_2), 2.55 (s, 3 H, CH_3), 3.22–3.32 (m, 2 H, CH_2), 3.32–3.42 (m, 2 H, CH_2), 3.42–3.51 (m, 2 H, CH_2), 3.51–3.62 (m, 2 H, CH_2), 3.77 (s, 3 H, CH_3O), 3.99–4.19 (m, 2 H, CH_2O), 4.41 (s, 2 H, CH_2), 4.45–4.55 (m, 2 H, OCH_2), 6.81–6.92 (m, 4 H, CH), 6.94 (d, J = 3.7 Hz, 1 H, CH), 7.13 (d, J = 3.7 Hz, 1 H, CH), 7.19–7.30 (m, 2 H, CH), 7.43–7.54 ppm (m, 2 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 15.6 (CH_3), 28.4 (3×CH_3), 28.6/29.2 (CH_2), 30.0 (CH_2), 45.6/46.2 (CH_2N), 46.8/47.2 (CH_2N), 55.2 (CH_3O), 66.4/66.6 (CH_2OPh), 67.5 ($PhCH_2O$), 72.6 (2×CH_2O), 79.7 (C), 113.7 (2×CH), 114.9 (2×CH), 122.5 (CH), 124.1 (C), 126.5 (C), 127.0 (2×CH), 127.5 (C), 128.2 (CH), 129.2 (2×CH), 130.4 (C), 131.9 (C), 138.6 (C), 138.9 (C), 145.4 (C), 155.3/155.6 (CO), 158.7 (CO), 159.1 ppm (CO). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –102.2 (s, 2 F), –118.4 (s, 2 F), –132.0 ppm (s, 2 F). ESI-MS, positive mode, *m/z* (rel. int., %): 1640.7 (100) $[2M+Na]^+$, 832.1 (84) $[M+H]^+$. HR-MS (ESI, positive mode): found: 810.2352; calcd. for $C_{40}H_{41}F_6NO_6S_2$: 810.2352 $[M+H]^+$.

Compound 28. Yield: 100 mg (48%) of grey powder. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 0.92 (s, 9 H, *t*BuSi), 1.38 (s, 9 H, *t*Bu), 1.70–1.84 (m, 2 H, CH_2), 2.10 (s, 3 H, CH_3), 2.96 (m, 2 H, CH_2), 3.31 (m, 2 H, CH_2), 3.41 (t, J = 6.2 Hz,

2 H, CH_2), 3.52 (t, J = 5.7 Hz, 2 H, CH_2N), 3.60 (m, 2 H, CH_2), 3.72 (s, 3 H, CH_3O), 4.12 (t, J = 5.7 Hz, 2 H, CH_2O), 4.36 (s, 2 H, CH_2), 6.84–6.91 (m, 2 H, CH), 6.94–7.02 (m, 3 H, CH), 7.19–7.26 (m, 2 H, CH), 7.28–7.43 (m, 7 H, CH), 7.49–7.59 ppm (m, 6 H, CH). ^{13}C NMR (75 MHz, [D$_6$]DMSO, 2 rotamers): δ =14.0 (CH_3), 18.6 (CSi), 26.4 (3×CH_3), 27.9 (3×CH_3), 28.6 (CH_2), 31.7 (CH_2), 44.6/45.4 (CH_2N), 46.1 (CH_2N), 54.9 (CH_3O), 63.2 (CH_2O), 65.9 (CH_2OPh), 66.9 ($PhCH_2O$), 71.5 (CH_2O), 78.6 (C), 113.5 (2×CH), 115.0 (2×CH), 122.8 (CH), 126.2 (CH), 126.4 (2×CH), 127.0 (C), 127.6 (4×CH), 129.0 (2×CH), 129.5 (2×CH), 130.4 (2×C), 131.9 (C), 133.2 (2×C-Si), 134.1 (C), 134.8 (4×CH), 135.3 (C), 142.4 (2×C), 154.6 (CO), 157.9 (CO), 158.6 ppm (CO). ^{19}F NMR (282 MHz, [D$_6$]DMSO): δ = –125.7 ppm (s, 4 F). ESI-MS, negative mode, *m/z* (rel. int., %): 1042.5 (100) $[M–H]^–$. HR-MS (ESI, positive mode): found: 1044.3610; calcd. for $C_{56}H_{61}F_4NO_8S_2Si$: 1044.3622 $[M+H]^+$.

Compound 29. Yield: 23 mg (18%) of yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (s, 9 H, *t*Bu), 2.44 (s, 3H, CH_3), 2.99 (t, J = 6.6 Hz, 2 H, CH_2), 3.33–3.42 (m, 2 H, CH_2), 3.42–3.49 (m, 2 H, CH_2), 3.49–3.61 (m, 2 H, CH_2), 3.77 (s, 3 H, CH_3O), 3.87 (t, J = 6.6 Hz, 2 H, CH_2), 4.00–4.14 (m, 2 H, CH_2), 4.40 (s, 2 H, CH_2O), 6.64 (s, 1 H, CH), 6.81–6.90 (m, 4 H, CH), 7.01 (d, J = 3.7 Hz, 1 H, CH), 7.10 (d, J = 3.7 Hz, 1 H, CH), 7.20–7.26 (m, 3 H, CH), 7.45–7.51 ppm (m, 2 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 15.2 (CH_3), 28.4 (3×CH_3), 28.6/29.2 (CH_2), 32.5 (CH_2), 45.6/46.2 (CH_2N), 46.9/47.2 (CH_2N), 55.2 (CH_3O), 62.8 (CH_2O), 66.3/66.6 (CH_2OPh), 67.5 ($PhCH_2O$), 72.6 (CH_2O), 79.7 (C), 113.7 (2×CH), 114.8 (2×CH), 122.3 (CH), 126.7 (CH), 126.9 (2×CH), 128.3 (CH), 129.2 (2×CH), 130.0 (C), 130.4 (C), 134.4 (C), 134.8 (2×C), 138.6 (C), 143.7 (C), 155.3/155.6 (CO), 158.3 (CO), 158.7 ppm (CO). ESI-MS, positive mode, *m/z* (rel. int., %): 1296.8 (56) $[2M+Na]^+$, 660.2 (100) $[M+Na]^+$. $C_{35}H_{43}NO_6S_2$, 637.3.

4-Bromo-3-(2-(*tert*-butyldiphenylsilyloxy)ethyl)-5-methyl-3-trimethylsilylthiophene (30): The bromide **6** (0.54 g, 1.0 mmol) in anhydrous THF (4 mL) was subjected to bromine-lithium exchange with 2.5 M solution of *n*BuLi in hexane (0.4 mL, 1.0 mmol) at –78 °C for 30 min followed by the addition of Me_3SiCl (1.3 mL, 10.0 mmol). The mixture was stirred at room temperature overnight, quenched with brine, and diluted with Et_2O (20 mL). The organic layer was separated, dried and evaporated under reduced pressure. The title compound was isolated by chromatography (50 g SiO_2) with hexane/EtOAc (4:1) to yield 0.52 g (98%) of colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.21 (s, 9 H, $SiCH_3$), 1.01 (s, 9 H, *t*BuSi), 2.30 (s, 3 H, CH_3), 2.90–3.05 (m, 2 H, CH_2), 3.63–3.76 (m, 2 H, CH_2O), 7.23–7.42 (m, 6 H, CH), 7.54–7.68 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 0.0 (3×CH_3), 15.2 (CH_3), 19.0 (CSi), 26.7 (3×CH_3), 34.5 (CH_2), 63.5 (CH_2O), 114.5 (CBr), 127.5 (4×CH), 129.4 (2×CH), 131.9 (C), 133.7 (2×C-Si), 135.5 (4×CH), 138.4 (C), 143.1 ppm (C). $C_{26}H_{35}BrOSSi_2$ (530.1), CI-MS (NH_3), positive mode, m/z (rel. int., %): 550 (100) and 548 (90) $[M+NH_4]^+$, 533 (56) and 531 (50) $[M+H]^+$.

Photochromic compound 31: To a solution of compound **30** (0.48 g, 0.90 mmol) in anhydrous THF (5 mL), 2.5 M solution of *n*BuLi in hexane (0.4 mL, 1.0 mmol) was added at –78 °C, and the mixture was stirred for 30 min at –78 °C. Then a solution of heptafluorocyclopentene **23** (0.19 g, 0.18 mmol) in THF (2 mL) was added. After 2 h, the reaction mixture was quenched with brine, diluted with EtOAc (20 mL), washed with brine, and dried. After evaporation of the solvents, the residue was applied on silica gel, and eluted with hexane/EtOAc (4:1 → 2:1) to yield 65 mg of the title compound as green foam (yield: 24%; according to ^{1}H NMR, contains ca. 20 mol.% of the debrominated derivative **24**). $C_{82}H_{95}F_6NO_7S_3Si_3$ (1499.5), ESI-MS, positive mode, m/z (rel. int., %): 1522.3 (100) $[M+Na]^+$.

***tert*-Butyl *N*-[3-(*tert*-butyldiphenylsilyloxy)propyl]-*N*-[2-[4-[3-[2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl]thiophen-2-yl]phenoxy]ethyl] carbamate (41):** To a solution of compound **34** (0.44 g, 1.5 mmol) in anhydrous THF (15 mL), 2.5 M solution of *n*BuLi in hexane (0.66 mL, 1.65 mmol) was added dropwise at –78 °C under argon, and the mixture was stirred for 1 h at –78 °C. Then $B(OiPr)_3$ (0.42 g, 2.25 mmol) was added, and the mixture was stirred for 1 h at –78 °C and 2 h at room temperature. After addition of water (0.5 mL), compound **16** (0.66 g, 1.0 mmol), Ph_3P (42 mg, 0.16 mmol), $Pd(dba)_2$ (23 mg, 0.04 mmol), and 20% aq. Na_2CO_3 (15 mL) were introduced, and the mixture was heated at 78 °C (bath temp.) for 18 h in a flask equipped with a reflux condenser and a bubble-counter. Then it was diluted with EtOAc (50 mL), the organic phase was separated, washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The title compound was isolated by chromatography (50 g SiO_2) eluting with hexane/EtOAc (8:1) to yield 0.17 g (23%) of yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (s, 9 H, *t*BuSi), 1.42 (s, 9 H, *t*Bu), 1.48–1.75 (m, 6 H, 3×CH_2, H-3/4/5), 1.75–1.89 (m, 2 H, $NCH_2CH_2CH_2O$), 2.94 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.39–3.51 (m, 3 H, $NCH_2CH_2CH_2O$ and C*H*H-6), 3.54–3.66 (m, 3 H, OCH_2CH_2N and C*H*HO), 3.67–3.81 (m, 3 H, $NCH_2CH_2CH_2O$ and CH*H*-6), 3.95 (dt, *J* = 7.1, 9.6 Hz, 1 H, CH*H*O), 4.03–4.16 (m, 2 H, OCH_2CH_2N), 4.59 (t, *J* = 3.3 Hz, 1 H, CHO), 6.88–6.94 (m, 2 H, CH), 7.03 (d, *J* = 5.2 Hz, 1 H, CH), 7.19 (d, *J* = 5.2 Hz, 1 H, CH), 7.36–7.42 (m, 8 H, CH), 7.64–7.69 ppm (m, 4 H, CH). ^{13}C NMR (75.5 MHz, $CDCl_3$, 2 rotamers): δ = 19.2 (CSi), 19.4 (CH_2-4), 25.4 (CH_2-5), 26.8 (3×CH_3, *t*BuSi), 28.4 (3×CH_3, *t*BuO), 29.1 (CH_2CH_2O), 30.6 (CH_2-3), 31.2/31.8 ($NCH_2CH_2CH_2O$), 45.4/46.3 (CH_2N), 46.9/47.2 (CH_2N), 61.6 (CH_2OSi), 62.0 (CH_2-6), 66.4/66.8 (OCH_2CH_2N), 67.6 (CH_2CH_2O), 79.6 (C), 98.6 (CHO), 114.4 (2×CH), 123.1 (CH), 126.9 (C), 127.6 (4×CH), 129.5 (CH), 129.6 (2×CH), 130.6 (2×CH), 133.7 (2×C), 134.3 (C), 135.5 (4×CH), 139.0 (C), 155.6 (CO), 158.2 ppm (CO). ESI-MS, positive mode, m/z (rel. int., %): 766.4 $[M+Na]^+$ (100). HR-MS (ESI, positive mode): found: 766.3578; calcd. for $C_{43}H_{57}NO_6SSi$: 766.3568 $[M+Na]^+$.

***tert*-Butyl *N*-methyl-*N*-[2-[4-[5'-methyl-4'-(heptafluorocyclopent-1-enyl)-4-[2-(tetrahydro-2*H*-pyran-2-yloxy)ethyl]-2,2'-bithiophen-5-yl]phenoxy]ethyl] carbamate (45):** According to the method used for the preparation of heptafluorocyclopentene **23**, bromide **44** (0.32 g, 0.50 mmol), 2.5 M solution of *n*BuLi in hexane (0.22 mL, 0.55 mmol), and C_5F_8 (0.7 mL, 5.0 mmol) afforded the title compound as yellowish oil. It was isolated by chromatography (100 g SiO_2) eluting with hexane/EtOAc (4:1); yield: 0.25 g (66%; according to HPLC, this substance contained ca. 20% of the debrominated derivative **46** formed from bromide **44**). HPLC: 70→100% A (30→0% B) for 0–20 min, 100% A for 20–25 min, t_R = 22.4 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 9 H, *t*Bu), 1.49–1.89 (m, 6 H, 3×CH_2, H-3/4/5), 2.45/2.46 (s, 3 H, CH_3), 2.91 (t, *J* = 6.9 Hz, 2 H, CH_2CH_2O), 3.00 (s, 3 H, CH_3N), 3.42–3.52 (m, 1 H, C*H*H-6), 3.56–3.68 (m, 3 H, OCH_2CH_2N, CH_2CHO), 3.71–3.82 (m, 1 H, CH*H*-6), 3.96 (dt, *J* = 6.9, 9.5 Hz, 1 H, CH_2CHHO), 4.05–4.19 (m, 2 H, OCH_2CH_2N), 4.61 (t, *J* = 3.3 Hz, 1 H, CHO), 6.89–6.97 (m, 2 H, 2×CH), 7.07 (s, 1 H, CH), 7.11 (s, 1 H, CH), 7.38–7.44 ppm (m, 2 H, 2×CH). ESI-MS, positive mode, *m/z* (rel. int., %): 772.2 $[M+Na]^+$ (100). HR-MS (ESI, positive mode): found: 772.1972; calcd. for $C_{35}H_{38}F_7NO_5S_2$: 772.1972 $[M+Na]^+$.

Betaine 48-THP was isolated as a by-product (orange powder) in the synthesis of compound **47** in an almost equal amount. ^{1}H NMR (300 MHz, [D_6]DMSO, 70 °C): δ = 1.33–1.53 (m, 4 H, CH_2), 1.53–1.69 (m, 2 H, CH_2), 2.51/2.52 (s, 3 H, CH_3), 3.16 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.34–3.47 (m, 1 H, C*H*HO), 3.57–3.68 (m, 1 H, C*H*HO), 3.69–3.82 (m, 1 H, C*H*HO), 3.91–4.06 (m, 1 H, C*H*HO), 4.58–4.62 (m, 1 H, CHO), 7.47 (s, 1 H, CH), 7.59 (s, 1 H, CH), 8.29 (d, *J* = 7.2 Hz, 2 H, CH), 9.30 ppm (d, *J* = 7.2 Hz, 2 H, CH). ^{13}C NMR (75.5 MHz, [D_6]DMSO, 70 °C): δ = 13.8 (CH_3), 18.7 (CH_2-4),

24.6 (CH_2-5), 29.4 (CH_2), 29.8 (CH_2-3), 32.0/32.4 (C), 61.1 (CH_2-6), 65.9 (CH_2O), 97.8 (CHO), 109.2 (3×C, C and 2×CF_2), 109.6 (CF_2), 110.2 (CF_2), 114.55 (CF_2), 119.6 (C), 124.3 (2×CH), 129.3 (2×CH), 135.1 (C), 133.4 (C), 138.7 (C), 141.0 (2×CH), 144.5 (C), 144.7 (C), 147.12 (C), 150.5 (=CF), 171.3 ppm (2×CO). ^{19}F NMR (282 MHz, [D_6]DMSO, 70 °C): δ = –106.4 (d, J = 12.6 Hz, 2 F), –117.2 (s, J = 16.4 Hz, 2 F), –126.5 (s, 5 F), –129.2 ppm (s, 2 F). ESI-MS, positive mode, *m/z* (rel. int., %): 768.1 $[M+Na]^+$ (100). HR-MS (ESI, positive mode): found: 768.0696; calcd. for $C_{31}H_{22}F_{11}NO_4S_2$: 768.0707 $[M+Na]^+$.

Photochromic compound 49: The title compound was isolated as green foam in the synthesis of compound **45**. HPLC: 50→100% A (50→0% B) for 0–25 min, t_R (OF) = 8.5 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45 (s, 18 H, *t*Bu), 1.47–1.86 (m, 12 H, CH_2), 1.89–2.16 (m, 6 H, CH_3), 2.89 (s, 4 H, CH_2), 2.98 (s, 6 H, CH_3N), 3.38–3.52 (m, 2 H, 2×C*H*H-6), 3.61 (s, 6 H, 2×CH_2N and 2×CH*H*OTHP), 3.68–3.80 (m, 2 H, 2×CH*H*-6), 3.87–4.00 (m, 2 H, 2×CH*H*OTHP), 4.03–4.18 (m, 4 H, CH_2O), 4.59 (s, 2 H, CH), 6.85–6.97 (m, 4 H, CH), 7.07 (s, 2 H, CH), 7.09 (s, 2 H, CH), 7.34–7.46 ppm (m, 4 H, CH). ESI-MS, positive mode, *m/z* (rel. int., %): 1268.1 (26) $[M+H]^+$, 1309.2 (100) $[M+Na]^+$. HR-MS (ESI, positive mode): found: 1309.4225; calcd. for $C_{65}H_{76}F_6N_2O_{10}S_4$: 1309.4179 $[M+Na]^+$.

Photochromic compound 50: The title compound was isolated as green foam in the synthesis of compound **47**. HPLC: 30→100% A (70→0% B) for 0–25 min, t_R (OF) = 21.1 min. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.45–1.85 (m, 12 H, CH_2), 1.96/2.16 (s, 6 H, CH_3), 2.98 (t, J = 6.6 Hz, 4 H, CH_2), 3.41–3.52 (m, 2 H, 2×C*H*H-6), 3.60–3.80 (m, 4 H, 2×CH*H*-6 and 2×C*H*HO), 3.93–4.07 (m, 2 H, 2×CH*H*O), 4.57–4.63 (m, 2 H, CH), 7.13 (s, 2 H, CH), 7.15 (s, 2 H, CH), 7.42–7.48 (m, 4 H, CH), 8.58–8.66 ppm (m, 4 H, CH). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –110.08 (t, J = 5.0 Hz, 4 F), –131.80 ppm (quint, J = 5.0 Hz, 2 F). ESI-MS, positive mode, *m/z* (rel. int., %): 943.2 (100) $[M+H]^+$. HR-MS (ESI, positive mode): found: 943.2167; calcd. for $C_{47}H_{44}F_6N_2O_4S_4$: 943.2161 $[M+H]^+$.

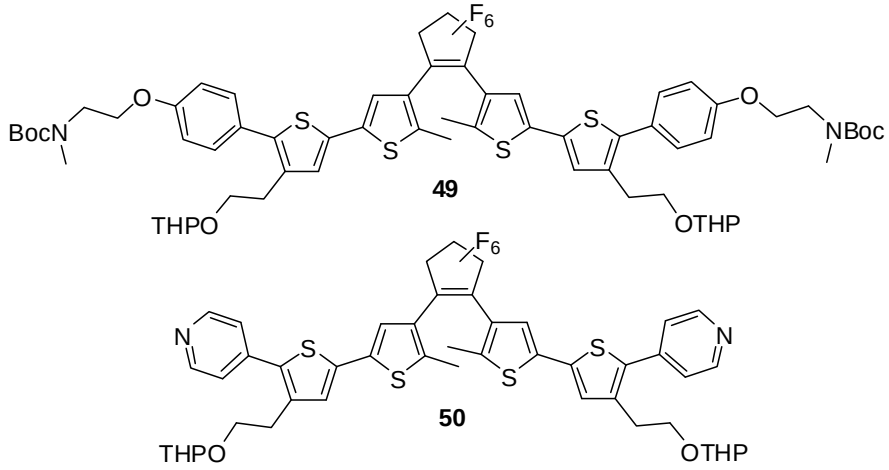

Figure S-1. Symmetric photochromic compounds formed along with heptafluorocyclopentenes **45** and **4**7 (see Schemes 12 and 13 in the main text).

Absorption Spectra

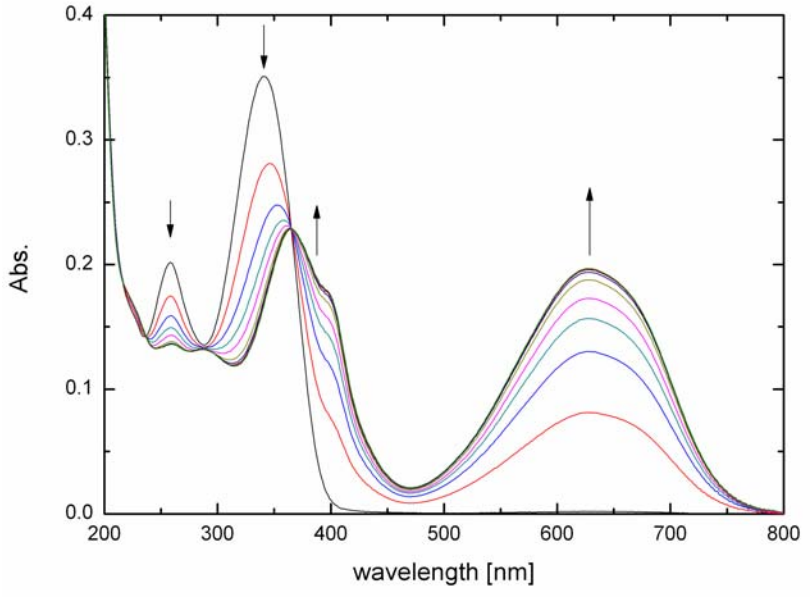

Figure S-2. Changes in the absorption spectra of diarylethene **52** in methanol upon irradiation with 366 nm light. The arrows indicate the directions of the changes.

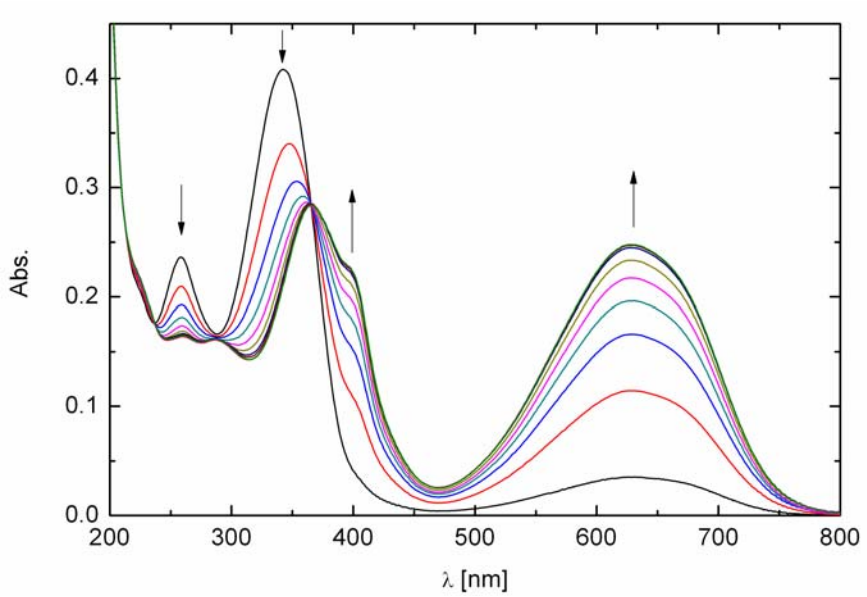

Figure S-3. Changes in the absorption spectra of diarylethene **54** in methanol upon irradiation with 366 nm light. The arrows indicate the directions of the changes.

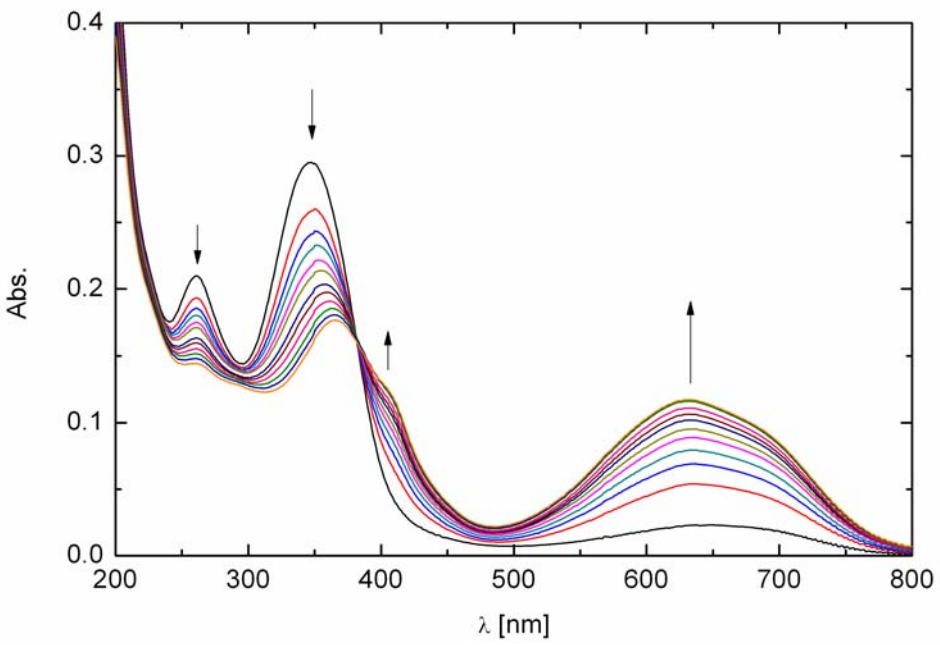

Figure S-4. Changes in the absorption spectra of diarylethene **54** in water upon irradiation with 366 nm light. The arrows indicate the directions of the changes.

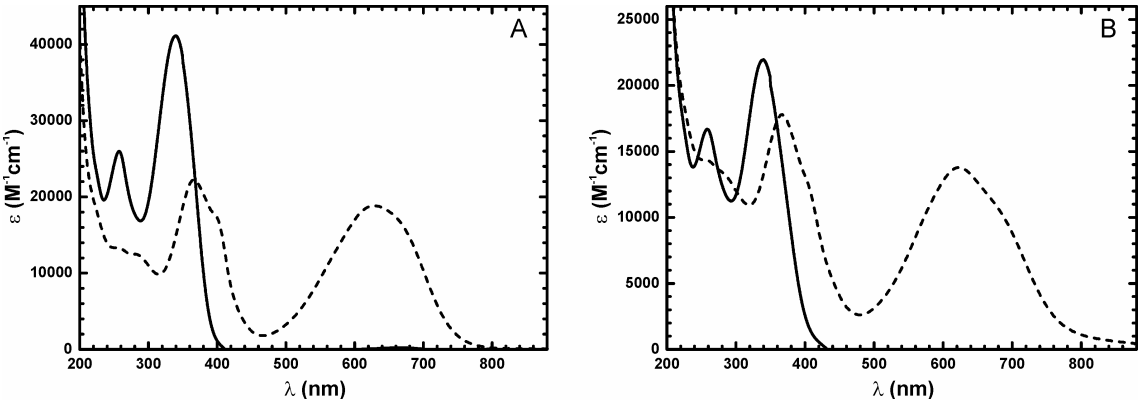

Figure S-5: Absorption coefficients of compound **57** in the open form (**57**-OF; solid lines) and the closed form (**57**-CF; dashed lines), in methanol (A) and water (B).