[Electronic Supplementary Information (ESI)]

Remote-Control Photocycloreversion of Dithienylethene Driven by Strong Push-Pull Azo Chromophores

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Characterization

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA600 spectrometer (600 MHz for proton and 150 MHz for carbon) by using acetone-d_6 or CDCl$_3$ as the solvent. Photoirradiation was carried out using a 300 W Compact-xenon lamp (Asahi Spectra, Max-302) as a light source. The UV-vis spectra of the samples were recorded using a Perkin-Elmer Lambda Bio-40 spectrophotometer at room temperature in 1 cm path-length quartz cuvettes. Emission spectrum was measured in THF solution at room temperature by using a HITACHI F-4500 fluorescence spectrophotometer. The thermal property was investigated with TA Instrument DSC 2920 at a heating rate of 10 ^{o}C/min under N$_2$ protection.

Synthesis
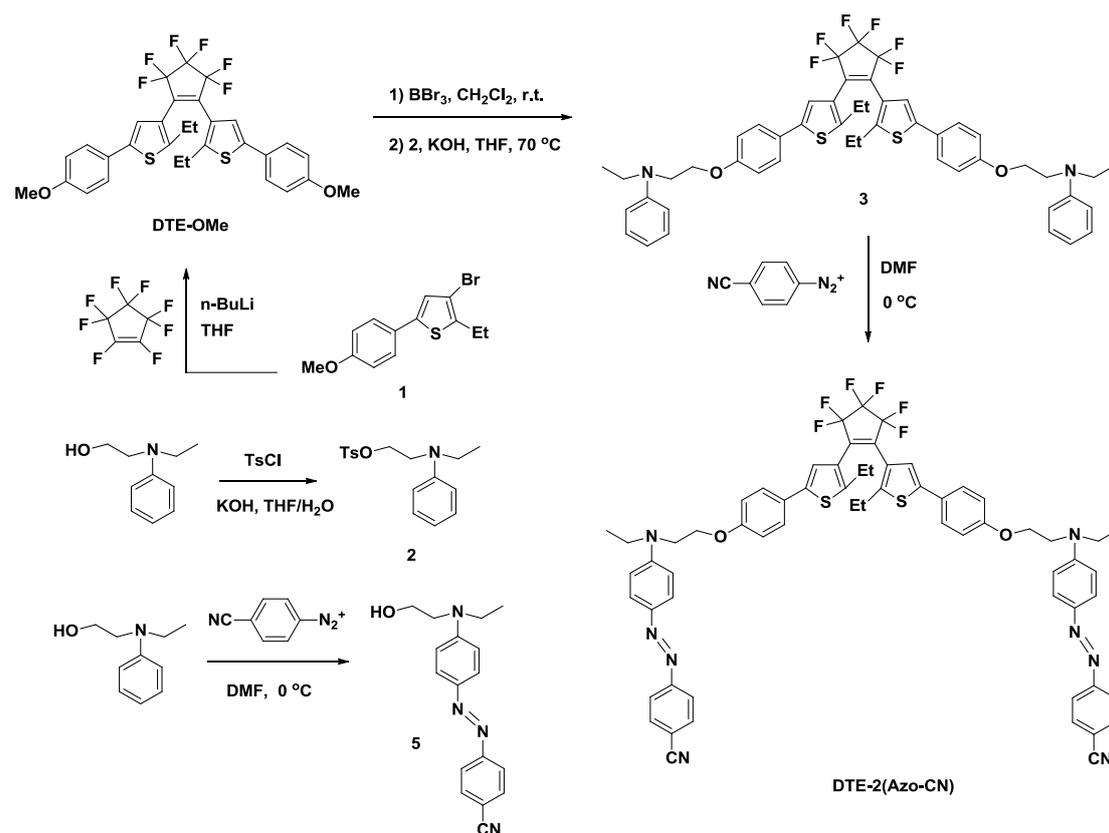
Scheme S1 The synthetic route of the DTE-2(Azo-CN).

DTE-2(Azo-CN) was synthesized according to the reaction scheme shown in Scheme S1.

1,2-Bis[5'-(4''-methoxyphenyl)-2'-ethylthien-3'-yl]perfluorocyclopentene

(DTE-OMe). 3-Bromo-2-ethyl-5-(4-methoxyphenyl)thiophene (**1**) was synthesized by the method reported previously[1]. To a anhydrous THF solution (30 mL) of **1** (1.5g, 5 mmol) was added 3.4 mL n-BuLi (1.6 M in a hexane solution , 5.44 mmol) at -78 °C under Ar. After 1 h, perfluorocyclopentene (0.53g, 2.5 mmol) was added to the reaction mixture, which was then further stirred at -78 °C for 1 h and allowed to warm to 25 °C. The resulting mixture was poured into water and extracted with ether. The combined organic extract was washed with water, dried over anhydrous $MgSO_4$,

filtered and evaporated under a reduced pressure. Then the residue was purified by column chromatography (SiO$_2$, CH$_2$Cl$_2$) to allow isolation of DTE-OMe in 70% yield.

^{1}H NMR (600 MHz, acetone-d_6): δ (ppm): 0.96 (t, 6H), 2.45 (q, 4H), 3.83 (s, 6H), 6.98 (d, 4H), 7.32 (s, 2H), 7.58 (d, 4H), ^{13}C NMR (150 MHz, acetone-d_6): δ (ppm) 160.5, 148.6, 143.3, 127.6, 126.7, 124.8, 122.0, 115.2, 55.7, 23.0, 15.9.

N-(4-methyl ethyl benzenesulfonate)-N-ethylaniline (**2**). 5 M aqueous NaOH (3 mL) was added dropwise into a mixture of N-Ethoxyl-N-ethylaniline (1.65 g, 10 mmol) and toluenesulfonyl chloride(2.00 g, 11 mmol) in tetrahydrofuran (THF, 25 mL) with violent stirring in ice-water bath. After reaction for 5 h at r.t., the mixture was poured into ice water (30 mL) and then was extracted from water with dichloromethane (50 mL). Organic layer was washed with saturated aqueous NaCl before dry over MgSO$_4$. Purification by column chromatography (silica gel, petroleum ether/dichloromethane = 5/1) yielded **2** as white solid in 60% yield. ^{1}H NMR (600 MHz, CDCl$_3$): δ (ppm) 1.09 (t, 3H), 2.41 (s, 3H), 3.29 (q, 2H), 3.56 (t, 2H), 4.13 (t, 2H), 6.54 (d, 2H), 6.66 (t, 1H), 7.16 (q, 2H,), 7.27 (d, 2H), 7.73 (d, 2H). ^{13}C NMR (150 MHz, CDCl$_3$): δ (ppm) 146.9, 145.0, 132.8, 130.0, 129.5, 128.0, 116.5, 111.9, 67.0, 49.0, 45.6, 21.8, 12.2.
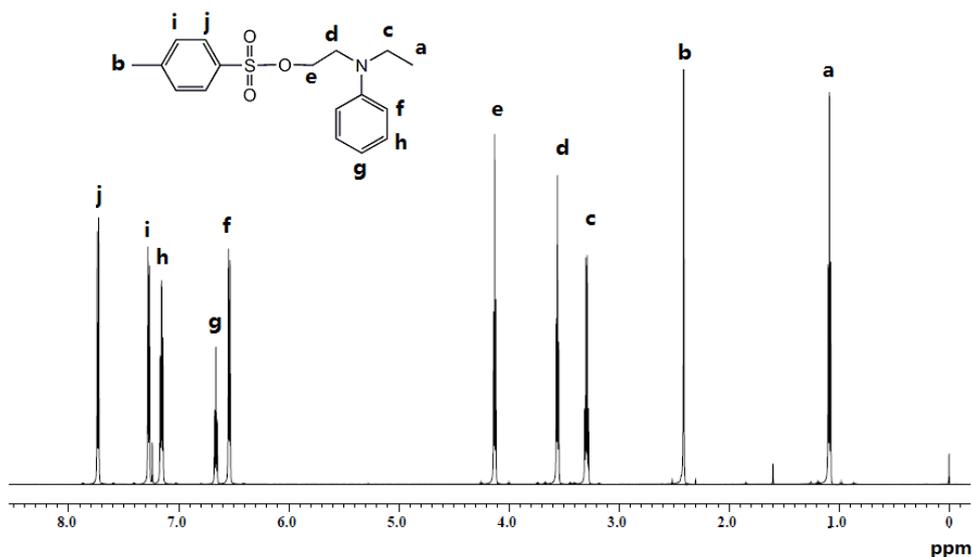
Figure S1 The ^{1}H NMR spectrum of the **2** in CDCl$_3$.

1,2-Bis [5'-(4''- (N-ethylanilino) ethoxy phenyl) -2'- ethylthien -3'- yl]

***perfluorocyclopentene* (3).** BBr$_3$ (0.6 mL) in dichloromethane (3 mL) was added

dropwise slowly into DTE-OMe (0.61 g, 1 mmol) dissolved in dichloromethane (20

mL) under N$_2$ atmosphere at 0 ^{o}C. After reaction for 8 h at r.t. and then quenched by

methanol, the mixture was poured into an excess of water and extracted from the

water using dichloromethane (100 mL). After desiccating and concentrating the

organic phase, the intermediate product as brown powder was obtained. At last, a

mixture of the intermediate product, **2** (0.80 g, 2.5 mmol) and KOH (0.28 g, 5 mmol)

in THF (40 mL) was heated at reflux for 3 h. The mixture was poured into an excess

of water and extracted from the water using dichloromethane (100 mL). The

combined organic layers were dried over MgSO$_4$. Purification by column

chromatography (silica gel, petroleum ether/dichloromethane = 1/1) yielded **3** as

viscous liquid in 75% yield. ^{1}H NMR (600 MHz, acetone-d_6): δ(ppm) 0.93 (t, 6H),

1.15 (t, 6H), 2.42 (q, 4H), 3.49 (q, 4H), 3.74 (t, 4H), 4.18 (t, 4H), 6.58 (t, 2H), 6.75 (d, 4H), 6.97 (d, 4H), 7.14 (t, 4H), 7.30 (s, 2H), 7.54 (d, 4H).
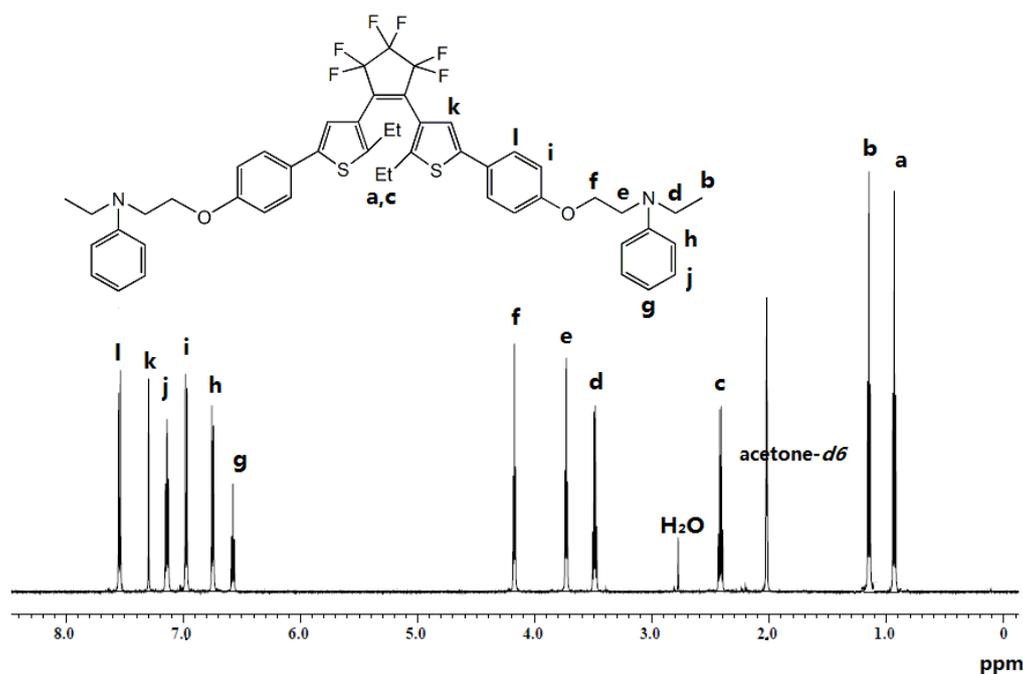

Figure S2 ^{1}H NMR spectrum of **3** in acetone-d_6.

DTE-2(Azo-CN) 4-aminobenzonitrile (0.1 g, 0.85 mmol) was dissolved in a mixture of acetic acid (2 mL) and sulfuric acid (0.1 mL) at 0 °C. NaNO$_2$ (0.07 g, 1.0 mmol) dissolved in 0.3 mL water was slowly dripped into the acidified 4-aminobenzonitrile solution. The mixture was stirred in an ice bath for 10 min to obtain a yellowish solution of the diazonium salts. **3** (0.1g, 0.12 mmol) was dissolved in 10 mL DMF and the solution was cooled down to 0 °C. The diazonium salt solution was added dropwise into the DMF solution. After reaction for 5 h, the raw product was obtained by pouring the reaction solution into 100mL deionized water. The precipitate was collected by filtration and washed with water until the neutral state was achieved. Purification by column chromatography (silica gel, dichloromethane) yielded

DTE-2(Azo-CN) as red powder in 85% yield. T_g: 80 °C. ^{1}H NMR (600 MHz, CDCl$_3$):

δ(ppm) 0.96 (t, 6H), 1.28 (t, 6H), 2.30 (q, 4H), 3.61 (q, 4H), 3.87 (t, 4H), 4.20 (t, 4H),

6.82 (d, 4H), 6.89 (d, 4H), 7.12 (s, 2H), 7.46 (d, 4H), 7.76 (d, 4H) , 7.88 (m, 8H); ^{13}C

NMR (150 MHz, CDCl$_3$): δ(ppm) 155.5, 143.8, 133.2, 127.1, 126.2, 122.8, 115.0,
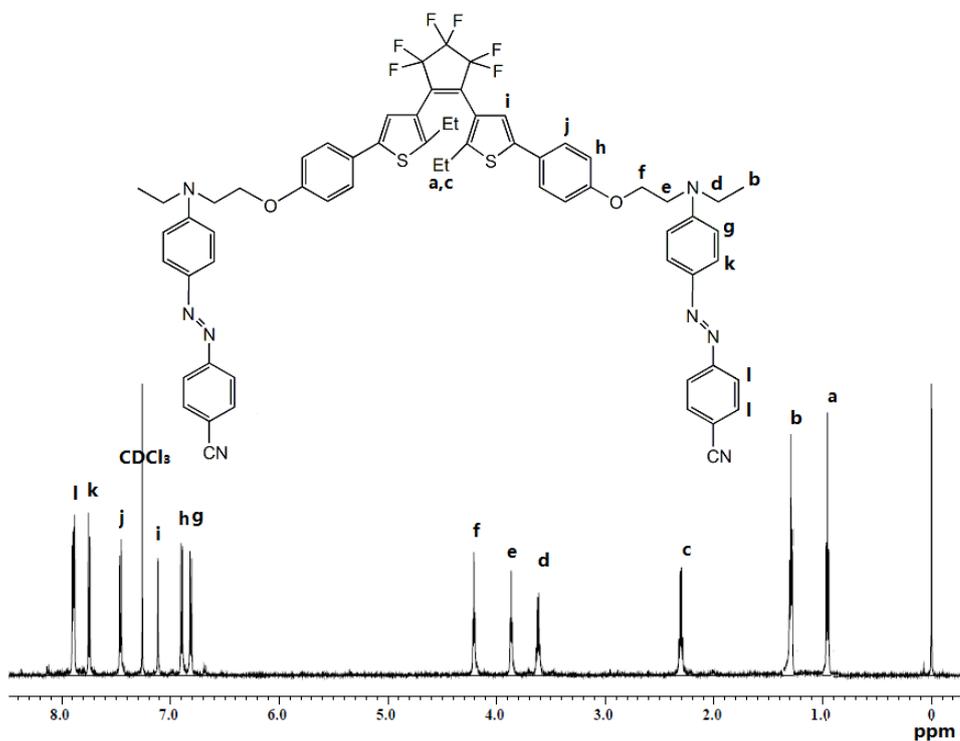
111.5, 65.23, 47.32, 22.54, 15.46, 12.46

Figure S3 ^{1}H NMR spectrum of DTE-2(Azo-CN) in CDCl$_3$.

4-(N-ethyl-N-ethoxylamino)-4'-cyanoazobenzene (5) 4-aminobenzonitrile (0.5 g,

4.3 mmol) was dissolved in a mixture of acetic acid (10 mL) and sulfuric acid (0.5 mL)

at 0 °C. NaNO$_2$ (0.35 g, 5.0 mmol) dissolved in 1.5 mL water was slowly dripped into

the acidified 4-aminobenzonitrile solution. The mixture was stirred in an ice bath for

10 min to obtain the solution of diazonium salts. N-Ethoxyl-N-ethylaniline (0.75 g,

4.5 mmol) was dissolved in 50 mL DMF and the solution was cooled down to 0 $^{\circ}$C.

The diazonium salt solution was added dropwise into above DMF solution. After

reaction for 5 h, the raw product was obtained by pouring the reaction solution into

100 mL deionized water. The precipitate was collected by filtration and washed with

water until the neutral state was achieved. Purification by column chromatography

(silica gel, dichloromethane) yielded **5** as red powder in 90% yield. ^{1}H NMR (600

MHz, CDCl$_3$): δ (ppm) 1.24(t, 3H), 3.54 (q, 2H), 3.60(t, 2H), 3.86(t, 2H), 6.77(d,

2H),7.71(d, 2H),7.84 (m, 4H); ^{13}C NMR (150 MHz, CDCl$_3$): δ (ppm) 155.4, 151.5,

143.5, 133.1, 126.1, 122.7, 119.0, 111.7,111.5, 60.2, 52.4, 45.9, 12.1.
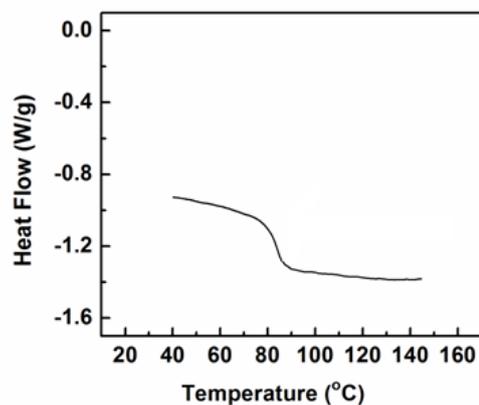
1. The thermal transition behavior of DTE-2(Azo-CN)

Figure S4 DSC curve of DTE-2(Azo-CN).

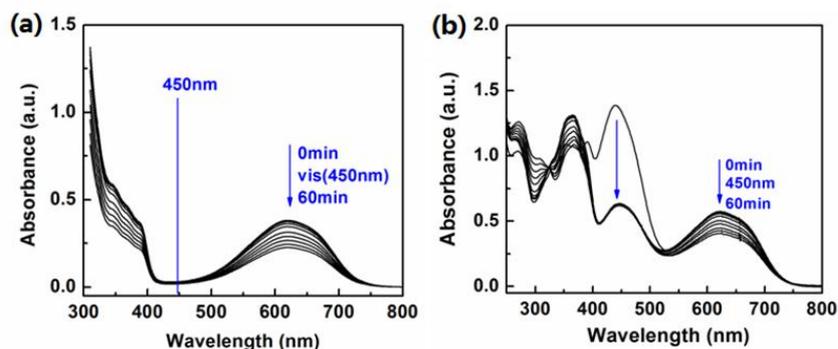2. UV-vis absorption and fluorescence spectra

Figure S5 UV-vis absorption spectral changes of (a) **DTE-OMe**$_{close}$ (3.3×10^{-5} M)

and (b) the mixture of **DTE-OMe**$_{close}$ (3.5×10^{-5} M) and Azo monomer **5** (7.0×10^{-5} M)

upon irradiation with visible light at 450 nm (2.3 mW cm^{-2}) for 0min, 1min, 2min,
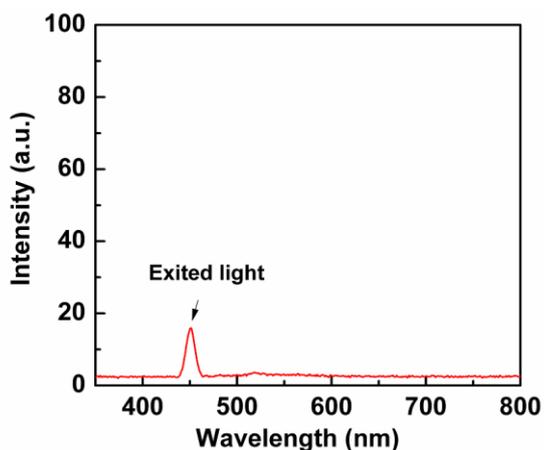
5min, 10min, 20min, 30min, 40min, 50min, 60min.

Figure S6 Emission fluorescence spectrum of azo monomer 5 in THF (7.0×10^{-5} M)

exited with 450 nm light.

3. Evaluation of ring opening conversion, photokinetic parameters

Absorbance (A) is proportional to the concentration (C) just like the following

formula:

$$\log(\frac{I_0}{I}) = A = \varepsilon CL$$

I_0 and I are the intensity of initial and transmitting light source, respectively. ε is a constant called molar absorption coefficient and L represents the thickness of liquid layer. So the ring opening reactions conversion of DTE_{close}-2(Azo-CN) can be calculated by this formula:

$$Conv. = \frac{C_0 - C}{C_0} = \frac{A_0 - A_t}{A_0} \qquad (Eq \quad S1)$$

A typed first-order photokinetic reaction was derived from the following formula:

$$-\frac{dC}{dt} = k_{c \to o} C \Rightarrow -\frac{dA}{dt} = k_{c \to o} A$$

$$\therefore \ln\left(\frac{A_0}{A_t}\right) = k_{c \to o} t \qquad (Eq \quad S2)$$

A_t and A_0 are absorbance at irradiation time t and the initial absorbance, respectively. $k_{c \to o}$ is the photokinetic parameters of ring-opening reactions.

[1] Y.N. He, Y. Yamamoto,W.S. Jin,T. Fukushima, A. Saeki, S. Seki, N. Ishii, T. Aida, *Adv. Mater.* 2010, 22, 829-832.