Experimental

Methyl-4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoate (4). 3-(2-(5-chloro-2-methylthiophen-3-yl)cyclopent-1-enyl)-2-methyl-5-phenylthiophene 3 (0.87 g, 2.36 mmol) in THF (40 ml) was treated with t-Buli (2.36 ml, 1.5 M in pentane, 3.54 mmol) under a N₂ atmosphere. After 1 h, B(OBu)₃ (0.95 ml, 3.54 mmol) was added and the mixture was stirred for 1 h at room temperature. A separate flask was charged with methyl 4-bromobenzoate (0.76 g, 3.54 mmol), [Pd(PPh₃)₄] (81 mg, 0.07 mmol), THF (50 ml), aqueous Na₂CO₃ (2 M, 10 ml) and ethylene glycol (10 drops). The mixture was heated to 80 °C and the preformed boronic ester was added slowly. The reaction mixture was heated at reflux overnight, cooled to room temperature, diluted with diethyl ether (50 ml) and washed with H₂O (50 ml). The aqueous layer was extracted with diethyl ether (50 ml). The combined organic layers were dried over Na₂SO₄. After evaporation of the solvent, the product was purified by column chromatography on silica gel (heptane) to afford 4 as a sticky oil (0.56 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.02 (s, 3H), 2.10 (m, 2H), 2.85 (t, J = 7.34, 7.69 Hz, 4H), 3.91 (s, 3H), 7.03 (s, 1H), 7.15 (s, 1H), 7.22 (t, J = 7.33, 7.34 Hz, 1H), 7.33 (t, J = 7.33, 8.07 Hz, 2H), 7.50 (d, J = 7.33 Hz, 2H), 7.54 (d, J = 8.43 Hz, 2H), 7.99 (d, J = 8.80 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.43 (q), 14.54 (q), 23 (t), 38.44 (t), 38.47 (t), 52.04 (q), 123.88 (d), 124.80 (d), 125.29 (d), 125.54 (d), 126.98 (d), 128.15 (s), 128.78 (d), 130.18 (d), 134.26 (s), 134.42 (s), 134.46 (s), 135.09 (s), 136.30 (s), 136.52 (s), 137.11 (s), 138.29 (s), 138.73 (s),
139.79 (s), 166.79 (s). EI-MS (m/z): 470 (M⁺, 100); HRMS calcd for C₂₉H₂₆O₂S₂ 470.1374, found 470.1399.

4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (5). Methyl-4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoate (4) (0.56 g, 1.21 mmol) and LiOH (0.15 g, 6 mmol) was added to 50 mL of MeOH/H₂O/THF (1:1:3 v/v/v). The suspension was stirred at room temperature for 10 h. The mixture was acidified carefully by dropwise addition of 2 M aq. HCl. The aqueous layer was extracted with dichloromethane (3x50 ml). The combined organic layer was washed with sat. aq. NaCl, dried over Na₂SO₄, and the solvent removed in vacuo. The product was recrystallized from dichloromethane/methanol, to yield compound 5 as a brown solid (0.49 g, 89%). ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.03 (s, 3H), 2.10 (m, 2H), 2.86 (t, J = 7.34, 7.33 Hz, 4H), 7.03 (s, 1H), 7.18 (s, 1H), 7.23 (m, 1H), 7.33 (t, J = 7.70, 7.33 Hz, 2H), 7.50 (d, J = 7.70 Hz, 2H), 7.58 (d, J = 8.43 Hz, 2H), 8.06 (d, J = 8.70 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 14.43 (q), 14.57 (q), 23.00 (t), 38.44 (t), 38.48 (t), 123.87 (d), 124.87 (d), 125.29 (d), 125.85 (d), 126.99 (d), 127.13 (s), 128.78 (d), 130.84 (d), 134.21 (s), 134.41 (s), 134.47 (s), 135.18 (s), 136.50 (s), 136.65 (s), 137.20 (s), 138.15 (s), 139.59 (s), 139.82 (s), 171.36 (s). EI-MS (m/z): 456 (M⁺, 100); HRMS calcd. for C₂₈H₂₄O₂S₂ 456.121, found 456.120. M.P. 170.7-171.7 °C.

4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)-N-propylbenzamide (2). 4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (5) (100 mg, 0.22 mmol) was suspended in CH₂Cl₂ (5 ml) and placed in ice bath. Subsequently N-
methylmorpholine (30 µl, 0.22 mmol) was added and the compound dissolved. Next 2-chloro-4,6-dimethoxytriazine (46 mg, 0.22 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C, and a second equivalent of N-methylmorpholine (30 µl, 0.22 mmol) was added followed by propylamine (43 µl, 0.44 mmol). Stirring was continued for 1 h at 0 °C, and subsequently overnight at room temperature. CH₂Cl₂ (50 ml) was added and the solution was washed with, respectively, 1M aq. HCl (2 x 20 ml), brine (1 x 20 ml), saturated aqueous bicarbonate solution (1 x 20 ml) and H₂O (1 x 20 ml). The organic phase was dried over Na₂SO₄ and after evaporation of the solvent a solid was obtained. After purification by column chromatography (EtOAc/heptane = 5:95) a brown solid was obtained (48 mg, 43%). ¹H NMR (400 MHz, CDCl₃) δ 0.98 (t, J = 7.33, 7.70 Hz, 3H), 1.64 (m, 2H), 2.00 (s, 3H), 2.02 (s, 3H), 2.09 (m, 2H), 2.85 (t, J = 7.70, 7.33 Hz, 4H), 3.41 (m, 2H), 6.15 (br, 1H), 7.03 (s, 1H), 7.10 (m, 1H), 7.22 (m, 1H), 7.33 (t, J = 7.33, 7.70 Hz, 2H), 7.50 (d, J = 6.97 Hz, 2H), 7.53 (d, J = 8.43 Hz, 2H), 7.72 (d, J = 8.43 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 11.42 (q), 14.00 (q), 14.49 (q), 22.93 (t), 23.00 (t), 38.41 (t), 38.49 (t), 41.74 (t), 123.90 (d), 125.04 (d), 125.15 (d), 125.28 (d), 126.95 (d), 127.40 (d), 128.45 (d), 128.75 (d), 131.71 (d), 132.79 (s), 134.33 (s), 134.43 (s), 134.46 (s), 135.01 (s), 135.81 (s), 136.54 (s), 136.99 (s), 137.32 (s), 138.32 (s), 139.74 (s), 166.94 (s). EI-MS (m/z): 497 (M⁺, 100); HRMS calcd for C₃₁H₃₆NOS₂ 497.185, found 497.184. M.P. 78-79 °C.

4-(5-Methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)-N-(2-(triethoxysilyl)ethyl)benzamide (1). 4-(5-methyl-4-(2-(2-methyl-5-phenylthiophen-3-yl)cyclopent-1-enyl)thiophen-2-yl)benzoic acid (5) (100 mg, 0.23 mmol) was suspended in CH₂Cl₂ (5 ml) and placed in ice bath. Subsequently N-methylmorpholine (25 ml, 0.23 mmol) was added suspension became a solution. Then 2-chloro-4,6-dimethoxytriazine (40 mg, 0.23 mmol) was added. The reaction mixture was stirred for 2 h at 0 °C, and a second equivalent of N-methylmorpholine (25 ml, 0.23 mmol) was added followed by n-aminopropyltriethoxysilane (0.16 ml, 0.69
Stirring was continued for 1 h at 0 °C, and overnight at room temperature. The reaction mixture was filtered and solvent removed in vacuo. The product was purified by flash column chromatography (1:1 EtOAc : Heptane) a sticky oil was obtained (0.11 g, 75%).$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.70 (m, 2H), 1.22 (m, 9H), 1.75 (m, 2H), 1.99 (s, 3H), 2.00 (s, 3H), 2.08 (m, 2H), 2.86 (m, 4H), 3.45 (m, 2H), 3.83 (m, 6H), 6.51 (br, 1H), 7.03 (s, 1H), 7.10 (s, 1H), 7.23 (m, 1H), 7.32 (t, $J$=7.33, 7.79 Hz, 2H), 7.51 (m, 4H), 7.73 (d, $J$=8.43 Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.78 (t), 14.40 (q), 14.49 (q), 18.25 (q), 22.74 (t), 22.84 (t), 38.41 (t), 38.44 (t), 42.17 (t), 58.49 (t), 123.88 (d), 124.98 (d), 125.09 (d), 125.26 (d), 126.95 (d), 127.45 (d), 128.52 (d), 128.75 (d), 131.64 (d), 132.83 (s), 134.33 (s), 134.41 (s), 134.45 (s), 134.97 (s), 135.76 (s), 136.55 (s), 136.97 (s), 137.24 (s), 138.37 (s), 139.73 (s), 166.88 (s). EI-MS (m/z): 659 (M$^+$, 100); HRMS calcd for C$_{34}$H$_{45}$NO$_4$S$_2$Si 659.256, found 659.257.

**Electrode Modification**

The ITO glass slides were treated with a 1 mM solution of compound 1 at reflux in dry toluene for 24 h. The modified ITO samples were then washed with HPLC-grade toluene, HPLC-grade methanol and HPLC grade $\textit{iso}$-propanol and dried with the stream of nitrogen.

**Electrochemistry**

Electrochemical measurements were carried out on a Model 630B Electrochemical Workstation (CHInstruments) using a saturated calomel reference electrode (SCE) and Pt wire as auxiliary electrode. The working electrodes were ITO-coated glass slides (Prazision Glas & Optik GmbH, Germany) or glassy carbon electrodes in the case of 2o/2c. The supporting electrolytes were n-Bu$_4$NPF$_6$ (TBAP) and n-TBA(CF$_3$SO$_3$) 0.1 M in CH$_2$Cl$_2$. 
Cyclic voltammetry of ITO glass before and after activation

**Figure S1.** Cyclic voltammogram of Ferrocene in 0.1 M TBAP/CH3CN recorded with ITO electrodes at the scan rate of 0.1 Vs⁻¹. Solid line, ITO before activation with basic H2O2 solution; dotted line, ITO after activation with basic H2O2 solution.

**Surface roughness determination**

A Dimension scanning probe microscope (Digital Instruments) was employed to observe the film morphology. The characterization was performed under ambient conditions by tapping mode AFM on several samples of 10-ITO and with different tips. The root mean square (RMS) surface roughness of the surface of 10-ITO as measured by atomic force microscopy (AFM) on areas typically of 1x1 µm² was 12 nm. For Figure S2a, the effective area was calculated to be 0.7764 µm² by WsXM software, which corresponds to a roughness factor of 1.2. AFM phase contrast images have been shown to be sensitive to material surface properties, such as chemical composition. Figure S2b is the phase contrast image corresponding to the topography shown on Figure S2a. It shows a different contrast than Figure S2a. This contrast corresponds to uncovered or monolayer-covered ITO areas. It shows that the organic coverage is homogeneously distributed over the surface.
Figure S2. AFM images of the monolayer/ITO surface. Scale: 0.8x0.8 µm². a) Topographic image b) Phase contrast image.

Cyclic voltammetry of 1o-ITO

Figure S3 Photoswitching of 1o-ITO, upon irradiation at 312 nm, and subsequently with >400 nm. a) 1o-ITO, b) after 312 nm irradiation of, c) after >400 nm irradiation, d) after 312 nm irradiation, e) after >400 nm irradiation f) after 312 nm irradiation, in 0.1 M TBA(CF₃SO₃)/CH₂Cl₂ at scan rate 2 V s⁻¹

Electrochemical conversion of 1c-ITO to 1o-ITO, oxidative ring-opening

Figure S4 Cyclic voltammetry of a) 1c-ITO (formed from 1o-ITO by irradiation with 312 nm light); b) 1o-ITO (after oxidative ring opening achedieved by repetitive cyclic voltammetry between 0.0 and 0.6 V at 0.1 V s⁻¹) in 0.1M TBA(CF₃SO₃)/CH₂Cl₂ at scan 0.5 Vs⁻¹ and c) after irradiation of oxidatively opened 1c-ITO with 312 nm light in 0.1 M TBA(CF₃SO₃)/CH₂Cl₂ at scan rate 2 Vs⁻¹.

Ring opening (oxidatively) is a thermodynamically disfavoured process. It occurs through disproportionation of the monocation of the closed form 1c⁺-ITO to the neutral compound e.g. 1c-ITO and the dication 1c²⁺-ITO. The dication 1c²⁺-ITO is in equilibrium with 1o²⁺-ITO albeit with the closed form highly favoured. In addition the dications 1c²⁺-ITO and 1o²⁺-ITO will undergo rapid electrochemical reduction to the monocation 1c⁺-ITO and neutral 1o-ITO compounds, respectively at below 0.6 V. although statistically unlikely, once ring opening does occur it is irreversible under the limited scanning range of 0-0.5 V. Hence, at high scan rates (> 1 V s⁻¹) the extent of disproportion of the monocation generated is low and the rapid reduction of the dication inhibits ring opening. At slower scan rates the equilibrium is driven towards the open form 1o-ITO, and overall ring open will be observed.

Cyclic voltammetry of 1o-ITO before and after photochemical ring-opening followed by photochemical ring closure monitored at 0.1 V s⁻¹.
Figure S5 Cyclic voltammetry of a) 1o-ITO and b) 1c-ITO after irradiation at 312 nm for 5 min. Inset: Repetitive photochemical switching of 1o-ITO to 1c-ITO. Data recorded in 0.1 M TBAPF$_6$/CH$_2$Cl$_2$ at scan rate 0.1 Vs$^{-1}$. 