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Supporting Information

Photochromic polymers bearing various diarylethene chromophores as the pendant: Synthesis, optical properties, and multicolor photochromism

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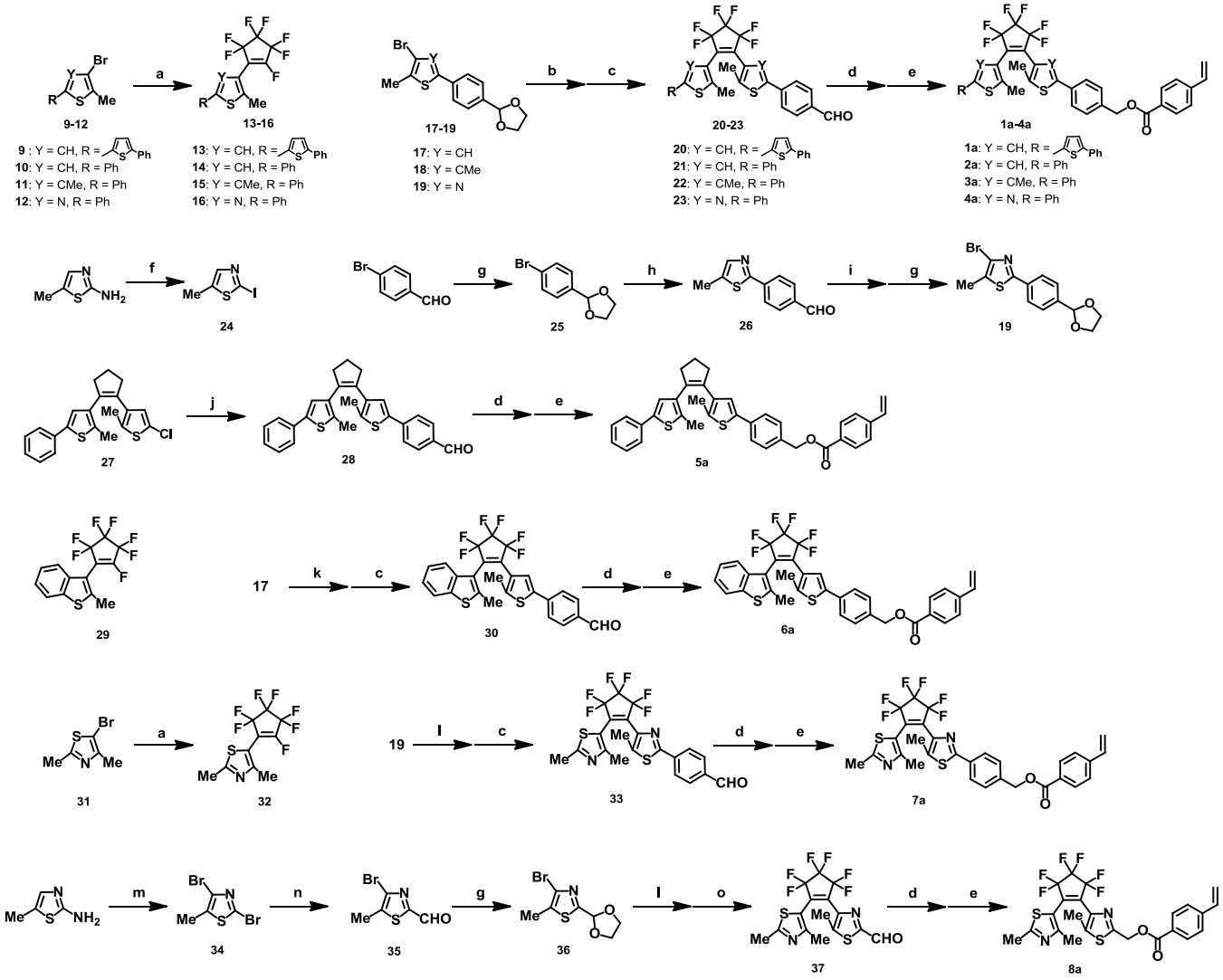
Materials. Diarylethene monomers and their relating compounds were synthesized according to Scheme S1.



Scheme S1. Synthetic scheme of **1a**-**8a**: (a) 1) *n*-BuLi/THF, 2) octafluorocyclopentene, −78 °C; (b) 1) *n*-BuLi/THF, 2) **13**, **14**, **15**, or **16**, −78 °C; (c) pyridinium *p*-toluenesulfonate/acetone, reflux; (d) KBH_4/ethanol, H_2O, r.t.; (e) *p*-vinyl benzoic acid, 4-(dimethylamino)pyridine, *N*,*N*′-dicyclohexyl-carbodiimide/THF, r.t.; (f) $NaNO_2$, KI/H_3PO_4, HNO_3, r.t., (g) ethylene glycol, *p*-toluenesulfonic acid monohydrate/toluene, reflux; (h) 1) *n*-BuLi/THF, 2) $B(OBu)_3$, −78 °C, 3) **24**, $Pd(PPh_3)_4$, Na_2CO_3aq/THF, reflux, 4) HCl, reflux; (i) Br_2/$CHCl_3$, MeCN, reflux; (j) 1) *n*-BuLi/THF, 2) $B(OBu)_3$, −78 °C 3) *p*-bromobenzaldehyde, $Pd(PPh_3)_4$, Na_2CO_3aq/THF, reflux; (k) 1) *n*-BuLi/THF, 2) **29**, −78 °C; (l) 1) *n*-BuLi/THF, 2) **32**, −78 °C; (m) $NaNO_2$, HBr, CuBr/H_3PO_4, HNO_3, r.t.; (n) *n*-BuLi, DMF/THF, −78 °C; (o) HCl/acetone, reflux.

Synthesis of 13.

Compound **9**[S1] (3.0 g, 9.0 mmol) was dissolved in dry THF (130 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (5.8 mL, 9.3 mmol) was dropwise added to the solution, and the mixture was stirred for 40 min. To the solution was quickly added octafluorocyclopentene (2 mL, 15 mmol), and the mixture was stirred for 1.5 h. Adequate amount of distilled water was added to the mixture to quench. The reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane 100%) to give 3.1 g of **13** in 76% yield.

13: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.46 (s, 3H, -C*H*$_3$), 7.10-7.63 (m, 8H, Aromatic H).

Synthesis of 15.

Compound **11**[S2] (9.0 g, 34 mmol) was dissolved in dry THF (430 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (25 mL, 41 mmol) was dropwise added to the solution, and the mixture was stirred for 1 h. To the solution was quickly added octafluorocyclopentene (7.7 mL, 56 mmol), and the mixture was stirred for 1.5 h. Adequate amount of distilled water was added to the mixture to quench. The reaction mixture was neutralized by dilute HCl, extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane 100%) to give 8.9 g of **15** in 70% yield.

15: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.11 (s, 3H, -C*H*$_3$), 2.00 (s, 3H, -C*H*$_3$), 2.38 (s, 3H, -C*H*$_3$), 7.25-7.42 (m, 5H, Aromatic H).

Synthesis of 16.

Compound **12**[S3] (5.0 g, 20 mmol) was dissolved in dry THF (100 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (13 mL, 21 mmol) was dropwise added to the solution, and the mixture was stirred for 1 h. To the solution was quickly

added octafluorocyclopentene (5.8 mL, 43 mmol), and the mixture was stirred for 1.5 h. Adequate amount of distilled water was added to the mixture to quench. The reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 9 / 1) to give 5.9 g of **16** in 81% yield.

16: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.54 (s, 3H, -C*H*$_3$), 7.43-7.95 (m, 5H, Aromatic H).

Synthesis of 19.

Compound **26** (2.0 g, 10 mmol) was dissolved in chloroform (15 mL) and acetonitrile (15 mL). To the solution was dropwise added bromine (1.1 mL, 22 mmol) at room temperature and refluxed for 6 h.[S4] The reaction mixture was neutralized by $NaHCO_3$, washed with aqueous sodium thiosulfate, extracted with chloroform, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 7 / 3) to give 1.2 g of bromo derivative in 49% yield. Formyl group in the compound (1.46 g, 5.2 mmol) was reprotected using ethylene glycol (4.0 g) in toluene in the presence of *p*-toluene sulfonic acid monohydrate (90 mg) as well as **17**[S5] to give 1.5 g of **19** in 88% yield.

19: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.44 (s, 3H, -C*H*$_3$), 4.02-4.17 (m, 4H, -C*H*$_2$-), 5.84 (s, 1H, -C*H*-), 7.50-7.92 (m, 4H, Aromatic H).

Synthesis of 20.

Compound **17**[S5] (2.1 g, 6.5 mmol) was dissolved in dry THF (100 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (4.1 mL, 6.6 mmol) was dropwise added to the solution, and the mixture was stirred for 40 min. To the solution was dropwise added a THF solution of **13** (3.0 g, 6.7 mmol), and the mixture was stirred for 3 h. Adequate amount of distilled water was added to the mixture to quench. The

reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 8 / 2) to give 3.4 g of the protected compound in 76% yield**.** The protecting group of the compound (3.0 g, 4.4 mmol) was removed in wet acetone (75 mL) in the presence of pyridinium *p*-toluenesulfonate (1.3 g, 5.2 mmol) as well as **21**[S5] to give 2.6 g of **20** in 95% yield.

20: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.96 (s, 3H, -C*H*$_3$), 2.03 (s, 3H, -C*H*$_3$), 7.09-7.93 (m, 13H, Aromatic H), 10.0 (s, 1H, -C*H*O).

Synthesis of 22.

Compound **18**[S6] (12 g, 18 mmol) was dissolved in dry THF (350 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (29 mL, 46 mmol) was dropwise added to the solution, and the mixture was stirred for 1 h. To the solution was dropwise added a THF solution (50 mL) of **15** (8.9 g, 14 mmol), and the mixture was stirred for 1 h. Adequate amount of distilled water was added to the mixture to quench. The reaction mixture was neutralized by dilute HCl, extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated in vacuo to give 10 g of the protected compound in 90% yield**.** The protecting group of the compound (1.2 g, 1.9 mmol) was removed in wet acetone (7 mL) in the presence of pyridinium *p*-toluenesulfonate (0.25g, 0.98 mmol) as well as **21**[S5] to give 1.1 g of **22** in > 99% yield.

22: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.11-2.46 (m, 12H, -C*H*$_3$), 7.29-7.89 (m, 9H, Aromatic H), 10.0 (s, 1H, -C*H*O).

Synthesis of 23.

Compound **19** (1.3 g, 4.1 mmol) was dissolved in dry THF (100 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (2.5 mL, 4.0 mmol) was dropwise added to the solution, and the mixture was stirred for 1.5 h. To the solution was

dropwise added a THF solution (10 mL) of **15** (2.0 g, 5.6 mmol), and the mixture was stirred for 4.5 h. Adequate amount of distilled water was added to the mixture to quench. The reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 6 / 4) to give 1.1 g of the protected compound in 44% yield**.** The protecting group of the compound (1.1 g, 1.8 mmol) was removed in wet acetone (30 mL) in the presence of pyridinium *p*-toluenesulfonate (810 mg, 3.2 mmol) as well as **21**[S5] to give 970 mg of **23** in 97% yield.

23: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.12-2.18 (m, 6H, -C*H*$_3$), 2.03 (s, 3H, -C*H*$_3$), 7.37-8.09 (m, 10H, Aromatic H), 10.1 (s, 1H, -C*H*O).

Synthesis of 24.[S7]

2-Amino-5-methylthiazole (1.9 g, 17 mmol) was slowly added to the mixed acid of phosphoric acid (30 mL) and nitric acid (30 mL). An aqueous solution (10 mL) of sodium nitrite (1.3 mg, 17 mmol) was dropwise added to the solution, and the mixture was stirred for 20 min. The reaction mixture was poured into an aqueous solution (100 mL) of potassium iodide (10 g) and stirred for 2-3 days. The mixture was neutralized by a NaOH aqueous solution and extracted with ether. The organic phase was washed with aqueous sodium thiosulfate, $NaHCO_3$ aqueous solution, brine, dried over $MgSO_4$ and evaporated in vacuo. The resulting crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 9 / 1) and recrystallization from the hexane solution to give 2.3 g of **24** in 60% yield**.**

24: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.47 (d, *J* = 1.2 Hz, 3H, -C*H*$_3$), 7.25 (q, *J* = 1.2 Hz, 1H, Aromatic H).

Synthesis of 26.

p-Bromobenzaldehyde (11 g, 60 mmol), ethylene glycol (40 g), and *p*-toluene

sulfonic acid monohydrate (1.0 g) were mixed with toluene (200 mL) and the mixture was refluxed for several hours. The reaction mixture was neutralized by a $NaHCO_3$ aqueous solution, extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo to give 13 g of **25** in 98% yield. **25** (2.3 g, 10 mmol) was dissolved in dry THF (60 mL) under Ar atmosphere at −78°C. 1.6 M *n*-BuLi hexane solution (6.5 mL, 10 mmol) was dropwise added to the solution, and the mixture was stirred for 1.5 h. To the solution was added $B(OnBu)_3$ (3.0 mL, 11 mmol), and the mixture was stirred for 1 h. Adequate amount of distilled water was added to the mixture to quench. To the solution were added **24** (2.4 g, 11 mmol), tetrakis(triphenylphosphine)palladium(0) (180 mg, 0.16 mmol), a 20% Na_2CO_3 aqueous solution (45 mL), and THF (50 mL), and the mixture was refluxed for 1-2 days. To the mixture was slowly added adequate amount of dilute HCl to remove the protecting group. After confirmation of deprotection on thin layer chromatography (TLC), the reaction mixture was neutralized by $NaHCO_3$, extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The resulting crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 7 / 3) to give 1.2 g of **26** in 53% yield.

26: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.55 (s, 3H, -CH_3), 2.56 (s, 3H, -CH_3), 2.03 (s, 3H, -CH_3), 7.57-8.10 (m, 5H, Aromatic H), 10.0 (s, 1H, -C*H*O).

Synthesis of 28.

Compound **27**[S8] (680 mg, 1.8 mmol) was dissolved in dry THF (15 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (1.3 mL, 2.0 mmol) was dropwise added to the solution, and the mixture was stirred for 45 min. To the solution was added $B(OnBu)_3$ (0.7 mL, 2.8 mmol), and the mixture was stirred for 1 h. Adequate amount of distilled water was added to the mixture to quench. To the solution were added *p*-bromobenzaldehyde (340 mg, 1.8 mmol), tetrakis(triphenylphosphine)palladium(0) (180 mg, 0.16 mmol), a 20% Na_2CO_3 aqueous solution (22 mL), THF (40 mL), and 20

drops of ethylene glycol, and the mixture was refluxed for 5 h. The reaction mixture was neutralized by dilute HCl, extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The resulting crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 9 / 1) to give 300 mg of **28** in 37% yield.

26: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.99 (s, 3H, -CH_3), 2.03 (s, 3H, -CH_3), 2.10 (quintet, J = 7.4 Hz, 2H, -CH_2), 2.85 (t, J = 7.4 Hz, 4H, -CH_2), 7.03-7.83 (m, 11H, Aromatic H), 9.96 (s, 1H, -C*H*O).

Synthesis of 30.

Compound **17**[S5] (910 mg, 2.8 mmol) was dissolved in dry THF (60 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (2.0 mL, 3.2 mmol) was dropwise added to the solution, and the mixture was stirred for 1 h. To the solution was dropwise added a THF solution of **29** (950 mg, 2.8 mmol), and the mixture was stirred for 1 h. Adequate amount of distilled water was added to the mixture to quench. The protecting group was removed by addition of HCl. The reaction mixture was neutralized, extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 8 / 2) to give 1.2 g of **30** in 70% yield.

30: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.98 (s, 3H, -CH_3), 2.31 (s, 3H, -CH_3), 7.31-7.86 (m, 9H, Aromatic H), 10.0 (s, 1H, -C*H*O).

Synthesis of 32.

Compound **31**[S3] (7.5 g, 39 mmol) was dissolved in dry THF (320 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (25 mL, 40 mmol) was dropwise added to the solution, and the mixture was stirred for 1.5 h. To the solution was quickly added a THF solution of octafluorocyclopentene (6.2 mL, 46.2 mmol), and the mixture was stirred for 1 h. The solution was allowed to warm to ambient temperature, and

adequate amount of distilled water was added to the mixture to quench. The reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 7 / 3) to give 6.3 g of **32** in 53% yield.

32: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.45 (s, 3H, -C*H*$_3$), 2.73 (s, 3H, -C*H*$_3$).

Synthesis of 33.

Compound **19** (1.9 g, 5.7 mmol) was dissolved in dry THF (50 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (4.0 mL, 6.4 mmol) was dropwise added to the solution, and the mixture was stirred for 1.5 h. To the solution was dropwise added a THF solution of **32** (3.5 g, 12 mmol), and the mixture was allowed to warm to ambient temperature. After stirred for 2.5 h, adequate amount of distilled water was added to the mixture to quench. The reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 1 / 1) to give 780 mg of the protected compound in 25% yield**.** The protecting group of the compound (780 mg, 1.5 mmol) was removed in wet acetone (25 mL) in the presence of pyridinium *p*-toluenesulfonate (660 mg, 2.6 mmol) as well as **21**[S5] to give 720 mg of **33** in > 99% yield.

33: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.98 (s, 3H, -C*H*$_3$), 2.13 (s, 3H, -C*H*$_3$), 2.70 (s, 3H, -C*H*$_3$), 7.92-8.06 (m, 4H, Aromatic H), 10.1 (s, 1H, -C*H*O).

Synthesis of 34.[S7]

2-Amino-5-methylthiazole (10 g, 88 mmol) was dissolved in phosphoric acid (100 mL) and nitric acid (50 mL) and the solution was cooled in ice bath. An aqueous solution (40 mL) of sodium nitrite (19 g, 270 mmol) was slowly added to the solution with vigorous stirring. After stirred for 20 min, the reaction mixture was poured into CuBr (13 g, 88 mmol) in hydrobromic acid (95 mL) and stirred for a few hours. The

mixture was neutralized by a NaOH aqueous solution and $NaHCO_3$, washed with aqueous sodium thiosulfate, extracted with ethyl acetate, washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by recrystallization from the hexane solution to give 14 g of **34** in 62% yield.

34: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.37 (s, 3H, -C*H*$_3$).

Synthesis of 35. [S9]

Compound **34** (3.9 g, 15 mmol) was dissolved in dry THF (80 mL) and under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (9.6 mL, 15 mmol) was dropwise added to the solution, and the mixture was stirred for 20 min. To the solution was added dimethylformamide (DMF) (3.0 mL, 39 mmol), and the mixture was stirred for 5 min. The mixture was allowed to warm to ambient temperature, and the reaction was quenched by addition of dilute hydrochloric acid. The reaction mixture was neutralized, extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 7 / 3) and recrystallization from the hexane and acetone solution to give 2.0 g of **35** in 63% yield.

35: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.54 (s, 3H, -C*H*$_3$), 9.85 (s, 1H, -C*H*O).

Synthesis of 37.

Compound **36** was synthesized by protection of **35** as well as **25**. **36** (1.2 g, 4.7 mmol) was dissolved in dry THF (30 mL) under Ar atmosphere at −78 °C. 1.6 M *n*-BuLi hexane solution (3.0 mL, 4.8 mmol) was dropwise added to the solution, and the mixture was stirred for 10 min. To the solution was dropwise added **32** (1.4 g, 4.7 mmol), and the mixture was allowed to warm to ambient temperature. After stirred for 4 h, adequate amount of distilled water was added to the mixture to quench. The reaction mixture was extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated

in vacuo. The crude product was purified by column chromatography on silica gel (hexane / ethyl acetate = 1 / 1) to give 370 mg of the protected compound in 17% yield**.** The protecting group of the compound was removed by refluxing in wet acetone in the presence of HCl to give 260 mg of **37** in 79% yield.

37: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.95 (s, 3H, -C*H*$_3$), 2.15 (s, 3H, -C*H*$_3$), 2.70 (s, 3H, -C*H*$_3$), 9.92 (s, 1H, -C*H*O).

Synthesis of Diarylethene Monomers.

The formyl group in **20**, **22**, **23**, **28**, **30**, **33**, and **37** was reduced to hydroxymethyl group using KBH_4, followed by esterification with *p*-vinyl benzoic acid to obtain diarylethene monomers **1a** and **3a**-**8a** as well as **2a**[S5].

1a: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.94 (s, 3H, -C*H*$_3$), 2.00 (s, 3H, -C*H*$_3$), 5.37 (s, 2H, -C*H*$_2$-), 5.39 (d, *J* = 11.1 Hz, 1H, Vinyl H), 5.87 (d, *J* = 17.6 Hz, 1H, Vinyl H), 6.75 (dd, *J* = 11.1, 17.6 Hz, 1H, Vinyl H), 7.10 (d, *J* = 3.8 Hz, 1H, Thienyl H), 7.16 (d, *J* = 17.6 Hz, 1H, Thienyl H), 7.22 (d, *J* = 3.8 Hz, 1H, Thienyl H), 7.27-8.06 (m, 14H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 762.1158 (M^+). Calcd. for $C_{41}H_{28}F_6O_2S_3$: 762.1156. Elemental analysis: Found: C, 64.65; H, 3.87. Calcd. for $C_{41}H_{28}F_6O_2S_3$: C, 64.55; H, 3.70.

3a: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.06-2.11 (m, 6H, -C*H*$_3$), 2.33-2.37 (m, 6H, -C*H*$_3$), 5.36 (s, 2H, -CH_2-), 5.37 (d, *J* = 10.7 Hz, 1H, Vinyl H), 5.85 (d, *J* = 17.3 Hz, 1H, Vinyl H), 6.73 (dd, *J* = 10.7, 17.3 Hz, 1H, Vinyl H), 7.22-8.06 (m, 13H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 708.1583 (M^+). Calcd. for $C_{39}H_{30}F_6O_2S_2$: 708.1591. Elemental analysis: Found: C, 66.37; H, 4.48. Calcd. for $C_{39}H_{30}F_6O_2S_2$: C, 66.09; H, 4.27.

4a: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.09 (s, 3H, -C*H*$_3$), 2.10 (s, 3H, -C*H*$_3$), 5.39 (s, 2H, -CH_2-), 5.40 (d, *J* = 10.8 Hz, 1H, Vinyl H), 5.88 (d, *J* = 17.6 Hz, 1H, Vinyl H), 6.76 (dd, *J* = 10.8, 17.6 Hz, 1H, Vinyl H), 7.38-8.06 (m, 13H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 683.1268 (MH^+). Calcd. for $C_{35}H_{25}F_6N_2O_2S_2$: 683.1262. Elemental

analysis: Found: C, 61.48; H, 3.60; N, 4.22. Calcd. for $C_{35}H_{24}F_6N_2O_2S_2$: C, 61.58; H, 3.54; N, 4.10.

5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.98 (s, 3H, -C*H*$_3$), 2.00 (s, 3H, -C*H*$_3$), 2.08 (quintet, *J* = 7.4 Hz, 2H, $CH_2CH_2CH_2$), 2.85 (t, *J* = 7.4 Hz, 4H, $CH_2CH_2CH_2$), 5.33 (s, 2H, C*H*$_2$), 5.37 (d, *J* = 11.0 Hz, 1H, Vinyl H), 5.85 (d, *J* = 17.6 Hz, 1H, Vinyl H), 6.73 (dd, *J* = 11.0, 17.6 Hz, 1H, Vinyl H), 7.03 (s, 1H, Thienyl H), 7.04 (s, 1H, Thienyl H), 7.20-8.06 (m, 13H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 572.1856 (M^+). Calcd. for $C_{37}H_{32}O_2S_2$: 572.1844. Elemental analysis: Found: C, 77.38; H, 5.62. Calcd. for $C_{37}H_{32}O_2S_2$: C, 77.59; H, 5.63.

6a: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.94 (s, 3H, -C*H*$_3$), 2.30 (s, 3H, -C*H*$_3$), 5.34 (s, 2H, CH_2), 5.39 (d, *J* = 10.9 Hz, 1H, Vinyl H), 5.87 (d, *J* = 17.7 Hz, 1H, Vinyl H) 6.75 (dd, *J* = 10.9, 17.7 Hz, 2H, Vinyl H), 7.16-8.05 (m, 13H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 654.1122 (MH^+). Calcd. for $C_{35}H_{24}F_6O_2S_2$: 654.1122. Elemental analysis: Found: C, 64.34; H, 3.97. Calcd. for $C_{35}H_{24}F_6O_2S_2$: C, 64.21; H, 3.69.

7a: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.97 (s, 3H, -C*H*$_3$), 2.10 (s, 3H, -C*H*$_3$), 2.70 (s, 3H, -C*H*$_3$), 5.39 (s, 2H, C*H*$_2$), 5.40 (d, *J* = 10.8 Hz, 1H, Vinyl H), 5.87 (d, *J* = 17.6 Hz, 1H, Vinyl H), 6.76 (dd, *J* = 10.8, 17.6 Hz, 1H, Vinyl H), 7.44-8.07 (m, 8H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 621.1106 (MH^+). Calcd. for $C_{30}H_{23}F_6N_2O_2S_2$: 621.1105. Elemental analysis: Found: C, 58.23; H, 3.60; N, 4.50. Calcd. for $C_{30}H_{22}F_6N_2O_2S_2$: C, 58.06; H, 3.57; N, 4.51.

8a: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.94 (s, 3H, -C*H*$_3$), 2.04 (s, 3H, -C*H*$_3$), 2.67 (s, 3H, -C*H*$_3$), 5.42 (d, *J* = 10.9 Hz, 1H, Vinyl H), 5.57 (s, 2H, C*H*$_2$), 5.89 (d, *J* = 17.7 Hz, 1H, Vinyl H), 6.76 (dd, *J* = 10.9, 17.7 Hz, 1H, Vinyl H), 7.46-8.07 (m, 4H, Aromatic H). FAB-MS (FAB$^+$): *m*/z 544.0714 (MH^+). Calcd. for $C_{24}H_{19}F_6N_2O_2S_2$: 545.0792. Elemental analysis: Found: C, 53.05; H, 3.47; N, 5.12. Calcd. for $C_{24}H_{18}F_6N_2O_2S_2$: C, 52.94; H, 3.33; N, 5.14.

Synthesis of 1a'-8a'.

Compounds **1a'-8a'** were prepared according to methods described in previous papers.[S2,S3,S8,S10]

1a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.96 (s, 3H, -C*H*$_3$), 2.00 (s, 3H, -C*H*$_3$), 7.08-7.63 (m, 14H, Aromatic H).

2a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.97 (s, 6H, -C*H*$_3$), 7.28 (s, 2H, Thienyl H), 7.2-7.6 (m, 10H, Aromatic H).[S10]

3a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.09 (two singlet peaks, 6H, -C*H*$_3$), 2.36 (two singlet peaks, 6H, -C*H*$_3$), 7.2-7.5 (m, 10H, Aromatic H).[S2]

4a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.10 (s, 6H, -C*H*$_3$), 7.3-8.0 (m, 10H, Aromatic H).

5a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.98 (s, 6H, -C*H*$_3$), 2.03-2.13 (m, 2H, $CH_2CH_2CH_2$), 2.84 (t, *J* = 7.5 Hz, 4H, $CH_2CH_2CH_2$), 7.03 (s, 2H, Thienyl H), 7.1-7.5 (m, 10H, Aromatic H).[S8]

6a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.93 (s, 3H, -C*H*$_3$), 2.30 (s, 3H, -C*H*$_3$), 7.17 (s, 1H, Thienyl H), 7.2-7.8 (m, 9H, Aromatic H).

7a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.98 (s, 3H, -C*H*$_3$), 2.09 (s, 3H, -C*H*$_3$), 2.70 (s, 3H, -C*H*$_3$), 7.4-7.9 (m, 5H, Aromatic H).

8a': ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.94 (s, 3H, -C*H*$_3$), 1.95 (s, 3H, -C*H*$_3$), 2.68 (s, 3H, -C*H*$_3$), 2.69 (s, 3H, -C*H*$_3$).

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