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# Supporting Information



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# Reversible Red Fluorescent Molecular Switches[**]

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## Description of the Synthesis

**General Remarks:** Melting points (uncorrected) were determined in capillaries using a SMP 10 apparatus (BIBBY STERLING LTD, UK). Routine NMR spectra were recorded with Varian MERCURY-300 and Bruker AM 250 spectrometers at 300 ($^1$H) and 75.5 MHz ($^{13}$C and APT), as well as at 250 ($^1$H) and 62.9 MHz ($^{13}$C and DEPT), respectively. $^1$H NMR spectra were also recorded with Varian INOVA 500 (500 MHz) and Varian INOVA 600 (600 MHz) instruments. All spectra are referenced to tetramethylsilane as an internal standard ($\delta$ = 0 ppm) using the signals of the residual protons of deuterated solvents: 7.26 for $CHCl_3$ and 2.50 for [$D_5$]DMSO. Multiplicities of signals are described as follows: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, $m_c$ = centrosymmetrical multiplet. Coupling constants (*J*) are given in Hz. EI-MS were recorded with MAT 95 (70 eV) and ESI-MS with LCQ spectrometers (Fa. Finnigan). HPLC-System (Knauer): Smartline pump 1000 (2×), UV-detector 2500, column thermostat 4000, mixing chamber, injection valve with 20 and 100 µL loop for the analytical and preparative columns, respectively; 6-port-3-channel switching valve; analytical column: Eurospher-100 C18, 5 µm, 250×4 mm; preparative column: Eurosphere-100 C18, 5 µm, 250×8 mm; solvent A: MeCN + 0.1% v/v TFA, solvent B: $H_2O$ + 0.1% v/v TFA. Injections of the irradiated solutions in EtOH allowed the direct measurements of the ratios of the open and closed forms at the photostationary state (detection at the isobestic point). Analytical TLC was performed on MERCK ready-to-use plates with silica gel 60 ($F_{254}$) and developed by molybdatophosphoric acid acid solution (5% in EtOH). Flash chromatography: MERCK silica gel, grade 60, 0.04-0.063 mm; fraction collector RETRIVER II (ISCO). Elemental analyses were carried out at Mikroanalytisches Laboratorium des Instituts für Organische und Biomolekulare Chemie der Georg-August-Universität Göttingen. THF and ether were dried with Na – benzophenone. Organic solutions were dried over $MgSO_4$. All reactions were carried out with magnetic stirring under positive argon pressure using the standard technique with vacuum – inert gas manifold, unless stated otherwise. Precise calculations of molecular masses for the highly resolved mass-spectra were based on the following assumptions: C 12.00000, H 1.007825, F 18.998403, N 14.003074, O 15.994915, S 31.972072.

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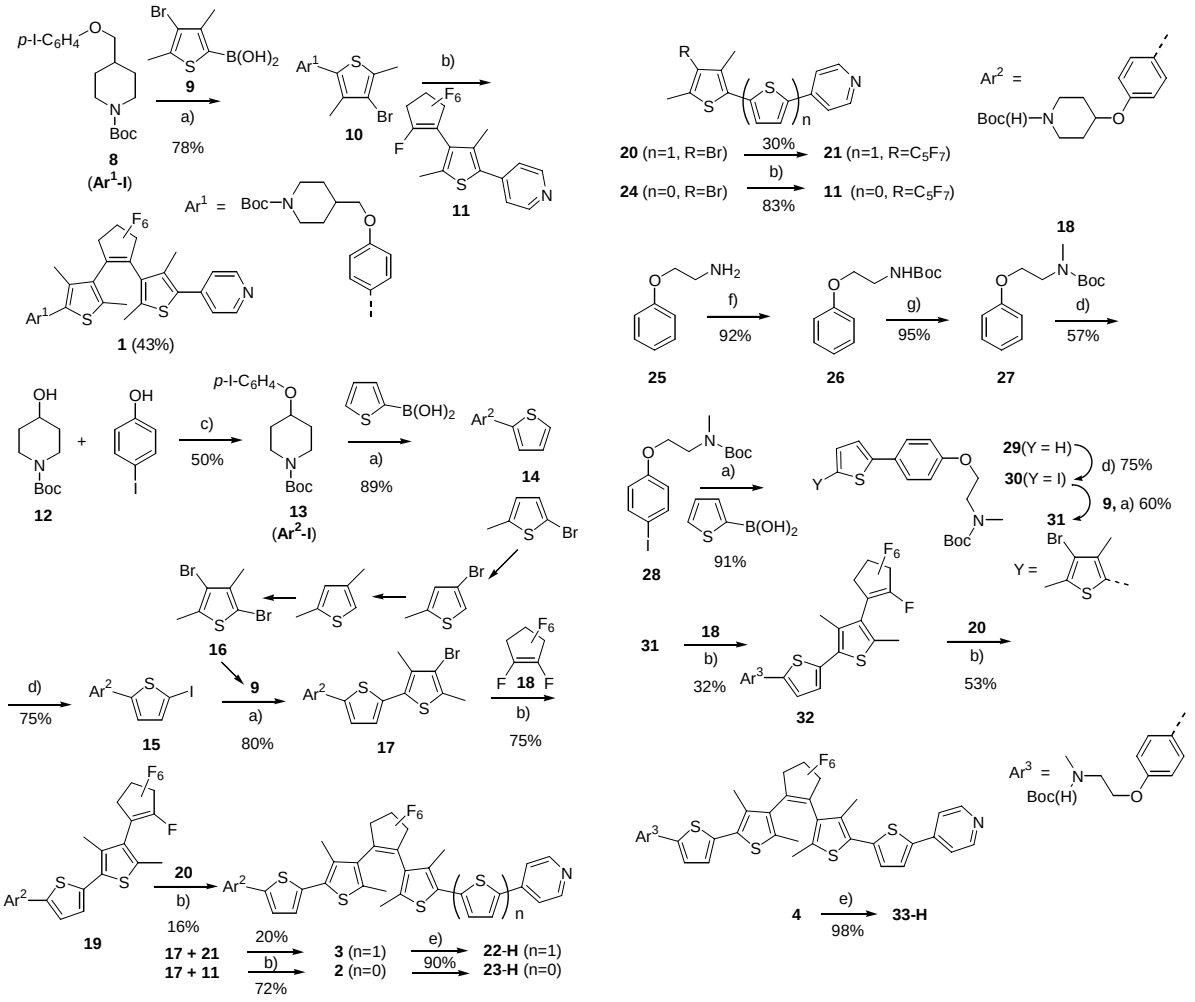

***Scheme 1.*** Synthesis of the photochromic units: a) $Pd(dba)_2$, $Ph_3P$, 20% aq. $Na_2CO_3$, THF, reflux; b) BuLi in hydrocarbon, -78 °C, THF; c) $Ph_3P$, *i*-PrOCO-N=N-$CO_2$Pr-*i*, THF, r. t., 24 h; d) ICl, AcOH, AcOK, 60 °C, 5 h; e) 4 M HCl in dioxane, r. t., 3 h; f) $Boc_2O$, $CHCl_3$, room temp.; g) MeI, $Ag_2O$, DMF, room temp.

**2-Bromo-5-methylthiophene** was prepared in 80% yield according to the published procedure.[1]

**4-Bromo-2-methylthiophene** was synthesized by a procedure of a "halogene dance":[2] *n*-BuLi (2.5 M in hexanes, 68.0 mL, 170 mmol) was added dropwise to the solution of *i*$Pr_2NH$ (17.2 g, 170 mmol) in THF (100 mL) at 0 °C within 30 min. This solution of LDA was left for warming-up to room temperature. In another 500 mL dry flask equipped with a dropping funnel and an argon inlet tube, a solution of 2-bromo-5-methylthiophene (30.0 g, 169 mmol) in 100 mL THF was prepared. The LDA solution was transferred to the dropping funnel under Ar and added dropwise at −78 °C within ca. 2 h to the solution in the flask. Then 20 mL of MeOH were slowly added for quenching. After warming-up to room temperature, saturated aq. $Na_4Cl$ was added (100 mL), followed by $Et_2O$ (400 mL). The organic layer was separated, washed with water, brine and dried. After the removal of solvents in vacuo, the residue was purified by distillation to yield 4-bromo-2-methylthiophene as a colourless

[1] Y. Goldberg, H. Alper, *J. Org. Chem.* **1993**, *58*, 3072−3075

[2] This procedure was similar to the method reported by J. Froehlich, C. Hameter and W. Kalt (*Monatsh. für Chemie* **1996**, *127*(3), 325−330) who isolated 4-bromo-2-methylthiophene in 53% yield.

oil (24.0 g, 80%) with b. p. 67–68 °C (20 mm Hg). $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.47 (d, *J* = 1.3, 3 H), 6.69 (d, *J* = 1.3, 1 H), 6.98 (m, 1 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm): δ = 15.3 (Me), 108.9, 120.3, 127.8, 141.1.

**2,4-Dimethylthiophene** was prepared by a modified procedure:[3] A three-necked flask equipped with a refluxed condenser and an inlet tube was charged with Ni(dppp)$Cl_2$ (150 mg, 0.32 mmol), 4-bromo-2-methylthiophene (12.4 g, 70 mmol) and 20 ml of dry ether. A solution of MeMgCl (2.85 M in THF, 49 mL, 0.14 mol) was added at +5 °C over 20 min with a help of a syringe pump. The yellow mixture was refluxed under nitgrogen for 22 h at 70 °C (bath temperature). After cooling to 0°C, the mixture was poured into the cold 2% aq. HCl solution (250 mL), and extraxcted with ether (3×50 mL). After drying, the solvent was evaporated at a normal pressure (bath tempertature did not exceed 50 °C), and the residue was subjected to fractional distillation to give a title compound as a colorless oil (6.2 g, 79%) with b. p. 138–140 °C. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.21 (d, *J* = 0.8, 3 H), 2.46 (d, *J* = 1, 3 H), 6.58 (d, *J* = 0.8, 1 H), 6.65 (quint, *J* = 1, 1 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm): δ = 15.2 (Me), 15.6 (Me), 118.1 (CH), 127.6(CH), 137.48, 139.5. MS (EI): *m/z* (rel. int., %) = 112 (70) [$M^{+\cdot}$], 111 (100) [$(M–H)^+$].

**2,4-Dibromo-3,5-dimethylthiophene** (**16**) was synthesized from 2,4-dimethylthiophene according to the published bromination method[4] with addition of 2 molar equivalents of AcONa. B. p. 120–125 °C (2 mm Hg). $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.17 (s, 3 H), 2.34 (s, 3 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm): δ = 15.4 (Me), 16.1 (Me) 104.7 (C-Br), 111.3 (C-Br), 133.8, 136.2. MS (EI): *m/z* (rel. int., %) = 272 (35) [$M(^{81}Br_2)^{+\cdot}$], 270 (90) [$M\ (^{81}Br + {}^{79}Br)^{+\cdot}$], 268 (35) [$M(^{79}Br_2)^{+\cdot}$], 110 (100).

**3,5-Dimethyl-4-bromothiophen-2-boronic acid (9)** was synthesized from 2,4-bromo-3,5-dimethyl thiophene as described for the similar compound (with triisopropyl borate instead of tributyl borate).[5] $^1$H NMR (250 MHz, [$D_6$] DMSO, ppm): δ = 2.29 (s, 3 H), 2.34 (s, 3 H), ~ 7.9 br.s (2 H). $^{13}$C NMR (62.9 MHz, [$D_6$] DMSO, ppm): δ = 15.6 (Me), 16.7 (Me), 114.3 (C-Br), 138.1 (C), 147.0 (C), 150.9 (C). Excessive drying of the freshly precipitated (wet) samples of this boronic acid leads to the loss of water and formation of the corresponding anhydride with chemical shifts of methyl groups, which differ from these of the acid **9** (in the $^1$H NMR spectrum).

***N-tert*-Butoxycarbonyl-4-[4-(3,5-dimethyl-4-bromothiophen-2-yl)phenoxymethyl]piperdine (10):** Iodide **8**[6] (0.75 g, 1.80 mmol), boronic acid **9** (0.604 g, 2.58 mmol), $Pd(dba)_2$ (57.5 mg, 0.10 mmol) and $Ph_3P$ (105 mg, 0.40 mmol) were placed into the Schlenk-flask with a reflux condenser and bubble-counter. This set-up was evacuated and flushed with argon several times. Then THF (8 mL) and 20% aq. $Na_2CO_3$ (8 mL) were added, and the mixture was refluxed overnight (bath temp. 95-98 °C). It was diluted with EtOAc (50 mL), organic layer was separated, dried, and evaporated in vacuo. The product was isolated as yellow oil (0.86 g) by chromatography on silica gel (120 g) with hexane/EtOAc mixture (6:1→ 4:1) as eluent. After solidification, the product was recrystallized from MeOH and gave 0.626 g (78%) of white solid (in 2 crops) with m.p. 120 °C. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.28 ("dq", *J* = 17 and 5, 2 H), 1.47 (s, 9 H), 1.82 (br. d, *J* = 13, 2 H), 1.98 ($m_c$, 1 H), 2.24 (s, 3 H), 2.41 (s, 3 H), 2.73 ("t", *J* = 13, 2 H), 3.82 (d, J = 6.5, 2 H), 4.15 (br. d, *J* = 13, 2 H), 6.91 (d, *J* = 8.8, 2 H), 7.30 (d, *J* = 8.8, 2 H). $^{13}$C NMR ($CDCl_3$, 62.9 MHz): δ = 15.1 (Me), 15.4 (Me), 28.4 (*t*Bu), 28.8 ($CH_2$), 36.2 (CH), 43.5 (br., $CH_2N$),

[3] M. Takeshita, M. Tashiro, *J. Org. Chem.* **1991**, *56*, 2837–2845
[4] M. Irie, K. Sakemura, M. Okinaka and K. Uchida, *J. Org. Chem.* **1995**, *60*, 8305–8309
[5] J. M. Lehn et al., *Chem.–Eur. J.* **1995**, *1*, 275–284
[6] R. N. Waterhouse, T. L. Collier, J. C. O'Brien, *J. Labelled Comp.* **1996**, *38*(7), 595–605.

72.3 ($CH_2O$), 79.3 (C-O), 113.4 (C), 114.5 (CH), 126.9 (C), 130.2 (CH), 131.6 (C), 134.4 (C), 154.8 (C), 158.5 (C); MS (EI): *m/z* (rel. int., %) = 481 (24) $[M(^{81}Br)]^{+\cdot}$, 479 (22) $[M(^{79}Br)]^{+\cdot}$, 284 (22), 282 (20), 142 (100), 98 (38), 57 (32). $C_{23}H_{30}BrNO_3S$ (480.49): calcd. C 57.49, H 6.29, N 2.92; found.

**3-Bromo-2,4-dimethyl-5-(4-pyridyl)thiophene (24):** Boronic acid **9** (3.08 g, 13.2 mmol), 4-bromopyridine hydrochloride (4.25 g, 21.9 mmol), $Pd(dba)_2$ (0.30 g, 0.52 mmol) and $Ph_3P$ (0.55 g, 2.1 mmol) were placed into the Schlenk-flask, which was evacuated, filled with Ar, and then THF (20 mL) and 20 % aq. $Na_2CO_3$ (20 mL) were added. The mixture was refluxed overnight (95–98 °C bath temp.), cooled and diluted with EtOAc (50 mL). Combined organic layers were dried, evaporated, and the title comp. was isolated by chromatography on $SiO_2$ (100 g); elution with $CH_2Cl_2$ + 1% v/v $Et_3N$ and acetone (0→10% v/v of acetone). Yield – 3.08 g (87%) of white solid after recrystallization from aq. MeOH, m.p. 93 °C. $^1$H NMR ($CDCl_3$, 250 MHz, ppm): δ = 2.33 (s, 3 H), 2.47 (s, 3 H), 7.32 ($m_c$, 2 H), 8.62 ($m_c$, 2 H). $^{13}$C NMR (75.5 MHz, $CDCl_3$, ppm): δ = 15.3 (Me), 15.9 (Me), 114.6 (C), 122.9 (CH), 131.5 (C), 134.5 (C), 134.6 (C), 142.0 (C), 150.1 (CH). EI-MS: *m/z* (rel. int., %) = 271 (4), 270 (11), 269 (100) $[M(^{81}Br)]^{+\cdot}$, 268 (26), 267 (100) $[M(^{79}Br)]^{+\cdot}$, 266 (15), 188 (76).

**2,4-Dimethyl-3-(perfluorocyclopenten-1-yl)-5-(4-pyridyl)thiophene (11):** Thienyl bromide **24** (3.21 g, 12.0 mmol) was dissolved in THF (70 mL) at room temperature, and the solution was cooled down to −78 °C with vigoros stirring. To the suspension, which was formed, *n*BuLi (2.5 M in hexanes, 5.0 mL, 16.5 mmol) was added dropwise. The red-brown suspension was stirred for 20 min at –78 °C, transferred to the syringe with a thick needle and was added quickly (while cold) to the vigorosly stirred solution of $C_5F_8$ (3.5 g, 16.5 mmol) in THF (30 mL) at –78 °C. During the addition the suspension of 3-thienyl lithium in the syringe became brighter. Addition was accompanied by the exothermic reaction, and the suspension of 3-thienyl lithium disappeared. The reaction solution was stirred for 30 min at –78 °C, and then quenched with the cold mixture of brine (100 mL) with 10 mL 0.5 M aq. $H_2SO_4$. The reaction mixture was allowed to warm up to room temperature and diluted with EtOAc (100 mL). The organic layer was separated, washed with brine (200 mL), dried and evaporated. The residue was taken-up in cyclohexane-EtOAc mixture (2:1) and purified on $SiO_2$ (100 g), eluting with cyclohexane-EtOAc (2:1→1:1). The title compound was isolated as a green solid (3.8 g, 83%) which was recrystallized from aq. MeOH to give a light brown solid with m.p. 96–97 °C. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.18 (s, 3 H), 2.43 (s, 3 H), 7.32 ($m_c$, 2 H), 8.63 ($m_c$, 2 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm):[7] δ = 14.1 (Me×2), 121.6 (C), 123.2 (CH), 133.7 (C), 134.2 (C), 141.4 (C), 142.1 (C), 150.2 (CH). EI-MS: *m/z* (rel. int., %) = 383 (4) [M+3], 328 (18) [M+2], 381 (100) $[M^{+\cdot}]$, 380 (19) $[M–H]^+$, 366 (14) $[M–CH_3]^+$, 303 (7). $C_{16}H_{10}NSF_7$ (381.31): calcd. C 50.40, H 2.64, N 3.67; found C 50.60, H 2.51, N 3.83.

***N*-*tert*-Butoxycarbonyl-4-(4-iodophenoxy)piperidine (13):** *p*-Iodophenol (2.20 g, 10 mmol), triphenylphosphine (2.73 g, 10.4 mmol), and *N*-Boc-4-hydroxypiperdine (ACROS ORGANICS, 2.10 g, 10.4 mmol) were dissolved in dry THF (20 mL), and diisopropyl azodicarboxylate (FLUKA, 2.12 g, 2.02 mL, 10.5 mmol) was added dropwise by cooling at such a rate, that the internal temperature did not exceed 25 °C. The mixture was stirred overnight at room temperature, evaporated in vacuo, and the residue was taken up in a small amount of dichlormethane and applied on top of the column with 115 g of $SiO_2$. Elution with hexane/ether mixture (4:1→ 2:1) afforded oil, which was dissolved in hot MeOH. Water (ca. 10–15 % v/v) was added and the solution was left at +5 °C. After ca. 16 h, white crystals were flitered-off and air-dried. Yield – 2.0 g (50 %), m. p. 89 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.43 (s, 9 H), 1.64–1.75 (m, 2 H), 1.83–1.92 (m, 2 H), 3.26–3.34 (m, 2 H), 3.60–3.69 (m, 2 H), 4.40 (m, 1 H), 6.65 (d, *J* = 9, 2 H), 7.46 (d, *J* = 9, 2 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm): δ = 28.4 (Me),

[7] Due to low intensities, signals of the fluorinated carbons were not detected.

30.3 ($CH_2$), 40.8 br. ($CH_2N$), 72.2 (CHO), 79.6 (C-O), 83.0 (C-I), 118.4 (CH), 138.3(CH), 154.7 (C), 157.0 (C). MS (EI): *m/z* (rel. int., %) = 403 (28) [$M^{+\cdot}$], 330 (10), 220 (36), 184 (73), 128 (32), 84 (82), 57 (100). $C_{16}H_{22}NIO_3$ (403.25): calcd. C 47.66, H 5.50, N 3.47; found C 47.54, H 5.50, N 3.47.

***N-tert*-Butoxycarbonyl-4-[4-(thiophen-2-yl)phenoxy]piperdine (14):** Iodide **13** (1.27 g, 3.15 mmol), thiophen-2-boronic acid (1.00 g, 7.82 mmol), $Pd(dba)_2$ (80.5 mg, 0.14 mmol) and $Ph_3P$ (147 mg, 0.56 mmol) were loaded into the Schlenk-flask with a reflux condenser and bubble-counter. This set-up was evacuated and flushed with argon several times. Then THF (10 mL) and 20% aq. $Na_2CO_3$ (10 mL) were added, and the mixture was refluxed overnight (bath temp. 95-98 °C). It was diluted with EtOAc (100 mL), organic layer was separated, dried, and evaporated in vacuo. The product was isolated by chromatography on silica gel (120 g) with hexane/EtOAc mixture (2:1→ 1:1) as eluent. Yield – 1.01 g (89%), m.p. 96–98 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.45 (s, 9 H), 1.66–1.80 (m, 2 H), 1.87–1.96 (m, 2 H), 3.29–3.37 (m, 2 H), 3.64–3.72 (m, 2 H), 4.47 ($m_c$, 1 H), 6.90 (d, *J* = 9, 2 H), 7.03 dd (*J* = 3.5 and 4.8, 1 H), 7.17–7.21 (m, 2 H), 7.51 (d, *J* = 9, 2 H). $^{13}$C NMR ($CDCl_3$, 62.9 MHz): δ=28.4 (Me), 30.4 ($CH_2$), 40.7 br. ($CH_2N$), 72.2 (CHO), 79.6 (C-O), 116.4 (CH×2), 122.1 (CH), 123.9 (CH), 127.2 (CH×2), 127.6 (C), 127.9 (CH), 144.1 (C), 154.8 (C), 156.7 (C). MS (EI): *m/z* (rel. int., %) = 361 (3) [M+2], 360 (9) [M+1], 359 (42) [$M^{+\cdot}$], 286 (8), 184 (10), 176 (100), 128 (19), 84 (38), 57 (43). $C_{20}H_{25}NO_3S$ (359.48): calcd. C 66.82, H 7.01, N 3.90; found C 66.75, H 6.77, N 3.67.

***N-tert*-Butoxycarbonyl-4-[4-(5-iodothiophen-2-yl)phenoxy]piperdine (15):** To the solution of the compound **14** (0.87 g, 2.4 mmol) and KOAc (1.2 g, 12 mmol) in AcOH (10 mL), 5.8 mL of the 0.47 M solution of ICl in AcOH was added dropwise (2.7 mmol ICl) at room temperature. After 2 hours, the mixture was diluted with ice-water (160 mL), the precipitated product was collected by filtration, washed with water and recrystallized from MeOH to afford 0.87 g (75%) of the title compound with m.p. 130–131 °C. $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.45 (s, 9 H), 1.66–1.79 (m, 2 H), 1.86–1.95 (m, 2 H), 3.29–3.37 (m, 2 H), 3.64–3.72 (m, 2 H), 4.47 ($m_c$, 1 H), 6.84 (d, *J* = 3.7, 1 H), 6.89 (d, *J* = 8.8, 1 H), 7.16 (d, *J* = 3.8, 1 H), 7.41 (d, *J* = 8.7, 2 H). $^{13}$C NMR ($CDCl_3$, 62.9 MHz, ppm): δ = 28.4 (Me), 30.4 ($CH_2$), 40.6 br. ($CH_2$), 71.1 (C-I), 72.1 (CH-O), 79.6 (C-O), 116.3 (CH), 123.6 (CH), 126.6 (C), 127.1 (CH), 137.7 (CH), 150.1 (C), 154.7 (C), 155.8 (C), 157.8 (C). MS (EI): *m/z* (rel. int., %) = 487 (3) [M+2], 486 (19) [M+1], 485 (92) [$M^{+\cdot}$], 412 (7), 302 (100), 184 (21), 131 (120), 128 (36), 84 (59), 57 (63). $C_{20}H_{24}INO_3S$ (485.38): calcd. C 49.49, H 4.98, N 2.88; found C 49.77, H 4.71, N 2.75.

***N-tert*-Butoxycarbonyl-4-[4-[5-(3.5-dimethyl-4-bromothiophen-2-yl)thiophen-2-yl]phenoxy]piperidine (17)** was prepared from the iodide (**15**) (0.853 g, 1.76 mmol), $Pd(dba)_2$ (41 mg, 0.071 mmol), $Ph_3P$ (74 mg, 0.28 mmol) and 3,5-dimethyl-4-bromothiophen-2-boronic acid (**9**, 0.64 g, 2.7 mmol) as described for the compound **14**. Reaction time – 36 h, yield – 0.77 g (80%) of yellow solid, m.p. 140 °C (aq. EtOH). $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.45 (s, 9 H), 1.68–1.80 (m, 2 H), 1.86–1.96 (m, 2 H), 2.36 (s, 3 H), 2.39 (s, 3 H), 3.28–3.39 (m, 2 H), 3.63–3.76 (m, 2 H), 4.47 ($m_c$, 1 H), 6.93 (d, *J* = 9, 2 H), 7.05 (d, *J* = 3.7, 1 H), 7.15 (d, *J* = 3.7, 1 H), 7.52 (d, *J* = 9, 2 H). $^{13}$C (62.9 MHz, $CDCl_3$, ppm): δ = 15.2 (Me), 15.9 (Me), 28.4 (Me), 30.4 ($CH_2$), 40.6 br. ($CH_2$), 72.2 (CH-O), 79.6 (C-O), 113.95 (C), 116.4 (CH), 122.4 (C), 126.5 (C), 127.0 (CH), 127.1 (C), 127.8 (C),132.3 (C), 132.8 (C), 134.5 (C), 144.0, 154.8 (C), 156.9 (C). MS (EI): *m/z* (rel. int., %) = 549/547 (3) [$M^{+\cdot}$], 487 (7), 486 (18), 485 (95), 412 (9), 302 (100), 184 (23), 131 (11), 128 (38), 84 (59), 57 (65). $C_{26}H_{30}BrNO_3S_2$ (548.56): calcd. C 56.93, H 5.51, N 2.55; found C 56.92, H 5.22, N 2.37.

***N-tert*-Butoxycarbonyl-4-[4-[5-[3,5-dimethyl-4-(perfluorocyclopentan-1-yl)thiophen-2-yl]thiophen-2-yl]phenoxy]piperdine (19):** Compound **17** (465 mg, 0.85 mmol) was dissolved in THF (7 mL), and a solution of *t*BuLi in

pentane (1.5 M, 10 mL, 1.5 mmol) was added dropwise at −78 °C to the yellow solution. After stirring for 15 min at −78 °C, the dark-green solution was quickly added by a syringe into the stirred solution of $C_5F_8$ (**18**, 2.3 g, 10.8 mmol) in THF (12 mL) at −78 °C. After stirring at −78 °C for 15 min, the reaction mixture was poured into the separation funnel with brine (50 mL) and AcOH (0.1 mL). The reaction flask was washed with EtOAc (3×30 mL), which was also transferred into the separation funnel. It was shaken, the organic layer was separated, evaporated, and the residue was purified on $SiO_2$ (50 g) with hexane/ether mixture (3:1→1:1) as an eluent. A yellow solid was isolated (518 mg) , which was recrystallized from MeOH to give 420 mg (75%) of the title compound with m.p. 134 °C. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.44 (s, 9 H), 1.66–1.83 (m, 2 H), 1.90–2.01 (m, 2 H), 2.33 (s, 3 H), 2.39 (s, 3 H), 3.30–3.41 (m, 2 H), 3.65–3.78 (m, 2 H), 4.49 ($m_c$, 1 H), 6.92 (d, *J* = 9, 2 H), 7.05 (d, *J* = 3.8, 1 H), 7.18 (d, *J* = 3.8, 1 H), 7.47 (d, *J* = 9, 2 H). MS (EI): *m/z* (rel. int., %) = 663 (8) [M+2], 662 (19) [M+1], 661 (56) [$M^{+\cdot}$], 480 (8), 479 (21), 478 (100), 477 (19), 286 (7), 128 (22), 84 (64), 57 (100). $C_{31}H_{30}NO_3S_2F_7$, HR-MS (ESI, positive mode): 684.14441 [M+Na] (found), 684.144475 (calculated).

**3-Bromo-2,5-dimethyl-5-[5-(4-pyridyl)thiophen-2-yl]thiophene (20)** was synthesized from 2-iodo-5-(4-pyridyl)thiophene[8] (0.74 g, 2.6 mmol) and 3-bromo-2,5-dimethylthiophen-2-boronic acid (**9**, 0.73 g, 3.1 mmol) in the presence of $Pd(dba)_2$ (59 mg, 0.10 mmol) and $Ph_3P$ (105 mg, 0.40 mmol) as described above for the compound **10**. Purified on $SiO_2$ (130 g) in $CH_2Cl_2$ (+1 % v/v $Et_3N$) followed by $CH_2Cl_2$/acetone mixture (8:2 with 1% v/v $Et_3N$). Yield – 0.75 g (82%), m. p. 143–144 °C (aq. MeOH). $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.02 (s, 3 H), 2.26 (s, 3 H), 7.08 (d, *J* = 4.3 Hz, 1 H), 7.43 (m, 3 H), 8.59 ($m_c$, 2 H). $^{13}$C NMR (75.5 MHz, $CDCl_3$, ppm): δ = 15.3 (Me), 16.0 (Me), 114.3 (C), 119.4 (CH), 125.7 (CH), 126.4 (CH), 127.1 (C), 133.3 (C), 133.7 (C), 138.1 (C), 140.4 (C), 140.9 (C), 150.4 (CH). EI-MS: *m/z* (rel. int., %) = 353 (6), 352 (14), 351 (100) $[M+H]^+$, 350 (22) [$M^{+\cdot}$], 349 (94), 348 (9), 270 (14), 237 (8), 204 (9), 122 (8), 71 (10), 69 (10). $C_{15}H_{12}BrNS_2$ (350.31): calcd. C 51.43, H 3.45, N 4.00; found C 51.67, H 3.26, N 3.79.

**2-[3,5-Dimethyl-4-(perfluorocyclopenten-1-yl)thiophen-2-yl]-5-(4-pyridyl)thiophene (21):** Bromide **20** (0.75 g, 2.1 mmol) was dissolved in THF (20 mL), and a solution of *t*BuLi in pentane (1.5 M, 1.5 mL, 2.25 mmol) was added dropwise at – 78 °C. The reaction mixture became dark-green, nearly black. After 15 min at −78 °C, the solution was rapidly added by a syringe to a vigorously stirred $C_5F_8$ (2.25 g, 11 mmol) in THF (10 mL), which was also kept at –78 °C. The reaction mixture became dark-brown. It was stirred at – 78 … – 50 °C for 1 h, quenched with brine (20 mL) containing a few drops of AcOH, diluted with EtOAc and, after evaporation of the organic layer, the title compound was isolated by repeated chromatography on $SiO_2$ (2 times with 120 g $SiO_2$ each time), eluting with $CHCl_3$ – acetone mixture (8:1 → 4:1). It was difficult to separate the title compound from the impurity with slightly lower $R_f$ (**20**, R = H). Yield – 290mg (30%) of a dark semi-solid with ca. 90% of the title compound. This compound seems to be unstable on $SiO_2$. After evaporation of the fractions with the compound **21**, the residue crystallizes only partially into a dark solid, which leaves a dark-red spot on the start of the analytical TLC. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 2.23 (s, 3 H), 2.39 (s, 3 H), 7.12 (d, *J* = 4, 1 H), 7.45 (d, *J* = 4, 1 H), 7.50 ($m_c$, 2 H), 7.59 ($m_c$, 2 H). EI-MS: *m/z* (rel. int., %) = 465 (10) [M+2], 464 (21) [M+1], 463 (100) [$M^{+\cdot}$], 462 (19) $[M–H]^+$. $C_{20}H_{12}NS_2F_7$, HR-MS (ESI, positive mode): 464.03693 $[M+H]^+$ (found), 464.03783 (calculated).

***tert*-Butyl *N*-2-phenoxyethyl carbamate (26):** A solution of *tert*-butyl pyrocarbonat (5.98 g, 27.4 mmol) in $CHCl_3$ (5 mL) was added dropwise to the solution of 2-phenoxyethyl amine (5.00 g), 27.4 mmol) in $CHCl_3$ (10 mL) by cooling with ice-water. After stirring for 16 h at room temperature, the solvent was evaporated, and the residue was distilled in vacuo to give 5.7 g (92%) of the title compound as a colorless solid; b. p. 92 °C (0.06 mm Hg), m. p. 30 °C. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ

[8] R. Nakajima, H. Iida, T. Hara, *Bull. Chem. Soc. Jpn.* **1990**, *63*(2), 636–637

= 1.45 (s, 9 H), 3.54 (q, *J* = 5.2, $CH_2N$, 2 H), 4.02 (t, *J* = 5.2, 2 H, $CH_2O$), 5.04 (br. s, 1 H, NH), 6.84–6.90 (m, 2 H), 6.91–7.00 (m, 1 H), 7.28–7.34 (m, 2 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm): δ = 28.4 (Me), 40.1 ($CH_2$), 67.0 ($CH_2$), 79.5 (C-O), 114.3 (CH), 121.0 (CH), 129.5 (CH), 156.1 (C-O), 158.4 (C=O). EI-MS: *m/z* (rel. int., %) = 237 (5) [$M^{+\cdot}$], 164 (10), 144 (12), 120 (12), 94 (53), 44 (17), 41 (12). $C_{13}H_{19}NO_3$ (237.29): calcd. C 65.80, H 8.07, N 5.90; found C 65.72, H 7.77, N 5.69.

***tert*-Butyl *N*-methyl-*N*-2-phenoxyethyl carbamate (27):** To the solution of compound **26** (5.46 g, 23.0 mmol) and MeI (22.9 g, 161 mmol) in DMF (40 mL), $Ag_2O$ (8.00 g, 34.5 mmol) was added by cooling with ice-water. After vigorous stirring for 46 h at room temperature, the reaction mixture was diluted with $CH_2Cl_2$ and filtered through the Celite® pad. The flilter-cake was washed with $CH_2Cl_2$ (2x50 mL), the combined filtrates were shaken with sat. aq. $Na_2S_2O_3$ (2x50 mL), water (6x50 mL), brine (100 mL) and dried. Solvents ($CH_2Cl_2$ and traces of DMF) were evaporated in vacuo, and the residue was kept at 0.01 mm Hg to yield the title compound as a yellowish solid with m. p. 48 °C (hexane). $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.45 (s, 9 H), 2.98 (s, 3 H, NMe), 3.54–3.65 (m, $CH_2N$, 2 H), 4.02–4.14 (m, 2 H, $CH_2O$), 6.84–7.00 (m, 3 H), 7.23–7.33 (m, 2 H). $^{13}$C NMR (62.9 MHz, $CDCl_3$, ppm): δ = 28.4 (Me), 35.0 (NMe), 48.3 ($CH_2N$), 65.3 ($CH_2O$), 79.6 (C-O), 114.3 (CH), 120.8 (CH), 129.5 (CH), 156.1 (C-O), 158.4 (C=O). EI-MS: *m/z* (rel. int., %) = 251 (2) [$M^{+\cdot}$], 178 (20), 158 (10), 102 (100), 94 (12), 77 (24), 58 (10), 57 (93), 44 (46), 41 (18). ESI-MS: *m/z* (rel. int., %) = 274 (100) $[M+Na]^+$. $C_{14}H_{21}NO_3$ (251.3): calcd. C 66.91, H 8.42, N 5.57; found C 66.92, H 8.58, N 5.37.

***tert*-Butyl *N*-[2-(4-iodophenoxy)ethyl]-*N*-methyl carbamate (28):** To the solution of the compound **27** (2.51 g, 10 mmol) and KOAc (1.03 g, 10.5 mmol) in AcOH (20 mL), 21 mL of the 0.5 M solution of ICl in AcOH was added dropwise at room temperature. The mixture was stirred for 24 h at 60 °C. After cooling, AcOH was evaporated in vacuo, the semi-solid residue was diluted with cold 5% aq. $Na_2SO_3$ (160 mL), and the precipitated product was collected by filtration, washed with water and air-dried to afford 2.15 g (57%) of the title compound as a yellow solid with m.p. 75 °C (hexane). $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.43 (s, 9 H), 2.94 (s, 3 H, NMe), 3.48–3.65 (m, $CH_2N$, 2 H), 3.92–4.15 (m, 2 H, $CH_2O$), 6.61–6.68 (m, 2 H, AA'XX'), 7.49–7.56 (m, 2 H, AA'XX'). $^{13}$C NMR (62.9 MHz, $CDCl_3$, 2 rotamers, ppm): δ = 28.4 (Me), 35.4/36.2 (NMe), 48.2 ($CH_2N$), 66.2/66.8 ($CH_2O$), 79.7 (C-O), 82.9 (C-I), 116.8 (CH), 138.2 (CH), 155.9 (C-O), 158.5 (C=O). EI-MS: *m/z* (rel. int., %) = 377 (2) [$M^{+\cdot}$], 220 (20), 102 (95), 58 (12), 57 (100), 44 (66), 41 (16). $C_{14}H_{20}INO_3$ (377.3): calcd. C 44.58, H 5.34, N 3.71; found C 44.39, H 5.09, N 3.94.

***tert*-Butyl *N*-methyl-*N*-[2-[4-(thiophen-2-yl)phenoxy]ethyl] carbamate (29)** was obtained from the iodide **28** (0,94 g, 2.5 mmol) and thiophene-2-boronic acid (0.38 g, 3 .0 mmol) as described above for the compound **14**. Yield – 0.76 (91%) of white solid with m. p. 90 °C (aq. MeOH) and $R_f$ = 0.4 (hexane – EtOAc, 2:1). $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.47 (s, 9 H), 2.99 (s, 3 H, NMe), 3.56–3.66 (m, $CH_2N$, 2 H), 4.04–4.18 (m, 2 H, $CH_2O$), 6.86–6.94 (m, 2 H, *J* = 8.8, AA'XX'), 7.05 (dd, *J* = 3.6 and 5.1, 1 H), 7.20 (dd, *J* = 1.1 and 3.6, 1 H), 7.22 (dd, *J* = 1.1 and 5.1, 1 H), 7.50–7.56 (m, 2 H, *J* = 8.8, AA'XX'). $^{13}$C NMR (75.5 MHz, $CDCl_3$, 2 rotamers, ppm): δ = 28.4 (Me), 35.4/36.2 (NMe), 48.3 ($CH_2N$), 66.2/66.8 ($CH_2O$), 79.7 (C-O), 114.7 (2xCH), 122.1 (CH), 123.9 (CH), 127.2 (2xCH), 127.5 (C), 127.9 (CH), 144.2 (C), 155.7 (C-O), 158.2 (C=O). EI-MS: *m/z* (rel. int., %) = 331 (8) [$M^{+\cdot}$], 260 (9), 177 (10), 176 (100), 102 (52), 57 (25). $C_{18}H_{23}NO_3S$ (331.3): calcd. C 64.84, H 6.95, N 4.20; found C 64.59, H 6.79, N 4.07.

***tert*-Butyl *N*-[2-[4-(5-iodothiophen-2-yl)phenoxy]ethyl]-*N*-methyl carbamate (30)** was obtained from the compound **29** (0,65 g, 2.0 mmol) as described above for the compound **28**. Yield – 0.67 (75%) of white solid with m. p. 117 °C (aq. EtOH). $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.47 (s, 9 H), 2.98 (s, 3 H, NMe), 3.52–3.68 (m, $CH_2N$, 2 H), 4.01–4.21 (m, 2 H,

$CH_2O$), 6.86 (d, *J* = 3.8, 1 H), 6.86–6.92 (m, 2 H, *J* = 8.8, AA'XX'), 7.18 (d, *J* = 3.6, 1 H), 7.39–7.44 (m, 2 H, *J* = 8.8, AA'XX'). $^{13}$C NMR (75.5 MHz, $CDCl_3$, 2 rotamers, ppm): δ = 28.4 (Me), 35.4/36.2 (NMe), 48.3 ($CH_2N$), 66.2/66.9 ($CH_2O$), 71.0 (C-I), 79.7 (C-O), 114.8 (2xCH), 123.6 (CH), 126.6 (C), 127.1 (2xCH), 137.8 (CH), 150.2 (C), 155.5/155.7 (C-O), 158.6 (C=O). EI-MS: *m/z* (rel. int., %) = 459 (11) [$M^{+\cdot}$], 302 (88), 210 (10), 102 (100), 58 (9), 57 (25). $C_{18}H_{22}INO_3S$ (459.3): calcd. C 47.07, H 4.83, N 3.95; found C 46.87, H 4.57, N 4.09.

***tert*-Butyl *N*-[2-[4-(4'-bromo-3',5'-dimethyl[2,2']bithiophen-5-yl)phenoxy]ethyl]-*N*-methyl carbamate (31)** was prepared from iodide **30** (0.64 g, 1.4 mmol) and boronic acid **9** (0.40 g, 1.7 mmol) as described for the compound **9**. $R_f$ = 0.34 (hexane – EtOAc, 3:1), yield – 0.44 g (60%) of the yellow solid with m. p. 80–81 °C (aq. EtOH). $^1$H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.47 (s, 9 H), 2.38 (s, 3 H), 2.42 (s, 3 H), 2.99 (s, 3 H, NMe), 3.55–3.68 (m, $CH_2N$, 2 H), 4.04–4.21 (m, 2 H, $CH_2O$), 6.87–6.95 (m, 2 H, *J* = 8.8, AA'XX'), 7.02 (d, *J* = 3.8, 1 H), 7.14 (d, *J* = 3.8, 1 H), 7.49–7.55 (m, 2 H, *J* = 8.8, AA'XX'). $^{13}$C NMR (75.5 MHz, $CDCl_3$, 2 rotamers, ppm): δ = 15.2, 15.9, 28.4 (Me), 35.3/36.1 (NMe), 48.3 ($CH_2N$), 66.2/66.9 ($CH_2O$), 77.2 (C), 79.7 (C-O), 114.8 (2xCH), 122.4 (CH), 126.6 (CH), 127.0 (2xCH), 127.8 (C), 132.3 (C), 132.9 (C), 134.5 (C), 144.1 (C), 150.2 (C), 155.5/155.7 (C-O), 158.4 (C=O). EI-MS: *m/z* (rel. int., %) = 523/521 (8) [$M^{+\cdot}$], 366 (40), 364 (36), 102 (100), 58 (14), 57 (54), 41 (18). $C_{24}H_{28}BrNO_3S_2$ (522.5): calcd. C 55.17, H 5.40, N 2.68; found C 54.93, H 5.13, N 2.89.

***tert*-Butyl *N*-[2-[4-[4'-(heptafluorocyclopent-1-enyl)-3',5'-dimethyl[2,2']bithiophen-5-yl]phenoxy]ethyl]-*N*-methyl carbamate (32):** Bromide **31** (0.44 g, 0.85 mmol) was placed into the dry reaction flask filled with Ar, it was closed with a septum, THF (5 mL) was added, and the solution was cooled down to –78 °C. *n*-BuLi (2.5 M in hexanes, 0.5 mL, 1.25 mmol) was added carefully with stirring, and the mixture was stirred for 20 min at –78 °C. Then it was transferred with a syringe to the cold (–78 °C) stirred solution of $C_5H_8$ (0.72 g, 3.4 mmol) in THF (5 mL), cold bath was removed, and the mixture was stirred for 6 h at room temperature. It was quenched with brine (10 mL) at 0 °C, diluted with EtOAc (30 mL), and the organic layer separated. The aqueous layer was extracted with EtOAc (2x15 mL). Combined organic solutions were dried, evaporated, and the residue was applied on $SiO_2$ (120 g). The title compound was isolated by elution with hexane – EtOAc mixture (4:1, $R_f$ = 0.23). Yield – 0.13 g of grey crystalline substance, with decomp. temp. > 80 °C. $^1$H NMR (250 MHz, $CDCl_3$, ppm): δ = 1.47 (s, 9 H), 2.22 (s, 3 H), 2.37 (s, 3 H), 2.99 (s, 3 H, NMe), 3.56–3.65 (m, $CH_2N$, 2 H), 4.05–4.18 (m, 2 H, $CH_2O$), 6.86–6.95 (m, 2 H, *J* = 1.9 and 8.8, AA'XX'), 7.05 (d, *J* = 3.8, 1 H), 7.16 (d, *J* = 3.8, 1 H), 7.48–7.55 (m, 2 H, *J* = 2.0 and 8.8, AA'XX'). $^{13}$C NMR (62.9 MHz, $CDCl_3$, 2 rotamers, signals of the fluorinated carbons were not recorded, ppm): δ = 13.9, 14.1, 28.4 (Me), 34.0/36.1 (NMe), 48.1 ($CH_2N$), 63.6/66.2 ($CH_2O$), 79.6 (C-O), 114.7 (2xCH), 121.0 (C), 122.3 (CH), 126.9 (C), 127.0 (2xCH), 129.9 (C), 132.5 (C), 133.4 (C), 137.5 (C), 139.6 (C), 155.7 (C-O), 158.5 (C=O). HR-MS (ESI, positive mode): 636.1472 [M+H] (found), $C_{29}H_{28}F_7NO_3S_2$+H, 636.1477 (calculated).

**Photochromic compound 1:** Bromide **10** (590 mg, 1.23 mmol) was dissolved in dry THF (10 mL), and the solution was cooled down to –78°C. *n*-BuLi (0.60 mL of 2.5 M solution in hexanes) was added dropwise, and the mixture was stirred for 15 min at –78°C. Then a solution of heptafluoride **11** (469 mg, 1.23 mmol) in THF (3 mL) was added dropwise at –78°C in such a way that the drops fell first onto a cold wall of the reaction flask. After stirring for 45 min at –78°C, the reaction mixture was let to warm-up to ca. 0°C, quenched with 5 mL of brine and 5 mL of 0.5 M aq. $H_2SO_4$, and diluted with EtOAc (20 mL). Organic layer was separated, dried, evaporated, and the compound **1** was isolated by chromatography on $SiO_2$ (EtOAc – cyclohexane 1:2 → 1:1). The brown oil (655 mg, ca. 70% crude oil) was dissolved in hot MeOH, the product was precipitated by adding water and dried in vacuo. Yield – 0.40 g (43%) of pale blue powder with m. p. 85–89 °C. $^1$H NMR (300 MHz, $CDCl_3$, 2 isomers, ppm): δ = 1.25 ("dq", *J* = 17 and 5, 2 H), 1.43 (s, 9 H), 1.80 (br. d, *J* = 14, 2 H), 1.92 (br. $m_c$, 1 H), 2.02

(br.s, 3 H), 2.12 s, 2.15 s (1:1, Σ 3 H), 2.32 (s, 3 H), 2.36 s, 2.37 s (1:1, Σ 3 H), 2.72 (br. "t", $J$ = 13, 2 H), 3.79 (d, $J$ = 7.5, 2 H), 4.15 (br. m, 2 H), 6.87 (d, $J$ = 9, 2 H), 7.23 (m, 4 H), 8.58 (br . d, $J$ = 7.5, 2 H). $^{13}$C NMR[9] (75.5 MHz, 2 isomers of the photochromic unit, $CDCl_3$, ppm): δ = 14.51, 14.58, 14.64, 14.74, 14.80, 14.86, 14.94, 14.98, 28.0 28.4 (3×Me), 28.8 (CH), 36.1 (NMe), 43.6 (br. $CH_2N$), 72.3 ($CH_2O$), 79.4 (C-O), 114.5 (2×CH), 123.0 (2×CH), 125.42/125.49 (C), 126.2 (C), 126.67/126.74 (C), 130.2 (CH), 131.06/131.19 (C), 133.2 (C), 134.33/134.1 (C), 136.3 (C), 138.0/138.3 (C), 140.9/141.1 (C), 141.6 (C), 150.0 (2×CH), 154.8 (C-O), 158.5 (C=O). MS (ESI): *m/z* (rel. int., %) = 763 (100) $[M+H]^+$ $C_{39}H_{40}N_2O_3S_2F_6$ (762.87): calcd. C 61.40, H 5.28, N 3.67; found 61.65, H 5.16, N 3.90. HR-MS (ESI, positive mode): 763.2458 [M+H] (found), 763.24628 (calculated). HPLC: 80 → 100% A (20 → 0% B) for 0–15 min, 100% A from 15–20 min, 1 mL/min, 40 °C, $t_R$ (OF) = 8.1 min, $t_R$ (CF) = 12.4 min, detection at 316 nm.

**Photochromic compound 2:** Bromide **17** (203 mg, 0.370 mmol) was dissolved in THF (3 mL), cooled to –78 °C, and to this solution 0.17 ml of 2.5 M *n*BuLi in hexanes (0.425 mmol) was added dropwise with stirring. The initially light-yellow solution first turned to be green, but, after the addition of *n*BuLi had been nearly complete, it again became yellow, with only a slight greenish touch. After 15 min at –78 °C, the solution of the pyridine derivative **11** (141 mg, 0.370 mmol) in 3 mL of THF was added in such a way, that the liquid first touched a cold wall of the flask above the lithiated thiophene **17**. After keeping for an hour at – 78 °C, the cold bath was removed, and the reaction was left for warming-up to ca. 0 °C. It was quenched by addition of brine (1 mL) with 2 or 3 drops of AcOH, diluted with EtOAc (15 mL), organic layer was separated, concentrated in vacuo and applied on top of the column with $SiO_2$ (50 g). Elution with hexane – EtOAc (1/1 → ¼) afforded 220 mg (72%) of the title compound as a green-yellow foam. This compound is easy to detect on TLC; its spots turn to be blue by irradiation at 254 or 365 nm. $^1$H NMR (500 MHz, open form, $CDCl_3$, ppm): δ = 1.45 (s, 9 H), 1.71–1.77 (br. m, 2 H), 1.90 (br. m, 2 H), 2.14 s, 2.16 s (Σ 3 H), 2.19 (s, 3 H), 2.32 (s, 3 H), 2.38 s, 2.39 s (Σ 3 H), 3.33 ($m_c$, 2 H), 3.67 (m, 2 H), 4.47 ($m_c$, 1 H), 6.89 (d, $J$ = 8.6, 2 H), 6.99 (d, $J$ = 3.7, 1 H), 7.10 (d, $J$ = 3.8, 1 H), 7.30 ($m_c$, 2 H), 7.48 (d, $J$ = 8.6, 2 H), 8.59 ($m_c$, 2 H). $^1$H NMR (500 MHz, closed form, $CDCl_3$, ppm): δ = 1.54 (s, 9 H), 1.76 (br. m, 2 H), 1.91 (br. m, 2 H), 2.02 (br. s, 3 H), 2.22 s (3 H), 2.23 (s, 3 H), 2.29 (br. s, 3 H), 3.35 ($m_c$, 2 H), 3.68 ($m_c$, 2 H), 4.50 ($m_c$, 1 H), 6.92 (d, $J$ = 8.6, 2 H), 7.21 (d, $J$ = 4.1, 1 H), 7.27 (d, $J$ = 4.1, 1 H), 7.29 (dm, $J$ = 6, 2 H), 7.53 (d, $J$ = 8.7, 2 H), 8.67 (dm, $J$ = 5.6, 2 H). MS (EI): *m/z* (rel. int., %) = 830 (15) $[M^{+\cdot}]$, 730 (22), 647 (100), 349 (5), 84 (38), 41 (62). $C_{42}H_{40}N_2O_3S_3F_6$, HR-MS (ESI, positive mode): 831.2179 $[M+H]^+$ (found), 831.2188 (calculated). HPLC: 90 → 100% A (10 → 0% B) for 0–15 min, 100% A from 15–20 min, 1 mL/min, 25 °C, $t_R$ (OF) = 9.3 min, $t_R$ (CF) = 16.7 min, detection at 367 nm.

**Photochromic compound 3:** *Preparation from 3-thienyl bromide **17** and 4-pyridinobithienyl heptafluorocyclopentane **21**.* Bromide **17** (331 mg, 0.604 mmol) was dissolved in THF (3 mL), and to this solution *t*BuLi (1.5 M in pentane, 0.45 mL, 0.675 mmol) was added dropwise at –78 °C. The color of the solution changed from pale yellow to orange. After keeping for 15 min at –78 °C, a solution of **21** (280 mg, 0.605 mmol) in THF (3 mL) was added dropwise. The reaction mixture became dark. After standard work-up (see above), the title compound was isolated from the complex mixture by chromatography on SiO2 (120 g), eluting with hexane – EtOAc (1:1 → 0:1). Starting bromide **17** (or its mixture with the compound with H instead of Br) elutes with highest $R_f$ (ca. 180 mg), then comes the starting compound **21** (100 mg) followed by the title compound (110 mg, 20%) which was isolated as brown foam. Its spot turns to be dark-green by irradiation on the TLC-plate (254/365 nm). In EtOAC the closed form has a slightly higher $R_f$-value than the open form.

*Preparation from heptafluorocyclopentene **19** and 3-thienyl bromide **20**.* Bromide **20** (245 mg, 0.700 mmol) was dissolved in 10mL of THF and cooled to – 78 °C. To this suspension, a solution of *t*BuLi in pentane (1.5 M; 1 mL, 1.5 mmol) was added

[9] Signals of the fluorinated carbon atoms with low intensities were not assigned.

gradually. The starting compound dissolved forming a very dark green solution. After 15 min, this solution was added from a syringe to the rapidly stirred cold (– 78 °C) solution of **19** (400 mg, 0.605 mmol) in THF (3 mL). After the standard work-up (see above by the preparation of compound **2**), the title compound was isolated from the complex mixture by chromatography (120 g of SiO2), eluting with ether – MeOH mixture (100:0 → 100:1 → 50:1). Yield – 87 mg (16%) of green foam. $^1$H NMR (300 MHz, open form, $CDCl_3$, ppm): δ = 1.46 (s, 9 H), 1.76 (br. m, 2 H), 1.91 (br. m, 2 H), 2.20 br. s, 2.22 s (Σ 6 H), 2.33 br. s, 2.35 (s, Σ 6 H), 3.34 (m, 2 H), 3.68 (m, 2 H), 4.47 ($m_c$, 1 H), 6.89 (2×d, *J* = 9, 2 H), 6.99 (d, *J* = 4, 1 H), 7.07 (br. d, *J* = 3.7, 1 H), 7.11 (br. d, *J* = 3.7, 1 H), 7.43 (m, 3 H), 7.45 (2×d, *J* = 9, 2 H), 8.56 (m, 2 H). $^1$H NMR (300 MHz, closed form, $CDCl_3$, ppm): δ = 1.46 (s, 9 H), 1.76 (br. m, 2 H), 1.91 (br. m, 2 H), 2.20 (s, 6 H), 2.28 s (br. s 6 H), 3.34 (m, 2 H), 3.67 (m, 2 H), 4.50 (m, 1 H), 6.93 (d, *J* = 8.9, 2 H), 7.21 (d, *J* = 4, 1 H), 7.27 (d, *J* = 4, 1 H), 7.31 (d, *J* = 3.7, 1 H), 7.48 (m, 2 H), 7.51 (d, *J* = 4, 1 H), 7.54 (d, *J* = 8.5, 2 H), 8.62 (m, 2 H). MS (EI): *m/z* (rel. int., %) = 913 (1) [M+1], 912 (2) [$M^{+\cdot}$], 812 (3) [M-Boc]$^+$, 729 (10), 56 (55), 44 (63), 41 (100). $C_{46}H_{42}N_2O_3S_4F_6$, HR-MS (ESI, positive mode): 913.2055 [M+H]$^+$ (found), 913.2068 (calculated). HPLC: 95 → 100% A (5 → 0% B) for 0–10 min, 100% MeCN from 10–12 min, 1 mL/min, 40 °C, $t_R$ (OF) = 9.2 min, $t_R$ (CF) = 12.4 min, detection at 368 nm.

**Photochromic compound 4:** Bromide **20** (79 mg, 0.23 mmol) in THF (4 mL) was subjected to halogen – lithium exchange at –78 °C with *t*BuLi (0.15 mL of 1.5 M solution in pentane, 0.23 mmol), and after 30 min compound **32** (95 mg, 0.15 mmol) in THF (1 mL) was added dropwise. After the standard work-up (see above by the preparation of compound **2**), the title compound was isolated by chromatography (120 g of $SiO_2$), eluting with hexane – EtOAc mixture (2:3). Yield – 70 mg (53%) of light-yellow solid. $^1$H NMR (300 MHz, open form, 2 isomers, $CDCl_3$, ppm): δ = 1.46 (s, 9 H), 2.19–2.56 (br. s, 3 H), 2.32–2.39 (br. s, 3 H), 2.98 (s, 3 H, NMe), 3.56–3.65 (m, 2 H, $CH_2N$), 4.05–4.18 (m, 2 H, $CH_2O$), 6.86–6.93 (AA'XX', *J* = 8.8, 2 H), 7.01 (d, *J* = 3.8, 1 H), 7.09 ("dd", *J* = 1.5 and 3.8, 1 H), 7.13 ("dd", *J* = 1.2 and 3.8, 1 H), 7.44 (d, *J* = 3.8, 1 H), 7.44–7.47 (m, 2 H), 7.47–7.53 (AA'XX', *J* = 8.8, 2 H), 8.56–8.60 (m, 2 H). $^{13}$C NMR (75.5 MHz, 2 rotamers × 2 isomers of the photochromic unit, $CDCl_3$, ppm): δ = 14.9, 15.3, 28.0 28.4 (3×Me), 29.7 (Me), 35.5/36.2 (NMe), 48.3 ($CH_2N$), 66.2/66.9 ($CH_2O$), 79.7 (C-O), 114.8 (2×CH), 119.5 (2×CH), 122.4 (CH), 125.7 (CH), 125.9/126.0 (C), 126.2/126.3 (C), 126.6 (CH), 126.8 (CH), 126.9 (2×CH), 129.2 (C), 130.0 (C), 132.3 (C), 133.4 (C), 133.9 (C), 134.0 (C), 137.6 (C), 138.4/138.5 (C), 139.4/139.5 (C), 140.5 (C), 140.9 (C), 144.1 (C), 150.4 (2×CH), 155.6 (C-O), 158.5 (C=O). $C_{44}H_{40}N_2O_3S_4F_6$, HR-MS (ESI, positive mode): 887.1899 [M+H]$^+$ (found), 887.1904 (calculated). HPLC: 80 → 100% A (20 → 0% B) for 0–15 min, 100% MeCN from 15–20 min, 2 mL/min, 25 °C, $t_R$ (OF) = 11.8 min, $t_R$ (CF) = 16.3 min, detection at 369 nm.

**Deprotection of the *tert*-butoxycarbonyl derivatives 2–4: synthesis of amines 23-H, 22-H and 33-H.** Starting compounds **2**–**3** (0.05–0.1 mmol) were dissolved in $CH_2Cl_2$ (0.5 mL), and the solution of HCl (4 M) in dioxane (2 mL) was added at 0°C. Reaction mixtures were let to warm-up to room temperature with stirring. After keeping at room temperature for 3 h, TLC displayed the full conversion of the starting material. (Before applying on TLC, a very small amount of the reaction mixture was basidified with 1 drop of sat. aq. $Na_2CO_3$ and extracted by a few drops of EtOAc.) Photochromic (green under UV) spots of amines stay on the start or move only very slowly in EtOAc. Corresponding hydrochlorides may precipitate from the solution. Solvents were evaporated in vacuo, and the residue was triturated with dry ether. Ether was decanted from the precipitated HCl-salt, it was dried in vacuo, and used in the final coupling step without further purification. **22-H**: $C_{41}H_{34}N_2OS_4F_6$ (*HCl), HR-MS (ESI, positive mode): 813.15283 [M+H]$^+$ (found), 813.15365 (calculated); **33-H**: $C_{39}H_{32}F_6N_2OS_4$ (*HCl), HR-MS (ESI, positive mode): 787.1372 [M+H]$^+$ (found), 787.1380 (calculated)

**Coupling of rhodamine 101 with amines 22-H, 23-H and 33-H: synthesis of the adducts 5–7**. Amines (**22-H, 23-H** or **33-H**, 2.5–5·$10^{-2}$ mmol, ca. 20–40 mg of hydrochlorides) were dissolved in dry $CH_2Cl_2$ (1–2 mL), an equal molar amount of **Rh 101** (12.3–24.6 mg) was added with stirring followed by the double molar equivalent of HATU (5·$10^{-2}$–$10^{-1}$ mmol, 19–38 mg) and 2–3 drops of $Et_3N$. The mixture was left overnight with stirring under Ar. Then it was diluted with $CH_2Cl_2$ (ca. 20 mL, washed with 0.1 M aq. $H_2SO_4$, water, sat. aq. $NaHCO_3$ (5 mL each time) and dried. After evaporation of the solvent, the blue glassy residue was purified on silica gel (50–100 g) with $CH_2Cl_2$ – MeOH mixture (ca 20:1 → 10:1) as an eluent. Rh 101 has a much lower $R_f$s than the coupling products **5–7**. Purity of the coloured fractions was controlled by HPLC.

**Adduct 5:** *N*-Boc-derivative **2** (54 mg, 6.5·$10^{-2}$ mmol) after deprotection was coupled with 25 mg of **Rh101** (5.1·$10^{-2}$ mmol) in the presence of HATU (38 mg, 0.10 mmol), $Et_3N$ (3 drops) in $CH_2Cl_2$, and after work-up and isolation with $CH_2Cl_2$/MeOH (20:1) afforded a dark violet solid, which was washed with ether and dried in vacuo; yield – 41 mg of **5** (66%). $^1$H NMR (500 MHz, 2 isomers, $CDCl_3$, ppm): δ = 1.59 (m, 2 H, $H^3$ in piperidine), 1.77 (m, 2 H, $H^{3'}$ in piperidine), 1.92 (m, 4 H, 2×$CH_2$ in Rh), 2.07 (m, 4 H, 2×$CH_2$ in Rh), 2.17 (s, 6 H, 2×Me), 2.31 (s, 3 H, Me), 2.39 (s, 3 H, Me), 2.67 (m, 4 H, 2×$CH_2$ in Rh), 3.00 (m, 4 H, 2×$CH_2$ in Rh), 3.28–3.66 (m, 12 H, 4×$CH_2$ in rhodamine + $H^{2,2'}$ in piperidine), 4.58 ($m_c$, 1 H, CH-O), 6.63 (br. s, 1 H, H-4 in Rh), 6.71 (br. s, 1 H, H-4' in Rh), 6.88 (d, *J* = 8, 2 H), 6.96 (2×d = t, *J* = 3.4, 1 H, $H^\beta$ in thiophene), 7.08 (d, *J* = 4, 1 H, $H^\beta$ in thiophene), 7.26 (m, 1 H), 7.39 (m, 2 H), 7.46 (d, *J* = 8, 2 H), 7.51 (m, 1 H), 7.61 (m, 2 H), 8.59 (m, 2 H). $C_{69}H_{61}N_4O_3S_3F_6$(+)*OH(–) [1203(+)*17(–)], MS (ESI, positive mode): *m/z* (rel. int., %) = 1206 (14) $[M+3]^+$, 1205 (29) $[M+2]^+$, 1204 (66) $[M+1]^+$, 1203 (100) $[M]^+$; HR-MS (ESI, positive mode): 1203.38097 [$M^+$] (found), 1203.3810 (calculated); 602.19389 $[M^+ + H^+]^{2+}$ (found), 602.19491 (calculated). HPLC: 80 → 100% A (20 → 0% B) for 0–15 min, 100% MeCN from 15–20 min, 1 mL/min, 25 °C, $t_R$ (OF) = 13.2 min, $t_R$ (CF) = 18.4 min, detection at 368 nm.

**Adduct 6:** Compound **22-H*HCl** (42 mg, 5.0·$10^{-2}$ mmol), 19 mg **Rh101** (3.9·$10^{-2}$ mmol) and HATU (34 mg, 8.9·$10^{-2}$ mmol) were mixed in $CH_2Cl_2$ (3 mL) and $Et_3N$ was added (3 drops). $R_f$ of **6** is ca. 0.5 in $CH_2Cl_2$/MeOH (15:1). Yield – 39 mg (77%) of a dark solid after column chromatography and washing with ether and drying in vacuo. $^1$H NMR (600 MHz, 2 isomers, $CDCl_3$, ppm): δ = 1.61 (m, 2 H, $H^3$ in piperidine), 1.78 (m, 2 H, $H^{3'}$ in piperidine), 1.92 (m, 4 H, $CH_2$ in Rh), 2.08 (m, 4 H, $CH_2$ in Rh), 2.16 s, 2.18 s, 2.21 s (1:1:2, Σ 6 H, Me), 2.32 s, 2.33 s, 2.34 s (2:1:1, Σ 6 H, Me), 2.66–2.71 (m, 4 H, $CH_2$ in Rh), 3.00 (m, 4 H, $CH_2$ in Rh), 3.28–3.36 (m, 2 H, $H^2$ in piperidine), 3.44–3.47 (m, 6 H, $CH_2$-N in Rh), 3.56–3.68 (m, 4 H, $H^{2'}$ in piperidine + $CH_2$-N in Rh), 4.58 (m, 1 H, CH-O), 6.62 (br. s, 1 H, H-4 in Rh), 6.72 (br. s, 1 H, H-4' in Rh), 6.89 (d, *J* = 8.6, 2 H), 6.96 (d, *J* = 3.6, 1 H), 7.08 (2×d, *J* = 3.6, 1 H), 7.10 (m, 1 H), 7.26 (br. d, *J* = 6.7, 1 H), 7.45 (2×d, *J* = 8, 2 H), 7.50–7.57 (m, 3 H), 7.62 (m, 3 H), 8.54 (br. s, 2 H). $C_{73}H_{63}N_4O_3S_4F_6$(+)*OH(–) [1285(+)*17(–)], MS (ESI, positive mode): *m/z* (rel. int., %) = 1289 (10) $[M+4]^+$, 1288 (32) $[M+3]^+$, 1287 (56) $[M+2]^+$, 1286 (76) $[M+1]^+$, 1285 (38) $[M]^+$; HR-MS (ESI, positive mode): 1285.3681 [$M^+$] (found), 1285.3687 (calculated). HPLC: 80 → 100% A (20 → 0% B) for 0–15 min, 100% MeCN from 15–20 min, 1 mL/min, 40 °C, $t_R$ (OF) = 16.2 min, $t_R$ (CF) = 18.0 min, detection at 370 nm.

**Adduct 7:** Compound **33-H*HCl** (9 mg, 1.2·$10^{-2}$ mmol), 5 mg **Rh101** (1.2·$10^{-2}$ mmol) and HATU (9 mg, 2.4·$10^{-2}$ mmol) were mixed in $CH_2Cl_2$ (3 mL) and $Et_3N$ was added (4 mg, 4.8·$10^{-2}$ mmol). $R_f$ of **7** is ca. 0.1 in $CH_2Cl_2$/MeOH (10:1). Yield – 12 mg (80%) of a violet solid after column chromatography and washing with ether and drying in vacuo. $^1$H NMR (300 MHz, 2 isomers, $CDCl_3$, ppm): δ = 1.85–1.97 (m, 4 H, $CH_2$ in Rh), 1.97–2.14 (m, 4 H, $CH_2$ in Rh), 2.21–2.28 (br. s, Σ 6 H, Me), 2.34–2.41 (br. s, Σ 6 H, Me), 2.62–2.73 (m, 4 H, $CH_2$ in Rh), 2.82–2.94 (m, 4 H, $CH_2$ in Rh), 3.11–3.14 ("m", 3 H, N-Me), 3.25–3.58 (m, 10 H, $CH_2$-N in Rh and photochromic unit), 3.95–3.98 (m, 2 H, $CH_2O$), 6.62–6.68 (m, 2 H, *J* = 8.8, CH), 6.74 (br. s,

2 H, H-4' in Rh), 7.05 (d, *J* = 3.8, 1 H), 7.11 (d, *J* = 3.8, 1 H), 7.18 ("dd", *J* = 1.5 and 3.8, 1 H), 7.32–7.37 (m, 1 H), 7.44–7.52 (m, 5 H), 7.55–7.60 (m, 1 H), 7.64–7.70 (m, 2 H), 8.56–8.62 (m, 2 H). $C_{71}H_{61}N_4O_3S_4F_6$(+)*OH(–) [1259(+)*17(–)], HR-MS (ESI, positive mode): 1259.3514 [$M^+$] (found), 1259.3531 (calculated). HPLC: 80 → 100% A (20 → 0% B) for 0–15 min, 100% MeCN from 15–20 min, 1 mL/min, 40 °C, $t_R$ (OF) = 18.0 min, $t_R$ (CF) = 18.8 min, detection at 368 nm.

**Optical Measurements**

***General methods***

Absorption and fluorescence stationary measurements were carried out in a Varian Cary 4000 UV-Vis spectrophotometer, and in a Varian Cary Eclipse fluorescence spectrophotometer, respectively. Sealed quartz cuvettes of 1 cm path length were used in all experiments. Emission spectra were corrected for instrument response.

Time resolve fluorescence measurements where performed in time-correlated single photon counting mode using a Microchannel Plate Photomultiplier Tube R3809U-50 (time resolution 50 ps, Hamamatsu Photonics) in conjunction with a Picoharp300 board (PicoQuant, Berlin, Germany) for detection, and a self-made software for data analysis including convolution with instrument response function. Excitation pulses were generated with a synchronized frequency-doubled optical parameter oscillator (OPO, APE GmbH, Berlin, Germany) tuned at 575 nm and coupled in a 30m single mode fiber (90 ps pulsewidth). The OPO was pumped by a MaiTai laser (Spectra-Physics, Mountain View, CA, USA). A bandpass filter HQ600/40 (AHF Analysentechnik, Tübingen, Germany) placed in front of the detector selected the emitted light to be collected.

Irradiation of the samples to drive the photochromic reactions was performed with a 200W Mercury lamp (LOT-Oriel GmbH & Co. KG, Darmstadt, Germany) equipped with a monochromator and a system of filters to select the appropriate wavelengths, or with a CW diode laser of 374 nm (iPulse-375, Toptica Photonics AG, Gräfelfing, Germany).

***Determination of the quantum efficiencies of the isomerization reactions***

The analysis of the kinetic data under continuous or semi-continuous irradiation depends on the wavelengths of the irradiation light used. In the UV range, both the OF and the CF absorbs. Thus, when the irradiation is performed in the UV, the resultant kinetics scheme can be represented by two components (OF and CF) and two quantum yields ($\Phi_{OF\rightarrow CF}$ and $\Phi_{CF\rightarrow OF}$).[10]

$$OF \underset{\Phi_{CF\rightarrow OF}}{\overset{\Phi_{OF\rightarrow CF}}{\rightleftharpoons}} CF$$

The expression for the photochemical reaction rate in this case is:

$$\frac{d[CF]}{dt} = -\frac{d[OF]}{dt} = \left(\Phi_{OF\rightarrow CF}^{\lambda-IRR}\,\varepsilon_{OF}^{\lambda-IRR} + \Phi_{CF\rightarrow OF}^{\lambda-IRR}\,\varepsilon_{CF}^{\lambda-IRR}\right) I_0^{\lambda-IRR}\,F^{\lambda-IRR}[OF] - \Phi_{CF\rightarrow OF}^{\lambda-IRR}\,\varepsilon_{CF}^{\lambda-IRR}\,I_0^{\lambda-IRR}\,F^{\lambda-IRR}[OF]_0 \quad \text{(e1)}$$

[10] M. H. Deniel, D. Lavabre, J. C. Micheau, in *Organic Photochromic and Thermochromic Compounds, Vol 2: Physicochemical Studies, Biological Applications, and Thermochromism* (Eds.: J. C. Crano, R. J. Guglielmetti), Kluwer Academic, Plenum Publishers, New York, **1999**, pp.167 – 209.

where $\Phi_{OF\rightarrow CF}^{\lambda-IRR}$ and $\Phi_{CF\rightarrow OF}^{\lambda-IRR}$ are the isomerization quantum yields for the forward and back reaction respectively, $\varepsilon_{OF}^{\lambda-IRR}$ and $\varepsilon_{CF}^{\lambda-IRR}$ the absorption coefficients of the open and close isomers respectively, $I_0^{\lambda-IRR}$ is the photonic flux expressed in M/s (moles of photons per litter per second), the factor $F^{\lambda-IRR}=\left(1-10^{-OD}\right)/OD$ (were OD is the optical density of the solution at the irradiation wavelength), $[CF]$ and $[OF]$ are the concentration of the closed and open isomers at any given time, and $[OF]_0$ is the concentration of the open isomer at time zero. All magnitudes except the concentrations are expressed at the irradiation wavelength *λ-IRR*, as the superscript denotes (in our case 313 nm, 365 nm or 375 nm).

Since the absorption of the sample usually changes with the irradiation time, equation e1 can not be analytically integrated. Exceptions are in the case when the irradiation wavelength corresponds to an isosbestic point, or in a very diluted sample where F→2.3. However in most of the experiments carried out in this work, the changes in F were small enough to consider it approximately constant. Thus, equation e1 can be integrated and an exponential dependence is obtained. Using the initial conditions $[CF]_0 = 0$ and $[OF]_0 = C_0$, the concentration of the CF at any time can be expressed as:

$$[CF]=C_0\left(\frac{\Phi_{OF\rightarrow CF}^{\lambda-IRR}\,\varepsilon_{OF}^{\lambda-IRR}}{\Phi_{APP.}^{\lambda-IRR}}\right)\left(1-\exp\left(-\Phi_{APP.}^{\lambda-IRR}\,I_{PS}^{\lambda-IRR}\,F_{PS}^{\lambda-IRR}\,t\right)\right) \tag{e2}$$

where $\Phi_{APP.}^{\lambda-IRR}=\left(\Phi_{OF\rightarrow CF}^{\lambda-IRR}\,\varepsilon_{OF}^{\lambda-IRR}+\Phi_{CF\rightarrow OF}^{\lambda-IRR}\,\varepsilon_{CF}^{\lambda-IRR}\right)$

The concentration of the CF instead of the OF was selected since it can be easily expressed as a function of the absorbance in the visible range, where the other isomer does not absorb. After reorganization of equation e2 and by substitution with the Lambert-Beer law, the absorption of the sample in the visible range at any irradiation time ( $A_{PS}^{\lambda-VIS}$ ) can be expressed according to the following equation:

$$A^{\lambda-VIS}=A_{PS}^{\lambda-VIS}\left(1-\exp\left(-\Phi_{APP.}^{\lambda-IRR}\,I_{PS}^{\lambda-IRR}\,F_{PS}^{\lambda-IRR}\,t\right)\right)=A_{PS}^{\lambda-VIS}\left(1-\exp\left(-k^{\lambda-IRR}\,t\right)\right) \tag{e3}$$

where $A_{PS}^{\lambda-VIS}=C_0\,\varepsilon_{CF}^{\lambda-VIS}\,\alpha_{PS}^{\lambda}=C_0\,\varepsilon_{CF}^{\lambda-VIS}\left(\frac{\Phi_{OF\rightarrow CF}^{\lambda-IRR}\,\varepsilon_{OF}^{\lambda-IRR}}{\Phi_{APP.}^{\lambda-IRR}}\right)$ is the absorption of the sample in the visible range in the photostationary state, and $k^{\lambda-IRR}=\Phi_{APP.}^{\lambda-IRR}\,I_{PS}^{\lambda-IRR}\,F_{PS}^{\lambda-IRR}$ is the exponential characteristic constant. To extract the parameters from equation e3, in particular $\Phi_{OF\rightarrow CF}^{\lambda-IRR}$, the absorption coefficient of the CF has to be known in the visible range ( $\varepsilon_{CF}^{\lambda-VIS}$ ), as well as the absorption coefficients at the irradiation wavelengths of both isomers ( $\varepsilon_{OF}^{\lambda-IRR}$ and $\varepsilon_{CF}^{\lambda-IRR}$ ). Absorption coefficients of the OF were determined from solutions prepared by weighting a certain mass of the compound, but this procedure is more cumbersome for the CF, since isolation of a weighable amount of this isomer is usually not easy. We have independently measured the conversion in the photostationary state ($\alpha_{PS}$) from HPLC experiments, and the spectra of the CF was calculated from the spectra of the OF and of the photostationary state. $\Phi_{OF\rightarrow CF}^{\lambda-IRR}$ was then obtained by fitting the absorption of the sample in the maximum of the absorption band of the CF in the visible range at different irradiation times to equation e3. While a single kinetic determination only gives information about $\Phi_{APP.}^{\lambda-IRR}$, an independent determination of $\varepsilon_{CF}^{\lambda-VIS}$ (from $\alpha_{PS}$) allows the extraction of $\Phi_{OF\rightarrow CF}^{\lambda-IRR}$, from $A_{PS}^{\lambda-VIS}$ and $k^{\lambda-IRR}$.

Irradiation experiments were also performed in the visible range, to drive the reverse (ring-opening) reaction and obtain its quantum efficiency ( $\Phi_{OF\rightarrow CF}^{\lambda-IRR}$ ). In this spectral range, only the CF absorbs and thus kinetic scheme is simplified to a system of two components and one quantum yield.[10]

$$CF \xrightarrow{\Phi_{CF\rightarrow OF}} OF$$

The absorption of the sample at any irradiation time ( $A^{\lambda-VIS}$ ) can be expressed, under the same assumptions mentioned above, according to:

$$A^{\lambda-VIS} = A_0^{\lambda-VIS} \exp\left(-\Phi_{CF\rightarrow OF}^{\lambda-IRR}\, \varepsilon_{CF}^{\lambda-IRR}\, I_{PS}^{\lambda-IRR}\, F_{PS}^{\lambda-IRR}\, t\right) \quad \text{(e4)}$$

In equation e4, $A_0^{\lambda-VIS}$ is the absorption at t = 0, usually the absorption at the PS state, and the rest of the parameters are the same as already expressed but in this case defined at *λ-IRR* in the visible range (577 nm and 660 nm). The absorption was measured in the maximum of the absorption band of the CF (*λ-VIS*) and usually differs from *λ-IRR*. $\Phi_{OF\rightarrow CF}^{\lambda-IRR}$ was calculated from the exponential constant ( $\Phi_{CF\rightarrow OF}^{\lambda}\, \varepsilon_{CF}^{\lambda}\, I_{PS}^{\lambda}\, F_{PS}^{\lambda}$ ) obtained from fitting the kinetic data under irradiation with visible light to equation e4. In this case, only the knowledge of the absorption coefficient at irradiation wavelength ( $\varepsilon_{CF}^{\lambda-IRR}$ ) is necessary.

The photon flux at the irradiation wavelengths (UV and visible) were measured by chemical actinometry using 1,2-Bis(2,4-dimethyl-5-phenylthiophen-3-yl)perfluorocyclopentene[11] in hexane or the furylfulgide Aberchrome 670 in toluene[12] as reference compounds.

***Determination of the RET efficiencies between the fluorophore and both isomers of the photochromic compounds***

Since the emission efficiency of each isomer is different, the fluorescence intensity of each sample depends on the relative amount of each isomer, and can be expressed as a function of the conversion according to the following expression:[13]

$$F = F_{Fluorophore}\left[(1-\alpha)(1-E_{OF}) + \alpha\,(1-E_{CF})\right] \quad \text{(e5)}$$

where $F_{Fluorophore}$ is the fluorescence intensity of the fluorophore (donor) in the absence of RET, α is any given conversion ($0 \leq \alpha \leq 1$), and $E_{OF}$ and $E_{CF}$ are the RET efficiencies of the OF and CF as acceptors, respectively. Then, the fluorescence modulation (FM) between the initial (α = 0) and the photostationary state ($\alpha_{PS}$) is:

$$FM = 1 - \frac{F_{PS}}{F_0} = \alpha_{PS}\left(\frac{E_{CF} - E_{OF}}{1 - E_{OF}}\right) \quad \text{(e6)}$$

[11] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org. Chem.* **1995**, *60*, 8305-8309.
[12] Y. Yokoyama, T. Inoue, M. Yokohama, T. Goto, T. Iwai, N. Kera, I. Hitomi, Y. Kurita, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 3297-3303.
[13] L. Giordano, T. M. Joven, M. Irie, E. A. Jares-Erijman, *J. Am. Chem. Soc.* **2002**, *124*, 7481-7489.

were $F_0$ and $F_{PS}$ are the fluorescence signal in the initial and in the PS state, respectively.
RET efficiency for the open isomers ($E_{OF}$) were determined from time resolved fluorescence measurements as well as from stationary ones:

$$E_{OF} = 1 - \frac{\tau_{OF}}{\tau_{REF}} = 1 - \frac{\Phi_{Fl.}^{OF}}{\Phi_{Fl.}^{REF}} \quad \text{(e7)}$$

where $\tau_{OF}$ and $\tau_{REF}$ are the fluorescence lifetime of the OF of the photochromic fluorescent compound and the reference compound respectively, and $\Phi_{Fl.}^{OF}$ an $\Phi_{Fl.}^{REF}$ are the fluorescence quantum yields for the same compounds determined in stationary methods.[Valeur] Time resolved fluorescence decays yielded good fits to a single exponential function. The model compound **Rh-NC$_5$H$_{10}$** was used as the reference to determine the properties of the fluorophore in the absence of RET ($\tau_{REF}$ and $\Phi_{Fl.}^{REF}$). Rhodamine 101 (Fluka, fluorescence grade) was use as a reference to calculate the absolute values ($\Phi_{Fluo} = 1$).[14] Same results were obtained for $E_{OF}$ from both methods, time-resolved and stationary, within experimental errors.

RET efficiency for the close isomers ($E_{CF}$) can be derived from equation e6:

$$E_{CF} = \frac{FM}{\alpha_{PS}} + E_{OF}\left(1 - \frac{FM}{\alpha_{PS}}\right) \quad \text{(e8)}$$

The three parameters in equation e8 were determined independently: fluorescence modulation (FM) was measured from stationary measurements, $\alpha_{PS}$ was measured by HPLC, and $E_{OF}$ was calculated as described above.

Time resolved measurements were also performed at different conversions after irradiation with UV light. However, only one exponential term was sufficient to accuratly fit the data, the same obtained for the pure OF. The lifetime of the CF is either too short compared with the response time of the setup (≈ 100ps, FWHM), or the photon count rate resulting from this isomer is too low to be measured in reasonable integration times, particularly compared with the photon count rate of the OF, even when the last one is in a smaller amount (i.e. ≈ 2% in the PS state). This is consistent with the high $E_{CF}$ values obtained.

[14] T. Karstens, K. Kobs, *J. Phys. Chem.* **1980**, *84*, 1871-1872.