Electronic Supplementary Information

Photoswitchable fluorescent diarylethene derivatives with short alkyl chain substituents

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^b Division of Frontier Materials Science, Graduate School of Engineering Science, Center for Quantum Science and Technology under Extreme Conditions, Osaka University, Toyonaka, Osaka 560-8531, Japan **Analytical data of 1a, 3a and 4a:** In the following ¹H NMR data, ap and p indicate the proton signals assigned to antiparallel and parallel conformations of the open-ring isomers, respectively.

1,2-Bis(2-methyl-6-phenyl-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**1a**): $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 2.11 (3 H, s, CH₃, ap), 2.24 (3 H, s, CH₃, p), 7.22-7.28 (2 H, m, aromatic), 7.43-7.59 (10 H, m, aromatic), 7.64 (1 H, d, *J* = 7.6 Hz, aromatic, p), 7.80 (1 H, d, *J* = 7.6 Hz, aromatic, ap), 7.93 (1 H, s, aromatic, p), 7.98 (1 H, s, aromatic, ap). *m/z* 684 (M⁺). Found: C, 61.55; H, 3.42; S, 9.35. Calc. for C₃₅H₂₂F₆O₄S₂: C, 61.40; H, 3.24; S, 9.37%.

1,2-Bis(2-*n*-propyl-6-phenyl-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**3a**): $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 0.82 (3.9 H, t, *J* = 7.2 Hz, CH₃, ap), 1.08 (2.1 H, t, *J* = 7.2 Hz, CH₃, p), 1.34-1.43 (1.4 H, m, CH₂, p), 1.74-1.99 (2.6 H, m, CH₂, ap), 2.29-2.69 (4 H, m, CH₂), 7.20 (0.7 H, d, *J* = 8.0 Hz, aromatic, p), 7.29 (1.3 H, d, *J* = 8.0 Hz, aromatic, ap), 7.40-7.61 (10.7 H, m, aromatic), 7.81 (1.3 H, dd, *J* = 8.0 and 1.2 Hz, aromatic, ap), 7.89 (0.7 H, d, *J* = 1.2 Hz, aromatic, p), 7.97 (1.3 H, d, *J* = 1.2 Hz, aromatic, ap). *m*/*z* 740 (M⁺). Found: C, 63.40; H, 4.02; S, 8.93. Calc. for C₃₉H₃₀F₆O₄S₂: C, 63.23; H, 4.08; S, 8.66%.

1,2-Bis(2-*n*-butyl-6-phenyl-1-benzothiophen-1,1-dioxide-3-yl)perfluorocyclopentene (**4a**): $\delta_{\rm H}$ (400 MHz; CDCl₃; Me₄Si) 0.76 (3.9 H, t, *J* = 7.2 Hz, CH₃, ap), 1.00 (2.1 H, t, *J* = 7.2 Hz, CH₃, p), 1.05-1.36 (4.0 H, m, CH₂), 1.43-1.96 (4 H, m, CH₂), 2.26-2.68 (4 H, m, CH₂), 7.20 (0.7 H, d, *J* = 8.0 Hz, aromatic, p), 7.30 (1.3 H, d, *J* = 8.0 Hz, aromatic, ap), 7.40-7.61 (10.7 H, m, aromatic), 7.80 (1.3 H, dd, *J* = 8.0 and 1.2 Hz, aromatic, ap), 7.89 (0.7 H, d, *J* = 1.2 Hz, aromatic, p), 7.98 (1.3 H, d, *J* = 1.2 Hz, aromatic, ap). *m*/*z* 768 (M⁺). Found: C, 64.09; H, 4.44; S, 8.47. Calc. for C₄₁H₃₄F₆O₄S₂: C, 64.05; H, 4.46; S, 8.34%.



Fig. S1 Absorption spectra of **3a** (black dashed line), **3b** (black solid line) and photostationary states under irradiation with 330 nm light (black dotted line) and fluorescence spectra of **3b** under irradiation with 450 nm light (green solid line, uncorrected) in 1,4-dioxane $(2.0 \times 10^{-5} \text{ M})$.