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**Photochemical control of a highly efficient addition reaction between electron-rich
alkynes and tetracyanoethylene**

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Materials

All reagents were purchased from Kanto, Tokyo Kasei, Wako and Aldrich and used as received. 4-(4-Bromo-5-methylthiophen-2-yl)-*N,N*-dimethylaniline (**5**)¹ and 3,5-dibromo-2-methylthiophene (**7**)² were prepared according to the reported method.

General measurements

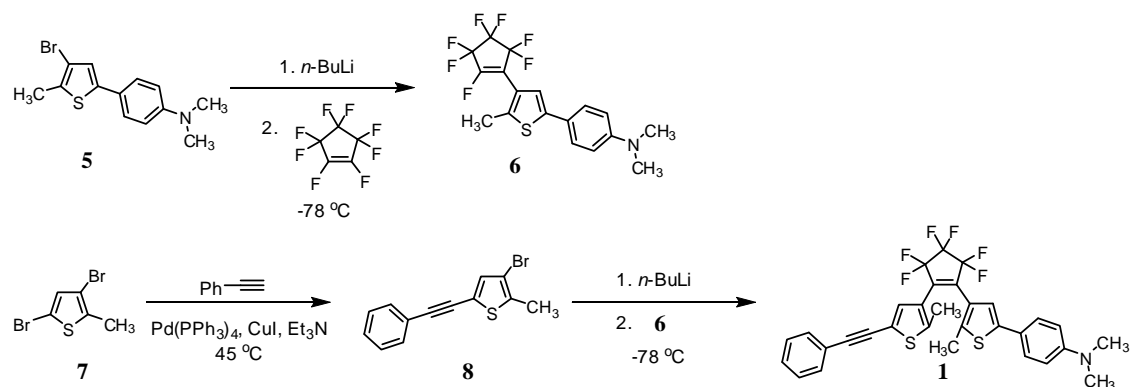
¹H and ¹³C NMR spectra were recorded on a JEOL model AL300 or a Bruker Biospin Avance400 spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from SiMe₄, using the solvent's residual signal as an internal reference. The resonance multiplicity is described as s (singlet), d (doublet) and m (multiplet). FR-IR spectra were recorded on a JASCO FT/IR-4100. Mass spectra were recorded on a Shimadzu GCMS-QP2010Plus spectrometer. Thermogravimetric analyses (TGA) were carried out on a Rigaku Thermoplus TG8120 under nitrogen flow at a heating rate of 10 °C min⁻¹. UV-Vis-NIR absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Electrochemical measurements were carried out on an ALS model 600C in dehydrated acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate ((*n*C₄H₉)₄NCIO₄) in a classical three-electrode cell at 20 °C. The working, reference and auxiliary electrodes were a platinum electrode (1.6 mm in diameter), Ag/AgNO₃/acetonitrile/(*n*C₄H₉)₄NCIO₄ and a platinum wire (BAS), respectively. All potentials are referenced to the ferrocene/ferrocene⁺ (Fc/Fc⁺) couple used as an internal standard.

X-Ray crystallographic analysis was carried out on a CCD-based X-ray diffractometer (Bruker AXS, SMART APEX) with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was cooled by a low temperature controller (Japan Thermal Engineering,

TC-190CP-CS-K). The data were collected as a series of ω -scan frames, each with a width of 0.3°/frame. The crystal decay was monitored by repeating the 50 initial frames at the end data collection and analyzing the duplicate reflections. Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects and decay. The cell constants were determined by the global refinement. The structure was solved by direct methods using SHELXS-90³ and refined by full-matrix least-squares on F^2 using SHELXL-97.⁴ The positions of hydrogen atoms were calculated geometrically and refined by the riding model.

Optimized molecular structures and electronic transitions were calculated by using the B3LYP functional and the 6-31G* basis set (Gaussian 03 program).⁵

Synthesis



Scheme S1 Synthesis of diarylethene **1**.

4-[4-(2,3,3,4,4,5,5-Heptafluorocyclopent-1-en-1-yl)-5-methylthiophen-2-yl]-N,N-dimethylaniline (**6**). To a solution of **5** (5.20 g, 17.6 mmol) in dry THF (350 mL), *n*-butyllithium hexane solution (1.6 M, 11.3 mL, 18.4 mmol) was added at $-78\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. The solution was stirred for 45 min at $-78\text{ }^{\circ}\text{C}$. After addition of perfluorocyclopentene (5.9 mL, 44 mmol), the reaction mixture was further stirred for 1.5 h at that temperature. The reaction was quenched by addition of water, and the product was extracted with diethyl ether ($\times 2$). The organic layer was washed with brine ($\times 3$), dried over MgSO_4 , filtered and evaporated. The crude product was purified by silica gel column chromatography (hexane : ethyl acetate = 90 : 10) to yield **6** (4.26 g, 59%). M.p. $136.5\text{--}137.5\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 2.44₅ (d, $J = 3.2$ Hz, 3 H, thienyl- CH_3), 2.99 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 6.71 (d, $J = 8.8$ Hz, 2 H, $-\text{C}_6\text{H}_4\text{N}$), 7.07 (s, 1 H, thienyl), 7.41 (d, $J = 8.8$ Hz, 2 H, $-\text{C}_6\text{H}_4\text{N}$). ^{13}C NMR (100 MHz, CDCl_3): δ 14.57, 40.37, 112.45, 112.65, 119.83, 120.21, 120.65, 121.45, 125.89, 126.52, 126.73, 140.95, 143.46, 150.32. IR (KBr): ν 2919, 2897, 2815, 1697, 1612, 1559, 1525, 1485, 1446,

1389, 1360, 1330, 1282, 1233, 1201, 1158, 1128, 1109, 1063, 1032, 975, 895, 808, 742, 668, 616. MS (EI): m/z 587 (M^+).

3-Bromo-2-methyl-5-(phenylethynyl)thiophene (**8**). To a degassed solution of **7** (27.5 g, 0.107 mmol) and phenylacetylene (3.78 g, 37.0 mmol) in triethylamine (300 mL), Pd(PPh₃)₄ (5.0 g, 4.33 mmol) and CuI (1.6 g, 8.40 mmol) were added under nitrogen. After the mixture was stirred for 18 h at 45 °C, the solution was cooled to 20 °C. Removal of the precipitated salt by filtration, evaporation and silica gel column chromatography (hexane) yielded **8** as white powder (8.17 g, 80%). ¹H NMR (300 MHz, CDCl₃): δ 2.40 (s, 3 H, -CH₃), 7.07 (s, 1 H, thienyl), 7.33-7.35 (m, 3 H, phenyl), 7.48-7.51 (m, 2 H, phenyl). ¹³C NMR (75 MHz, CDCl₃): δ 14.90, 81.68, 93.63, 108.95, 120.76, 122.58, 128.38, 128.58, 131.41, 134.05, 136.34. IR (neat): ν 2912, 2203, 1594, 1525, 1456, 1439, 1329, 1258, 1151, 1096, 1066, 1026, 995, 909, 814, 749, 685.

4-(4-{3,3,4,4,5,5-Hexafluoro-2-[2-methyl-5-(phenylethynyl)thiophen-3-yl]cyclopent-1-en-1-yl}-5-methylthiophen-2-yl)-N,N-dimethylaniline (**1**). To a solution of **8** (2.71 g, 9.77 mmol) in dry THF (50 mL), *n*-butyllithium hexane solution (1.6 M, 6.30 mL, 10.3 mmol) was added at -78 °C under a nitrogen atmosphere. The solution was stirred for 20 min at -78 °C. After a solution of **6** (4.00 g, 9.77 mmol) in dry THF (25 mL) was added, the reaction mixture was stirred for 1.5 h at -78 °C. The reaction was quenched by addition of water, and the product was extracted with diethyl ether. The organic layer was washed with brine (× 3), dried over MgSO₄, filtered and evaporated. The crude product was purified by silica gel column chromatography (hexane : ethyl acetate

= 90 : 10) to yield **1** (3.25 g, 57%). M.p. 96.0-97.0 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.93₁ (s, 3 H, thienyl-CH₃), 1.93₄ (s, 3 H, thienyl-CH₃), 2.99 (s, 6 H, N(CH₃)₂), 6.71 (d, *J* = 8.8 Hz, 2 H, -C₆H₄N), 7.07 (s, 1 H, thienyl), 7.28 (s, 1 H, thienyl), 7.34-7.36 (m, 3 H, phenyl), 7.41 (d, *J* = 8.8 Hz, 2 H, -C₆H₄N), 7.49-7.52 (m, 2 H, phenyl). ¹³C NMR (100 MHz, CDCl₃): δ 14.09, 14.45, 40.40, 81.63, 93.76, 112.47, 119.73, 121.50, 121.61, 122.54, 125.21, 125.35, 126.57, 128.41, 128.65, 131.43, 131.55, 139.20, 143.27, 143.36, 150.26. ¹³C{¹H} DEPT (90° NMR (CDCl₃): δ 112.47, 119.72, 126.57, 128.41, 128.65, 131.43. IR (KBr): ν 2951, 2916, 2851, 2812, 2205, 1608, 1550, 1521, 1475, 1443, 1396, 1357, 1335, 1268, 1187, 1160, 1133, 1113, 1086, 1067, 1046, 1010, 983, 953, 942, 900, 891, 811, 756, 739, 689, 670, 628. MS (EI): *m/z* 587 (M⁺), 572 (M-CH₃).

4-[4,4,5,5,6,6-Hexafluoro-9a,9b-dimethyl-8-(phenylethynyl)-5,6,9a,9b-tetrahydro-4H-indeno[5,4-b:6,7-b']bisthiophen-2-yl]-N,N-dimethylaniline (2). The closed-ring isomer **2** was prepared by photoirradiation to an acetonitrile solution of **1**, followed by isolation using HPLC (Hitachi L-7100 pump system equipped with a Hitachi L-7400 detector (349 nm), a silica gel column (Kanto, Mightysil RP-18(H)GP) and CH₃CN/MeOH 95:5 as an eluent at 7 mL min⁻¹). M.p. 132.6-134.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.15 (s, 3 H, CH₃), 2.16 (s, 3 H, CH₃), 3.06 (s, 6 H, N(CH₃)₂), 6.47 (s, 1 H, olefinic), 6.53 (s, 1 H, olefinic), 6.66 (d, *J* = 8.8 Hz, 2 H, -C₆H₄N), 7.34-7.37 (m, 3 H, phenyl), 7.45 (d, *J* = 8.8 Hz, 2 H, -C₆H₄N), 7.48-7.51 (m, 2 H, phenyl). ¹³C NMR (100 MHz, CDCl₃): δ 24.84, 25.70, 40.10, 65.93, 66.84, 83.98, 101.78, 110.19, 111.50, 120.44, 121.81, 123.75, 128.53, 128.80, 129.51, 131.80, 133.37, 144.57, 152.08, 152.30, 160.54. ¹³C{¹H} DEPT (90° NMR (CDCl₃): δ 110.19, 111.50, 123.76, 128.53, 128.80,

129.51, 131.80. IR (KBr): ν 2962, 2925, 2857, 2806, 2198, 1601, 1569, 1517, 1483, 1442, 1432, 1371, 1340, 1326, 1279, 1261, 1222, 1189, 1168, 1122, 1092, 1075, 1039, 986, 968, 945, 911, 878, 852, 828, 812, 760, 689, 669. MS (EI): m/z 587 (M^+).

2-[4-(2-{5-[4-(Dimethylamino)phenyl]-2-methylthiophen-3-yl]-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-5-methylthiophen-2-yl]-3-phenylbuta-1,3-diene-1,1,4,4-tetracarbonitrile (4). To a solution of the closed-ring isomer **2** (38.2 mg, 0.0650 mmol) in CH₃CN (8 mL), tetracyanoethylene (9.8 mg, 0.077 mmol) was added in the dark at room temperature. After 15 min, the solution was warmed in a water bath (45 °C) for 15 min to enhance the thermal ring-opening reaction. Evaporation and isolation using HPLC (Hitachi L-7100 pump system equipped with a Hitachi L-7400 detector (349 nm), a silica gel column (Kanto, Mightysil RP-18(H)GP) and CH₃CN/MeOH 98:2 as an eluent at 7 mL min⁻¹) yielded **4** (44.4 mg, 95%). M.p. 94.1-95.5 °C. ¹H NMR (400 MHz, CDCl₃): δ 1.89 (s, 3 H, thienyl-CH₃), 2.21 (s, 3 H, thienyl-CH₃), 3.00 (s, 6 H, N(CH₃)₂), 6.70 (d, J = 8.8 Hz, 2 H, -C₆H₄N), 6.98 (s, 1 H, thienyl), 7.38 (d, J = 8.8 Hz, 2 H, -C₆H₄N), 7.52-7.56 (m, 2 H, phenyl), 7.59 (s, 1 H, thienyl), 7.63-7.69 (m, 3 H, phenyl). ¹³C NMR (100 MHz, CDCl₃): δ 14.40, 15.51, 40.32, 80.64, 87.98, 110.86, 111.22, 112.06, 112.37, 118.92, 120.90, 124.46, 126.61, 128.58, 128.81, 129.12, 130.13, 130.62, 130.88, 131.89, 135.00, 137.91, 139.23, 144.51, 150.44, 155.13, 156.54, 165.69. ¹³C{¹H} DEPT (90° NMR (CDCl₃): δ 112.37, 118.91, 126.61, 129.12, 130.14, 135.01, 137.92. IR (KBr): ν 2961, 2920, 2852, 2807, 2226, 1733, 1609, 1557, 1523, 1474, 1423, 1396, 1361, 1338, 1270, 1229, 1194, 1167, 1139, 1113, 1092, 1047, 1032, 986, 953, 890, 870, 812, 740, 687, 668, 650, 629, 611. MS (EI): m/z 715 (M^+).

X-Ray crystal structure analysis

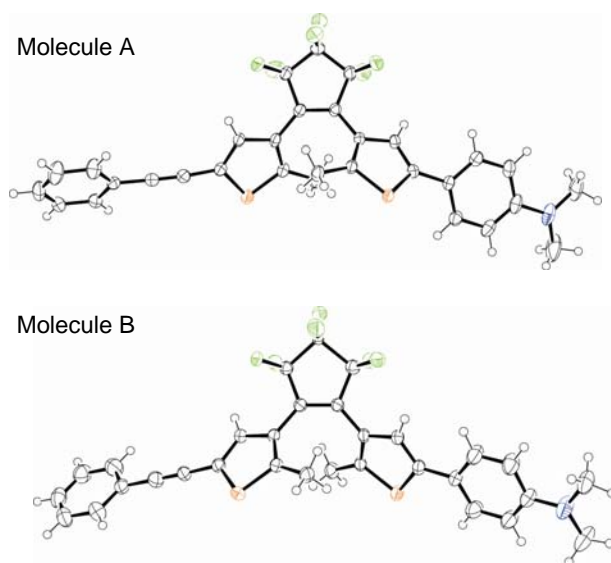


Fig. S1 ORTEP drawings of **1** with 50% thermal ellipsoids. Two molecules (A and B) are crystallographically independent. The hexafluorocyclopentene ring of molecule B is disordered in the ratio of 68 : 32. The minor structure is omitted for clarity. CCDC No. 824641.

Table S1 Crystal data of **1**

Formula	$C_{31}H_{23}F_6N_1S_2$
Formula weight	587.62
T / K	123(2)
Crystal system	Triclinic
Space group	$P \bar{1}$
$a / \text{\AA}$	11.2172(10)
$b / \text{\AA}$	14.1305(12)
$c / \text{\AA}$	18.2407(16)
$\alpha / ^\circ$	73.8990(10)
$\beta / ^\circ$	82.837(2)
$\gamma / ^\circ$	77.2150(10)
$V / \text{\AA}^3$	2702.8(4)
$\rho_{\text{calcd}} / \text{g cm}^{-3}$	1.444
Z	4
$R_1 (I > 2\sigma(I))$	0.0520
$wR_2 (I > 2\sigma(I))$	0.1371
R_1 (all data)	0.0656
wR_2 (all data)	0.1481

Photochromism of **1**

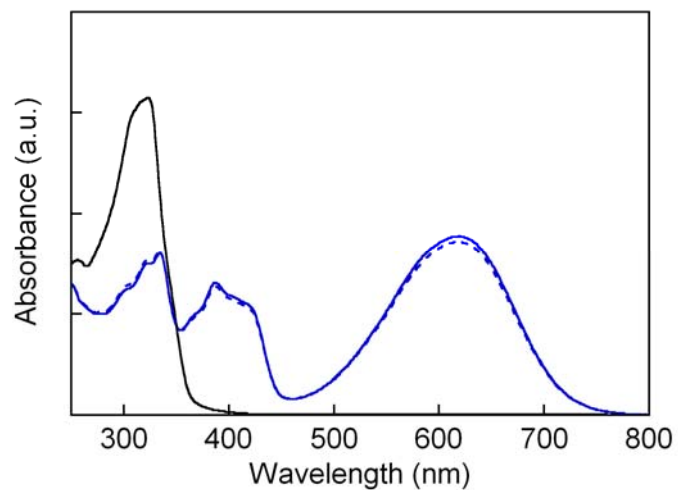


Fig. S2 Absorption spectra of **1** and **2** in hexane. Black solid line: open-ring isomer **1**, blue solid line: closed-ring isomer **2**, blue dashed line: photostationary state under irradiation with 322 nm light. The conversion ratio from **1** to **2** at the photostationary state was 97%.

Computational calculation

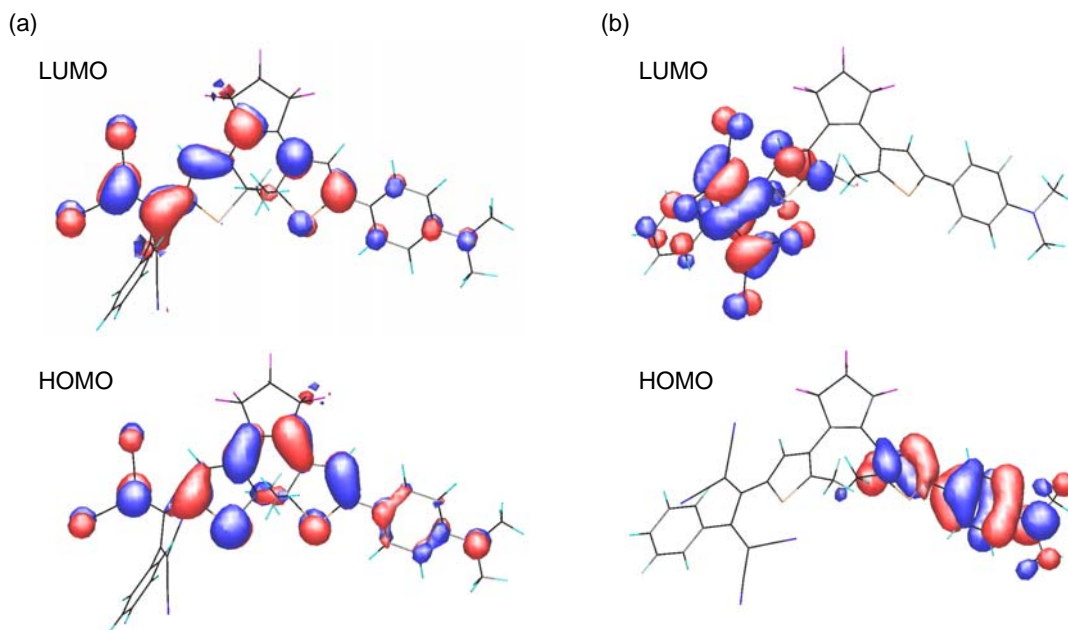


Fig. S3 HOMOs and LUMOs of (a) **3** and (b) **4** calculated by B3LYP/6-31G*.

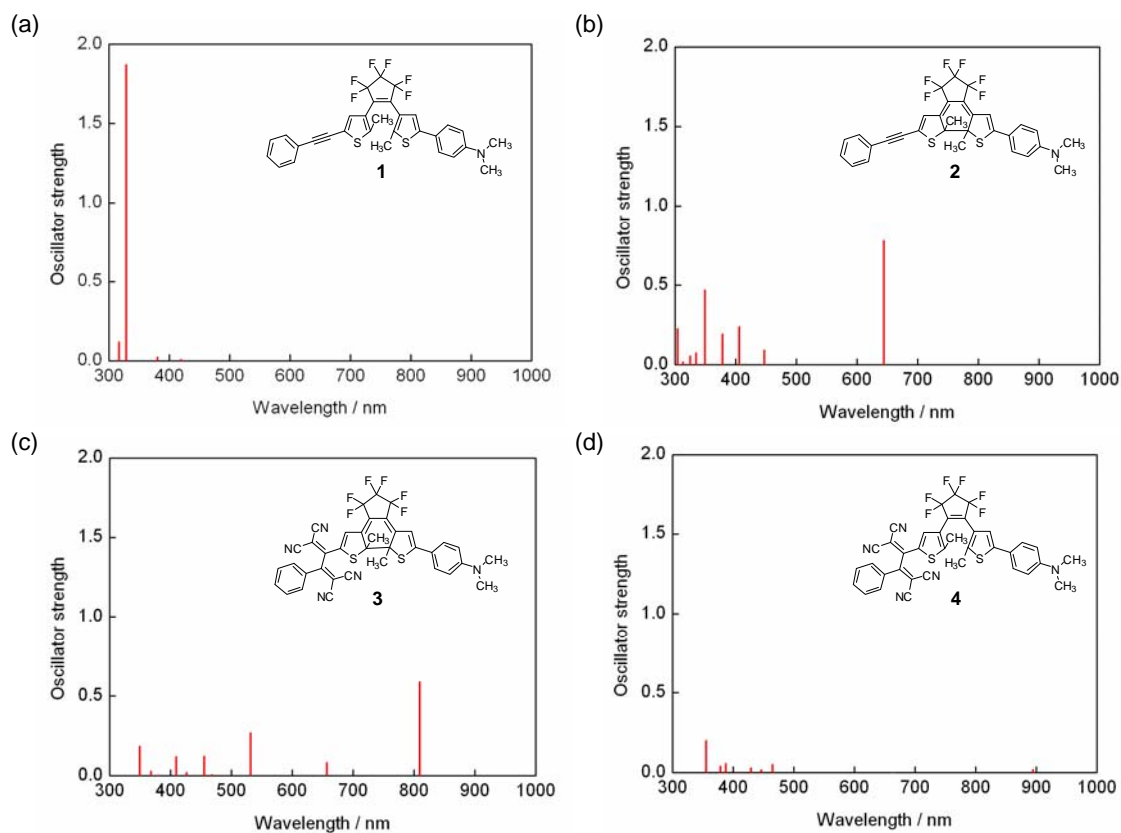


Fig. S4 Electronic absorption spectra of (a) **1**, (b) **2**, (c) **3** and (d) **4** calculated by time-dependent B3LYP/6-31G*.

Photochromism of **4**

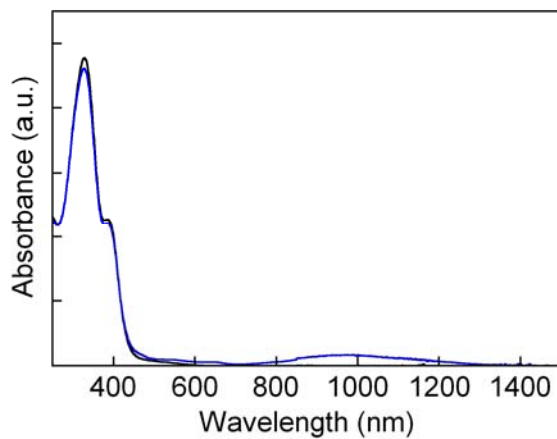


Fig. S5 Absorption spectra of **4** in 1,2-dichloroethane. Black line: before photoirradiation, blue line: after irradiation with 365 nm light.

Cyclic voltammograms

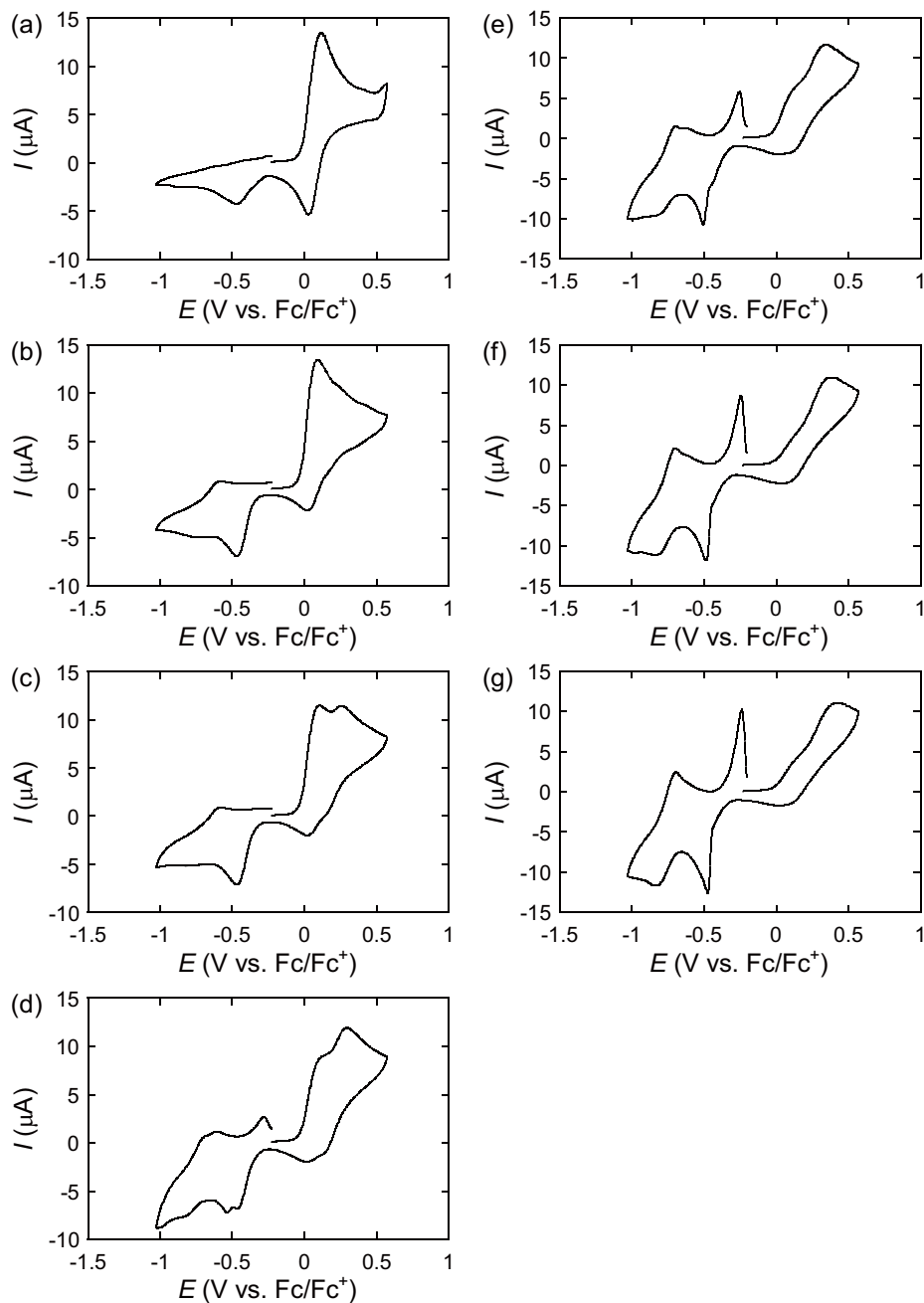


Fig. S6 Time-dependent changes in the CV curves of **2** and TCNE in acetonitrile with 0.1 M $(n\text{C}_4\text{H}_9)_4\text{NClO}_4$ at 20 °C (a, 0 min; b, 10 min; c, 20 min; d, 30 min; e, 40 min; f, 50 min; g, 60 min).

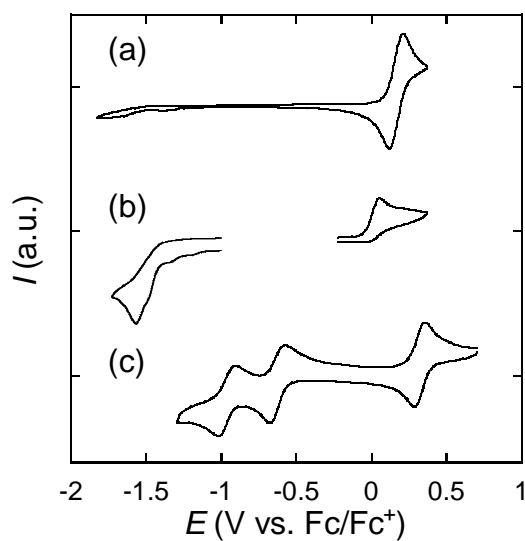


Fig. S7 Cyclic voltammograms of (a) **1**, (b) **2** and (c) **4** in acetonitrile with 0.1 M $(n\text{C}_4\text{H}_9)_4\text{NClO}_4$ at 20 °C.

Solvatochromism

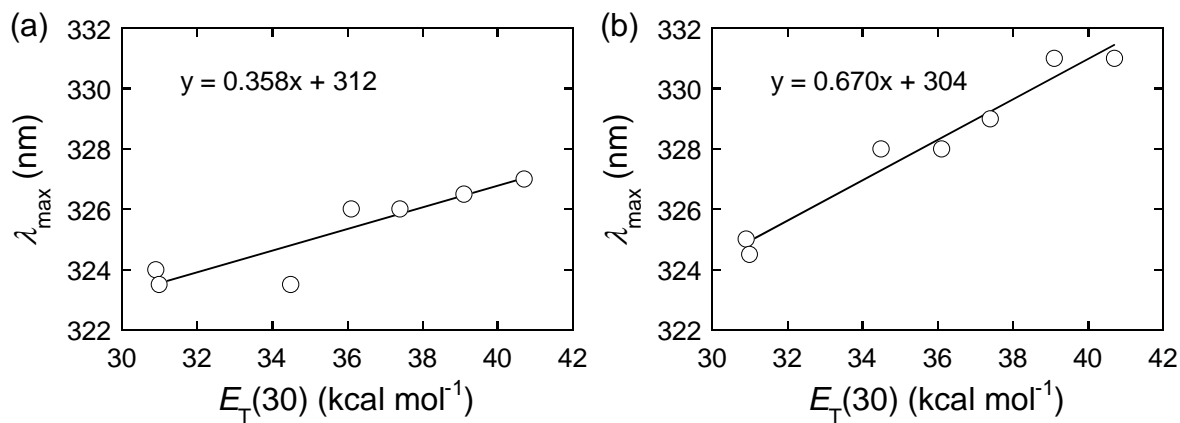


Fig. S8 Relationship between the solvent polarity parameter $E_T(30)$ and the absorption maximum of (a) **1** and (b) **4**.

Table S2 UV-Vis absorption data of **1** and **4** in various solvents.

Solvent	$E_T(30)$ (kcal mol ⁻¹)	1 λ_{\max} (nm)	4 λ_{\max} (nm)
Cyclohexane	30.9	324	325
Hexane	31.0	323.5	324.5
Diethylether	34.5	323.5	328
1,4-Dioxane	36.1	326	328
THF	37.4	326	329
Chloroform	39.1	326.5	331
Dichloromethane	40.7	327	331

Thermogravimetric analysis (TGA)

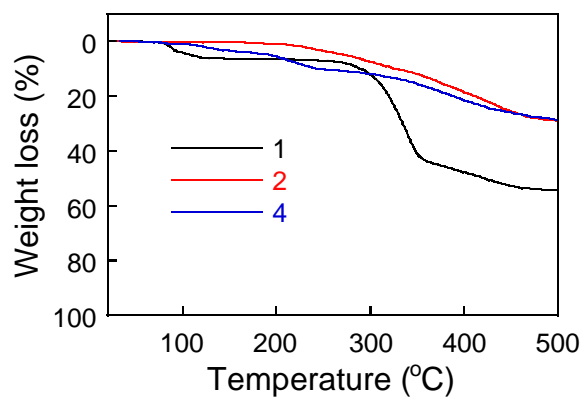


Fig. S9 Thermogravimetric analysis of **1**, **2** and **4** at the heating rate of 10 °C min⁻¹ under flowing nitrogen.

Table S3 Summary of thermal stability of **1**, **2** and **4**.

Compound	$T_{d5\%}$ (°C)	Weight loss at 500 °C (%)
1	109	55.1
2	272	30.3
4	193	30.0

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