Supporting Information

Enhancement of Cyclization Quantum Yields of Perfluorodiarylethenes via Weak Intramolecular Interactions

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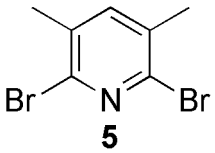
1. General methods

Chemical reagents were purchased from either Acros, Aldrich, Alfa Aesar, or TCI. and used without further purification. Solvents were from Beijing Chemical Works. Anhydrous solvents were of spectro-grade and purified by distillation prior to use. (2,5-Dimethyl-3-thienyl)perfluorocyclopentene (**7**) was synthesized according to Ref. 4c in the manuscript. All solution-phase reactions were performed under an atmosphere of dry argon or nitrogen. Reactions were monitored by analytical thin-layer chromatography on plates coated with 0.25 mm silica gel 60 F_{254} (Qingdao Haiyang Chemical). TLC plates were visualized by UV irradiation (254 nm). Flash column chromatography employed silica gel (32-63 μm, Qingdao Haiyang Chemcial) and Al_2O_3 (37-74 μm, J&K). Analysis by analytical HPLC employed an Agilent 1200 instrument fitted with a ZORBAX SIL column (5 μm particle size, 4.6 mm, 25 cm). Melting points were measured with a WRS-1B melting point apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Vertex-70 spectrometer. NMR spectra were obtained with a Bruker AV-400 spectrometer with teramethyl silane (TMS) as interal reference and $CDCl_3$ as solvent. Elemental analysis was measured with a PE CHN 2400 analyzer. Absorption spectra were obtained with an Agilent 8453 UV/VIS spectrometer. Photoirradiation was carried out with a SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Light of appropriate wavelengths was isolated by light filters. X-ray experiments of single-crystal were performed on a Bruker SMART APEX2 CCD area-detector equipped with graphite monochromatized Mo Kα radiation at room temperature (294 ± 2 K).

2. Synthesis and characterization data

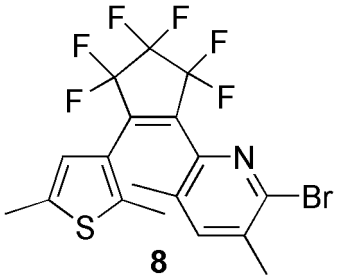


5

2,6-Dibromo-3,5-dimethylpyridine (5)

To a stirred oleum solution (40 mL) of compound 3,5-dimethylpyridine (5.35 g, 50 mmol) at 277 K was added Br_2 (5.64 mL, 110 mmol) dropwise. The solution was stirred for 30 min at this temperature. It was warmed to 353 K and refluxed for 36 h. The solution was cooled to room temperature, poured into water slowly, neutralized by aqueous NaOH. The crude product was

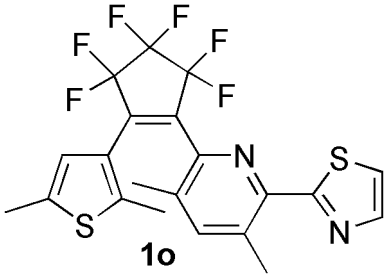
isolated by filteration. Column chromatography (dichloromethane) afforded **5** (10.71 g, 80%) as a white solid, mp 102-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (s, 1H, pyridine-H), 2.30 (s, 6H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.11, 139.51, 134.21, 20.96. IR (KBr, *v*, cm^{-1}): 3132, 1585, 1535, 1386, 1082, 974, 705.



8

1-(2,5-Dimethyl-3-thienyl)-2-(6-bromo-3,5-dimethyl-2-pyridyl)perfluorocyclopentene (8)

To a stirred solution of **5** (3.15 g, 11.87 mmol) in anhydrous THF (50 mL) was added dropwise a solution of 2.5 mol L^{-1} *n*-BuLi in hexane (5.12 mL, 12.80 mmol) at 195 K. The reaction was stirred for 30 min at 195 K, a solution of **7** (3.97 g, 13.06 mmol) in THF (5 mL) was added. The reaction solution was stirred for 1 h at this temperature. The reaction was allowed to warm to room temperature, and quenched with water (15 mL). The product was extracted with diethyl ether. The organic layers were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Column chromatography on Al_2O_3 (hexane) afforded diarylethene **8** (1.62 g, 29%) as a colorless crystal, mp 96–97 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 1H, pyridine-H), 6.64 (s, 1H, thiophene-H), 2.38 (s, 3H, $-CH_3$), 2.37 (s, 3H, $-CH_3$), 1.93 (s, 3H, $-CH_3$), 1.84 (s, 3H, $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.20, 141.66, 141.00, 140.54, 137.87, 135.98, 132.68, 124.51, 123.61, 21.72, 17.43, 15.04, 14.26; IR (KBr, *v*, cm^{-1}): 3128, 1637, 1587, 1400, 1274, 1126, 1188, 1060, 1004, 894, 826, 734, 707; LRMS, ESI^{+} *m/z* 470.1 (MH^{+}, $C_{18}H_{14}BrF_6NS$ requires 469.0); Anal. Calcd for $C_{18}H_{14}BrF_6NS$: Calcd C, 45.97; H, 3.00; N, 2.98. Found C, 45.91; H, 3.02; N, 2.96.

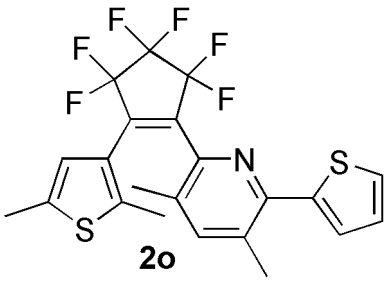


1o

1-(2,5-Dimethyl-3-thienyl)-2-(3,5-dimethyl-6-thiazole-2-yl-pyridin-2-yl)perfluorocyclopenten

e (1o)

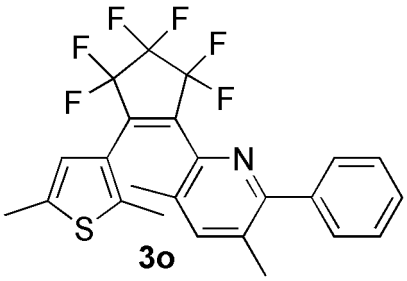
The solution of **8** (0.23 g, 0.49 mmol), 2-tributylstannylthiazole (1.83 g, 4.9 mmol), $Pd(PPh_3)_4$ of anhydrous toluene (25 mL) was refluxed for 24 h. The reaction was slowly cooled to room temperature, and concentrated in vacuo. Column chromatography on Al_2O_3 (hexane) afforded **1o** (0.16 g, 46%) as a colorless crystal, mp 119–120 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 3.2 Hz, 1H, thiazole-H,), 7.41 (d, 1H, J = 3.2 Hz, thiazole-H), 7.38 (s, 1H, pyrindine-H), 6.70 (s, 1H, thiophene-H), 2.79 (s, 3H, -CH_3), 2.40 (s, 3H, -CH_3), 1.90 (s, 3H, -CH_3), 1.87 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 147.2, 144.4, 143.7, 142.3, 140.5, 137.9, 133.2, 132.2, 124.4, 123.8, 121.5, 20.57, 17.85, 15.10, 14.20; IR (KBr, *v*, cm^{-1}): 3471, 2927, 1625, 1450, 1334, 1276, 1195, 1122, 1055, 987, 950, 839, 725; LRMS *m/z*, *ESI*$^+$,475.0 (MH^+, $C_{22}H_{17}F_6NS_2$ requires 474.0); Anal. Calcd for $C_{21}H_{16}F_6N_2S_2$: Calcd C, 53.16; H, 3.30; N, 5.90. Found C, 53.46; H, 3.30; N, 5.70.



2o

1-(2,5-Dimethyl-3-thienyl)-2-(3,5-dimethyl-6-thiophen-2-yl-pyridin-2-yl)perfluorocyclopentene (2o)

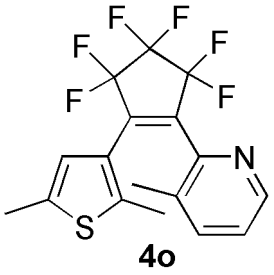
The solution of **8** (0.20 g, 0.43 mmol), 2-tributylstannylthiophene (1.58 g, 4.3 mmol), $Pd(PPh_3)_4$ of anhydrous toluene (25 mL) was refluxed for 24 h. The reaction was slowly cooled to room temperature, and concentrated in vacuo. Column chromatography on Al_2O_3 (hexane) afforded **2o** (0.11 g, 55%) as a colorless crystal, mp 145–146 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 3.6 Hz, 1H), 7.42 (d, J = 4.0 Hz, 1H), 7.30 (s, 1H, pyrindine-H), 7.13 (t, J = 4.4 Hz, 1H, thiophene-H), 6.70 (s, 1H, thiophene-H), 2.56 (s, 3H, -CH_3), 2.39 (s, 3H, -CH_3), 1.88 (s, 3H, -CH_3), 1.86 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 144.87, 144.56, 141.66, 140.44, 137.63, 130.94, 129.87, 127.84, 127.56, 126.78, 123.99, 116.06, 21.18, 17.61, 15.06, 14.23; IR (KBr, *v*, cm^{-1}): 3128, 1400, 1274, 1190, 1139, 1062, 987, 894, 847, 711; LRMS *m/z*, *ESI*$^+$, 474.1 (MH^+, $C_{22}H_{17}F_6NS_2$ requires 473.0); Anal. Calcd for $C_{22}H_{17}F_6NS_2$: Calcd C, 55.81; H, 3.62; N, 2.96. Found C, 55.92; H, 3.51; N, 2.91.



3o

1-(2,5-dimethyl-3-thienyl)-2-(3,5-dimethyl-6-phenyl-pyridin-2-yl)perfluorocyclopentene (3o)

3o was prepared by reacting **8** (0.5 g, 1.1 mmol) and phenylboronic acid (0.16 g, 1.3 mmol) in the presence of $Pd(PPh_3)_4$ and Na_2CO_3 in tetrahydrofuran (THF) (10 mL) for 24 h at 343 K under nitrogen atmosphere. The reaction was allowed to cool to room temperature. After being extracted with ether, the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on Al_2O_3 using hexane as eluent to afford 0.26 g of **3o** visible as a colorless crystal in 51% yield, mp 108–109 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 7.6 Hz, 2H, benzene-H), 7.38-7.47 (m, 3H, benzene-H), 7.35 (s, 1H, pyrindine-H), 6.71 (s, 1H, thiophene-H), 2.40 (s, 3H, -CH_3), 2.36 (s, 3H, -CH_3), 1.92 (s, 3H, -CH_3), 1.89 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.5, 144.8, 141.0, 140.3, 139.7, 137.5, 131.4, 129.1, 128.1, 128.0, 124.8, 124.1, 20.0, 17.8, 15.1, 14.3; IR (KBr, *v*, cm^{-1}): 3068, 2962, 2924, 2862, 1647, 1548, 1442, 1340, 1276, 1188, 1143, 1060, 894, 842, 736, 698; LRMS *m/z*, *ESI*$^+$, 468.1 (MH^+, $C_{22}H_{17}F_6NS_2$ requires 467.0); Anal. Calcd for $C_{24}H_{19}F_6NS$: Calcd C, 61.66; H, 4.10; N, 3.00. Found C, 61.96; H, 4.25; N, 3.11.

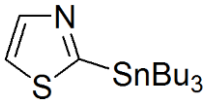


4o

1-(2,5-dimethyl-3-thienyl)-2-(3-methyl-2-pyridinyl)perfluorocyclopentene (4o)

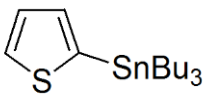
To a stirred anhydrous THF, 30 mL of compound **6** (0.54 g, 3.14 mmol) was added dropwise in a 1.6 mol L^{-1} *n*-BuLi/hexane solution (2.35 mL, 3.77 mmol) at 195 K under argon atmosphere. After 30 min, THF (2 mL) containing compound **7** (1.80 g, 5 mmol) was added and the reaction mixture was stirred for 2 h at this temperature. The reaction was allowed to warm to room temperature and quenched by addition of water. The product was extracted with diethyl ether. Then the combined

organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel using chloroform as the eluent to afford 0.22 g of compound **4o** visible as a red solid with an 8.6% yield. mp 79–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, 1H, J = 4.0 Hz, pyrindine-H), 7.48 (d, 1H, J = 7.8 Hz, pyrindine-H), 7.24 (dd, 1H, J_1 = 4.4 Hz, J_2 = 7.8 Hz, pyrindine-H), 6.66 (s, 1H, thiophene-H), 2.38 (s, 3H, -CH_3), 1.93 (s, 3H, -CH_3), 1.84 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 140.6, 138.5, 137.8, 133.5, 124.5, 124.0, 123.75, 18.32, 15.09, 14.19; IR (KBr, *v*, cm^{-1}): 2925, 1342, 1272, 1190, 1132, 1056, 990, 875, 805, 729; LRMS *m/z*, *ESI*$^+$, 378.2 (MH^+, $C_{22}H_{17}F_6NS_2$ requires 377.0); Anal. Calcd for $C_{17}H_{13}F_6NS$: Calcd C, 54.11; H, 3.47; N, 3.71. Found C, 53.98; H, 3.57; N, 3.49.



2-Tributylstannylthiazole

To a stirred solution of 2-bromothiazole (5.0 g, 30.48 mmol) in distilled DEE (50 ml), 2.4 mol/L *n*-BuLi/hexane (13.97 mL, 33.53 mmol) was added dropwise at 195 K under nitrogen atmosphere. Stirring was continued for 1 h, tributyltin chloride (10.93 g, 33.53 mmol) was added to the solution. The reaction mixture was stirred at 195 K for another 1h and then at rt for 12h. The reaction was quenched with water (30 mL), and the product was extracted with diethyl ether (15 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated in vacuo. Column chromatography on Al_2O_3 (hexane) afforded 2-tributylstannylthiazole as a yellow liquid (11.29 g, 99%).



2-Tributylstannylthiophene

To a stirred slurry of magnesium turnings (0.88 g, 36.80 mmol) in anhydrous THF (5 mL) at room temperature, a solution of 2-bromothiophene (5.0 g, 30.67 mmol) in anhydrous THF was added dropwise. The reaction was stirred for 3 h at room temperature. The mixture was cooled to 195 K, and tributyltin chloride (11 g, 33.74 mmol) was added dropwise. After 30 min, the reaction was allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with water

(40 mL), and the product was extracted with diethyl ether (15 mL × 3). The organic layers were combined, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Column chromatography on Al_2O_3 (hexane) afforded 2-tributylstannylthiophene as a yellow liquid (11.32 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.66 (m, 1H, thiophene-H), 7.27–7.28 (m, 1H, thiophene-H), 7.19–7.20 (d, 1H, thiophene-H) 1.53–1.60 (m, 6H, -CH_2), 1.29–1.38 (m, 6H, -CH_2), 1.08–1.12 (m, 6H, -CH_2), 0.87-0.95 (m, 9H, -CH_3).

3. Supplementary data

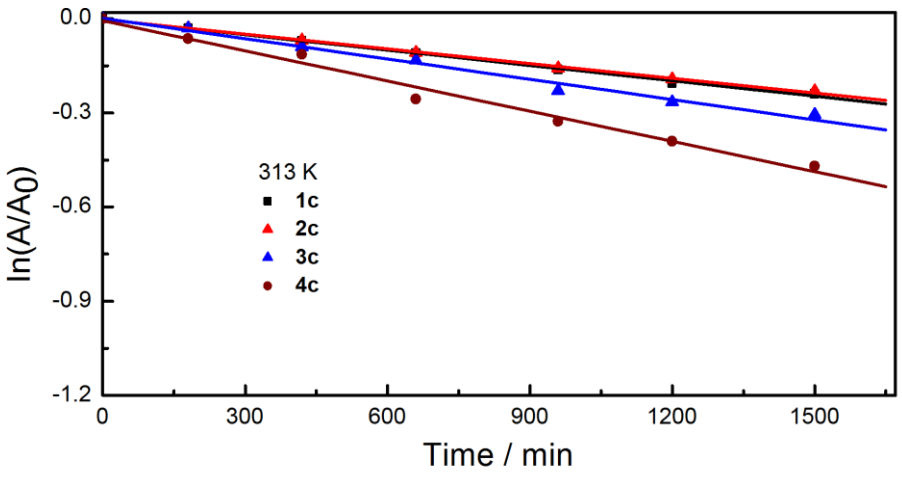


Figure S1. Thermal fading of **1c**–**4c** at 313 K in hexane.

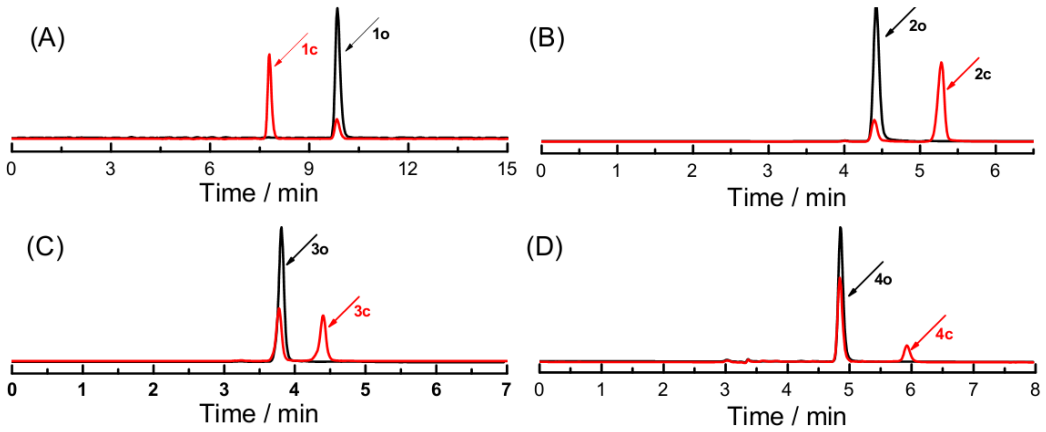


Figure S2. Photoconversion ratios of **1o–4o** in photostationary state in hexane by HPLC analysis: (A) **1o**, (B) **2o**, (C) **3o**, and (D) **4o**. Eluent: (hexane/CH_2Cl_2 80:20 *v*/*v* for **1**, hexane/*i*PrOH 99:1 *v*/*v* for **2**−**4**); flow rate = 1.0 mL min^{-1}.

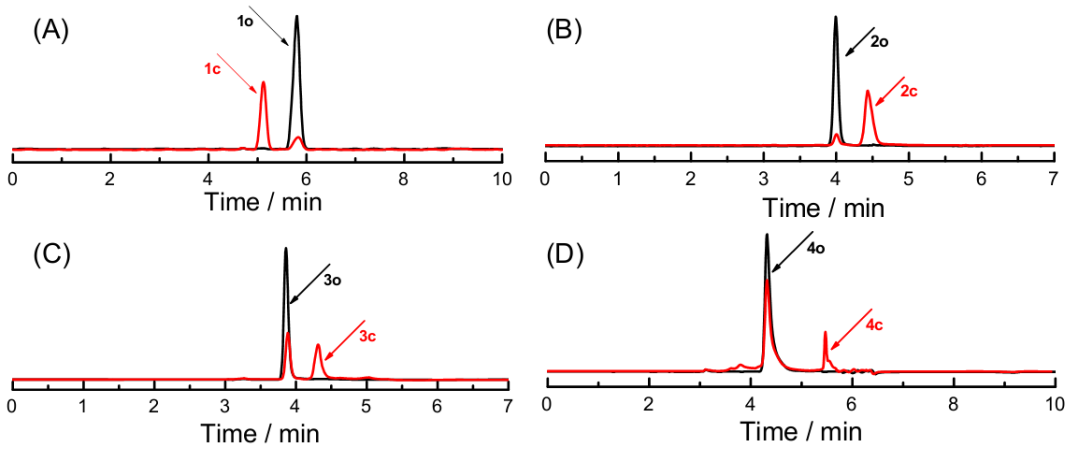


Figure S3. Photoconversion ratios of **1o–4o** in photostationary state in MeOH by HPLC analysis: (A) **1o**, (B) **2o**, (C) **3o**, and (D) **4o**. Eluent: (hexane/CH_2Cl_2 80:20 *v*/*v* for **1**, hexane/*i*PrOH 99:1 *v*/*v* for **2**−**4**); flow rate = 1.0 mL min^{-1}.

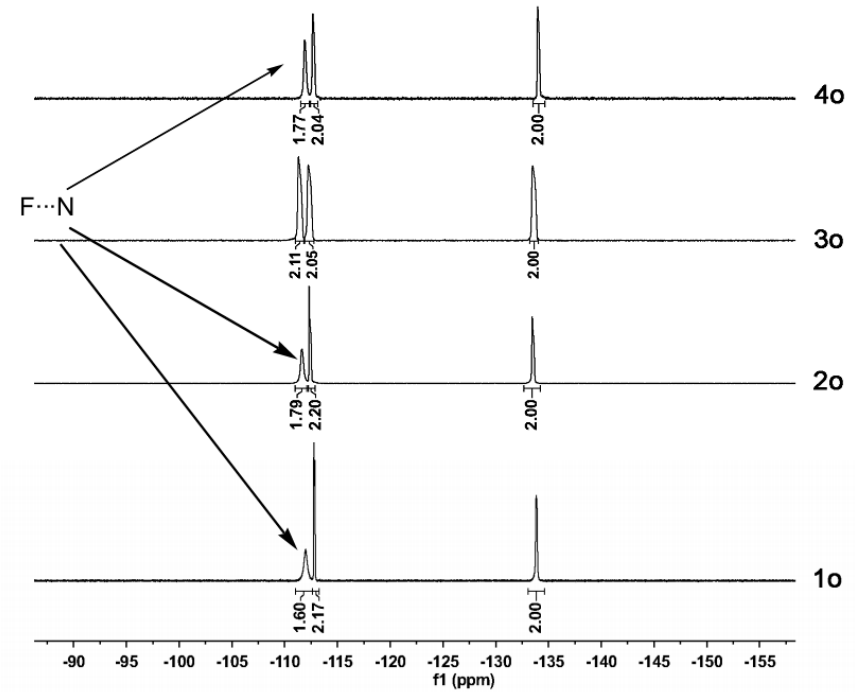


Figure S4. ^{19}F NMR (376 MHz) spectra of **1o**–**4o** in MeOH-d_4.

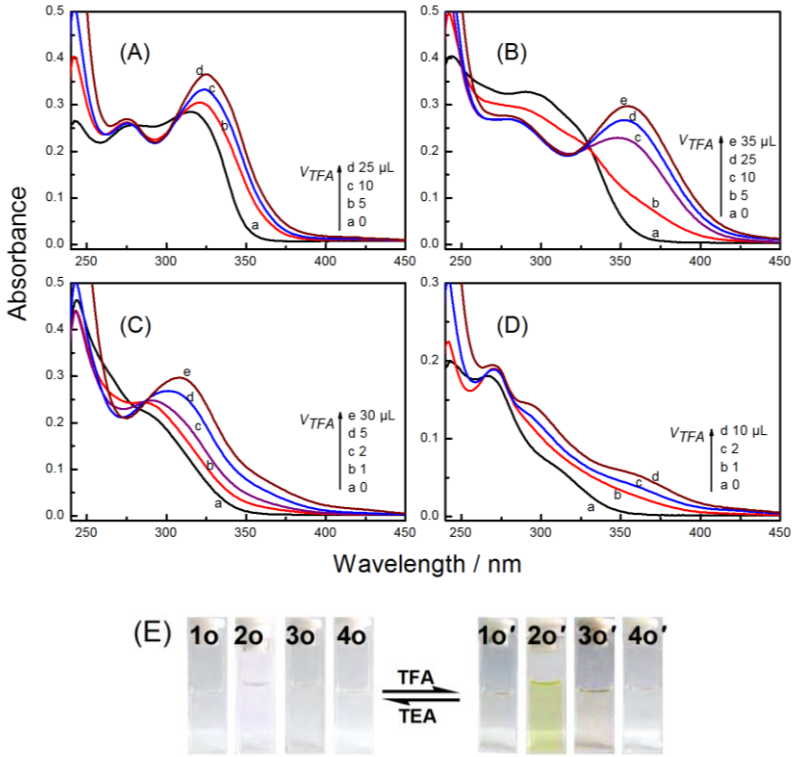


Figure S5. Absorption spectrum of **1o–4o** with stimulation of TFA in chloroform (2.0×10^{-5} mol L^{-1}): (A) **1o**, (B) **2o**, (C) **3o**, and (D) **4o**. Color changes of **1o–4o** with stimulation of TFA/TEA in chloroform (E).

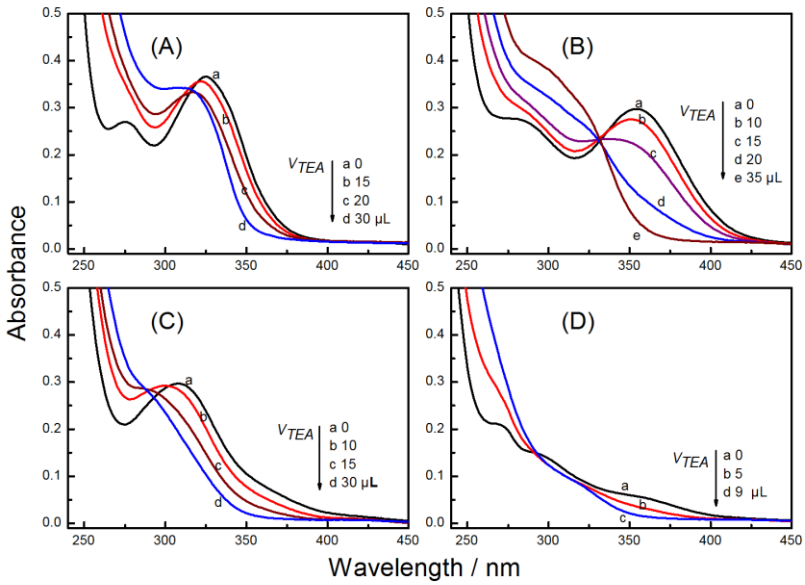


Figure S6. Absorption spectrum of diarylethenes **1o′–4o′** with addition TEA in chloroform (2.0×10^{-5} mol L^{-1}): (A) **1o′**, (B) **2o′**, (C) **3o′**, and (D) **4o′**.

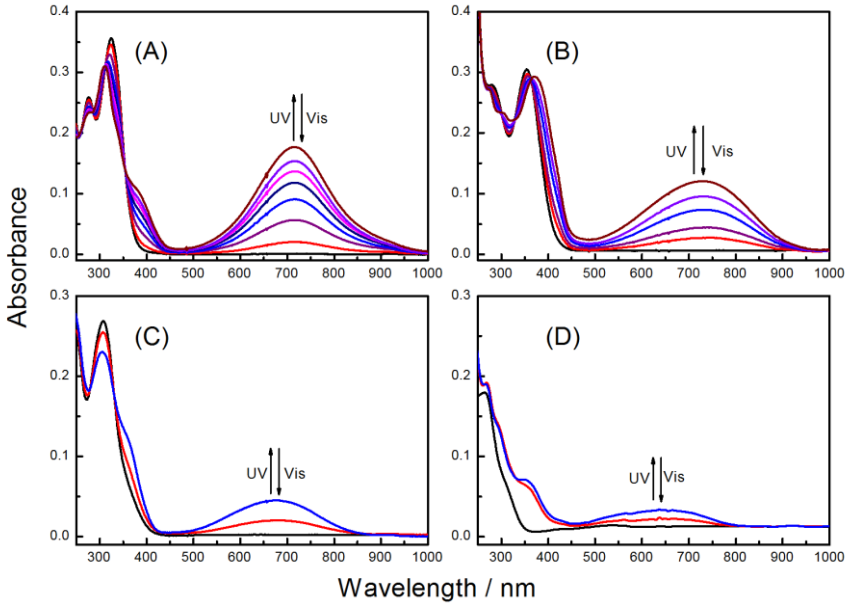


Figure S7. Absorption spectral of diarylethenes **1o′–4o′** with stimulation of light in chloroform (2.0×10^{-5} mol L^{-1}): (A) **1o′**, (B) **2o′**, (C) **3o′**, and (D) **4o′**.

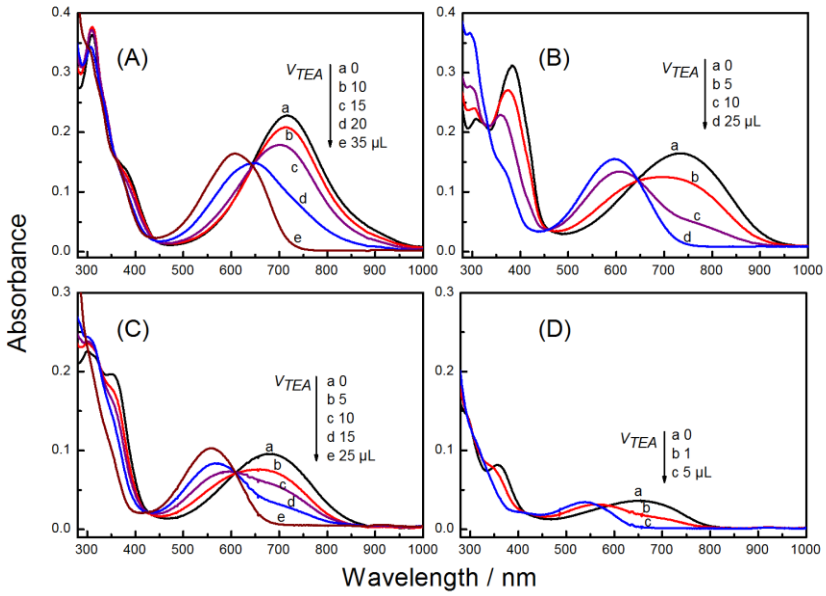


Figure S8. Absorption spectral of diarylethenes **1c′–4c′** with stimulation of TEA in chloroform (2.0×10^{-5} mol L^{-1}): (A) **1c′**, (B) **2c′**, (C) **3c′**, and (D) **4c′**.

4. Crystallography

The crystal of **1o** was mounted on glass fibre and transferred to an Xcalibur Eos Gemini. The crystals of **2o**–**4o** were mounted on glass fibre and transferred to a Bruker SMART CCD area detector. The crystallographic measurement for the crystal of **1o** was carried out using an Agilent Xcalibur E X-ray single crystal diffractometer, σ scan, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) under room temperature. The crystallographic measurement for the crystals of **2o**–**4o** was carried out using a Bruker SMART APEX2 CCD diffractometer, σ scan, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) under room temperature. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 values using the program SHELXS-97. All non-hydrogen atoms were subjected to anisotropic refinement. Hydrogen atoms were generated theoretically and ridden on their parent atoms in the final refinement. For the full-matrix least-squares refinements [I > 2σ(I)], the unweighted and weighted agreement factors of R1 = ∑(Fo-Fc)/Fo and wR2 = $[\sum(Fo^2-Fc^2)2/\sum wFo^4]^{1/2}$ were used. Further details on the crystal structures have been deposited in the Cambridge Crystallographic Data Centre as supplemental publication CCDC 899297 for **1o**, CCDC 879873 for **2o**, CCDC 899298 for **3o** and CCDC 918115 for **4o**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk).

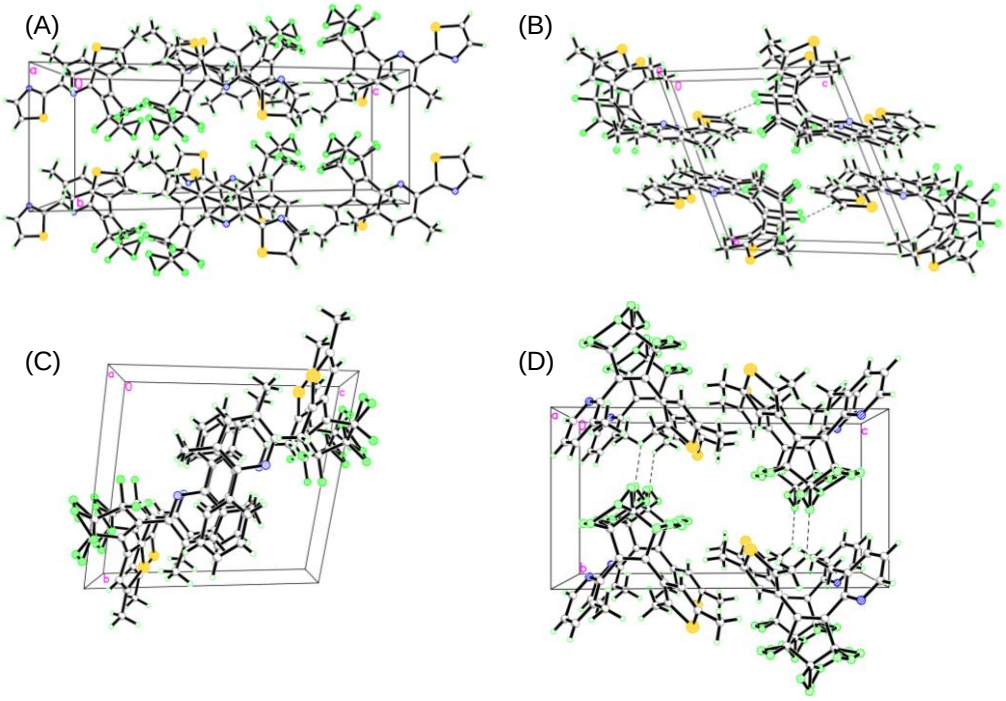


Figure S9. Packing views along the x direction of **1o**–**4o**: (A) **1o**, (B) **2o**, (C) **3o**, and (D) **4o**.

Table S1. Crystallographic parameters of **1o**–**4o**

	1o	**2o**	**3o**	**4o**
Formula	$C_{21}H_{16}F_6N_2S_2$	$C_{22}H_{17}F_6NS_2$	$C_{24}H_{19}F_6NS$	$C_{17}H_{13}F_6NS$
Formula weight	474.48	473.49	467.46	377.34
Temperature (K)	293(2)	296(2)	293(2)	293(2)
Crystal system	monoclinic	Triclinic	Triclinic	monoclinic
Space group	C2/c	P-1	P-1	P21/a
Unit cell dimensions				
a (Å)	22.8128(10)	8.8943(10)	9.2019(14)	11.9922(12)
b (Å)	8.4517(3)	11.9170(14)	11.350(2)	8.6729(5)
c (Å)	24.4912(10)	12.0266(14)	12.040(2)	16.3046(11)
α (º)	90.00	66.6080(10)	92.035(16)	90.00
β (º)	112.059(5)	68.4160(10)	105.450(16)	94.157(8)
γ (º)	90.00	78.7220(10)	111.628(16)	90.00
Volume ($Å^3$)	4376.4(3)	1086.1(2)	1114.0(4)	1691.3(2)
Z	8	2	2	4
Density(calcd)(g/cm^3)	1.440	1.448	1.394	1.482
Goodness-of-fit on F^2	1.087	1.051	1.193	1.059
Final R indices [I/2σ(I)]				
*R*1	0.0606	0.0686	0.0581	0.0899
*wR*2	0.1649	0.1895	0.1543	0.1474
R indices (all data)				
*R*1	0.0859	0.0795	0.0789	0.0542
*wR*2	0.1875	0.2049	0.1710	0.1204

5. NMR spectra

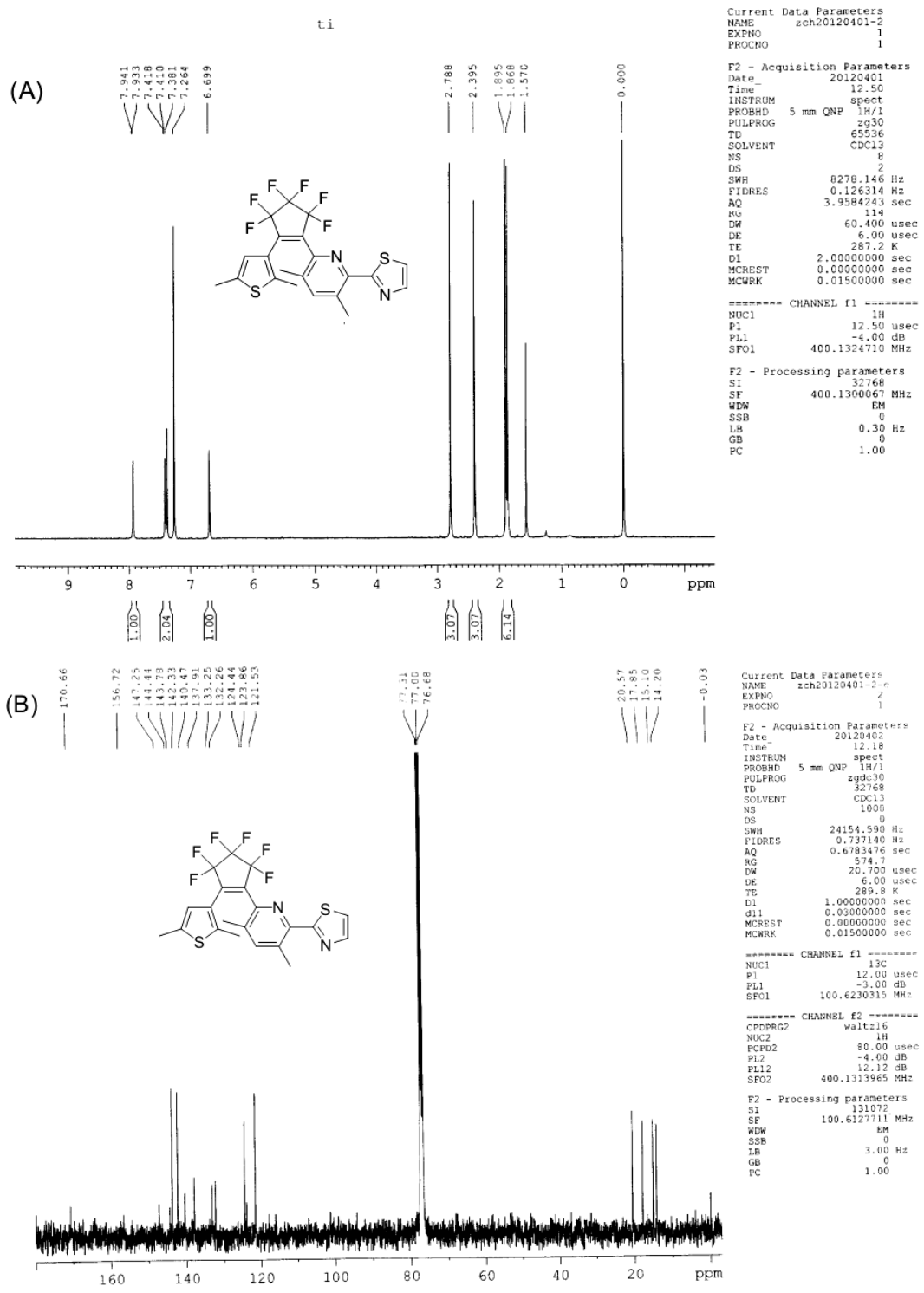


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **1o**.

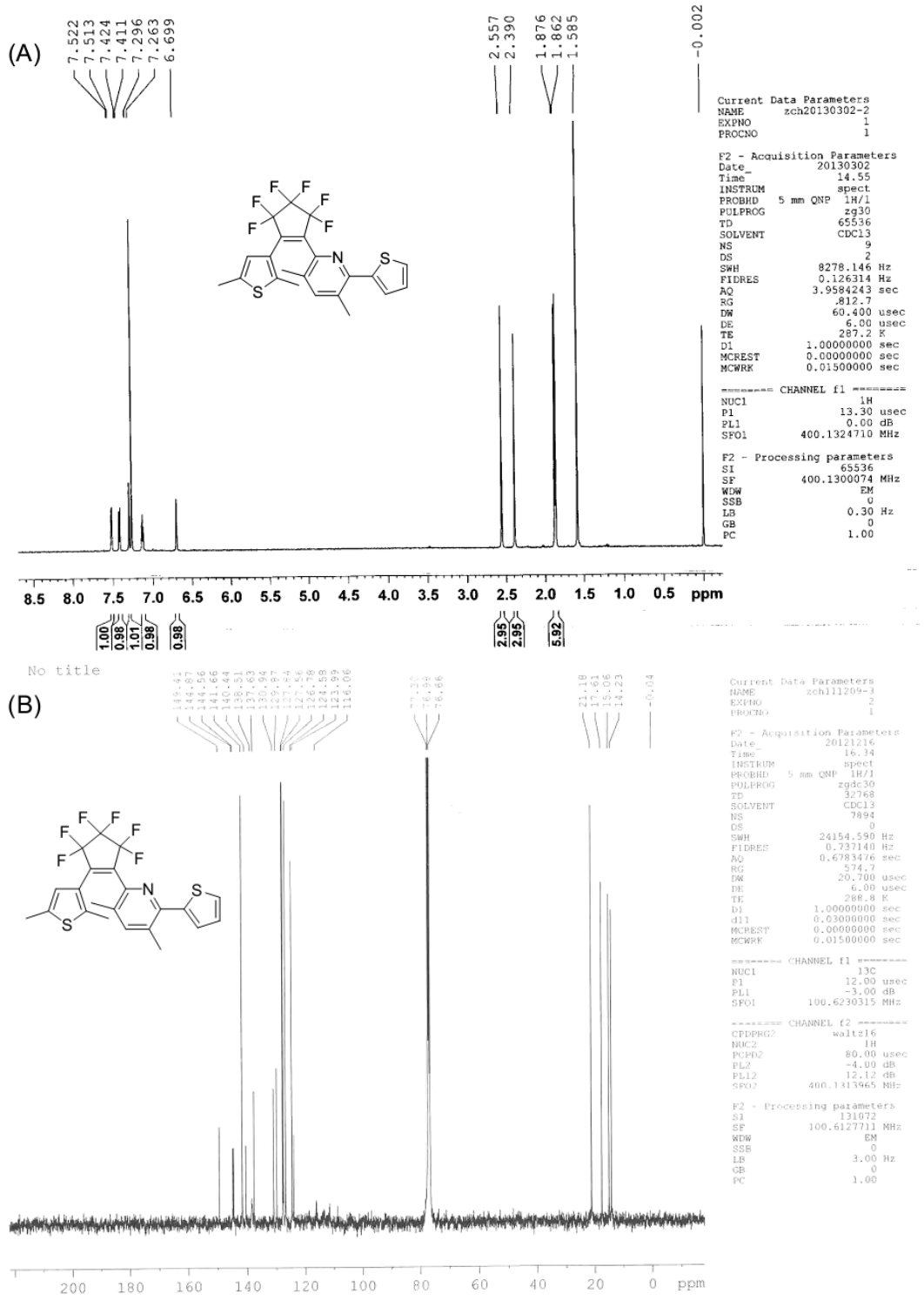


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **2o**.

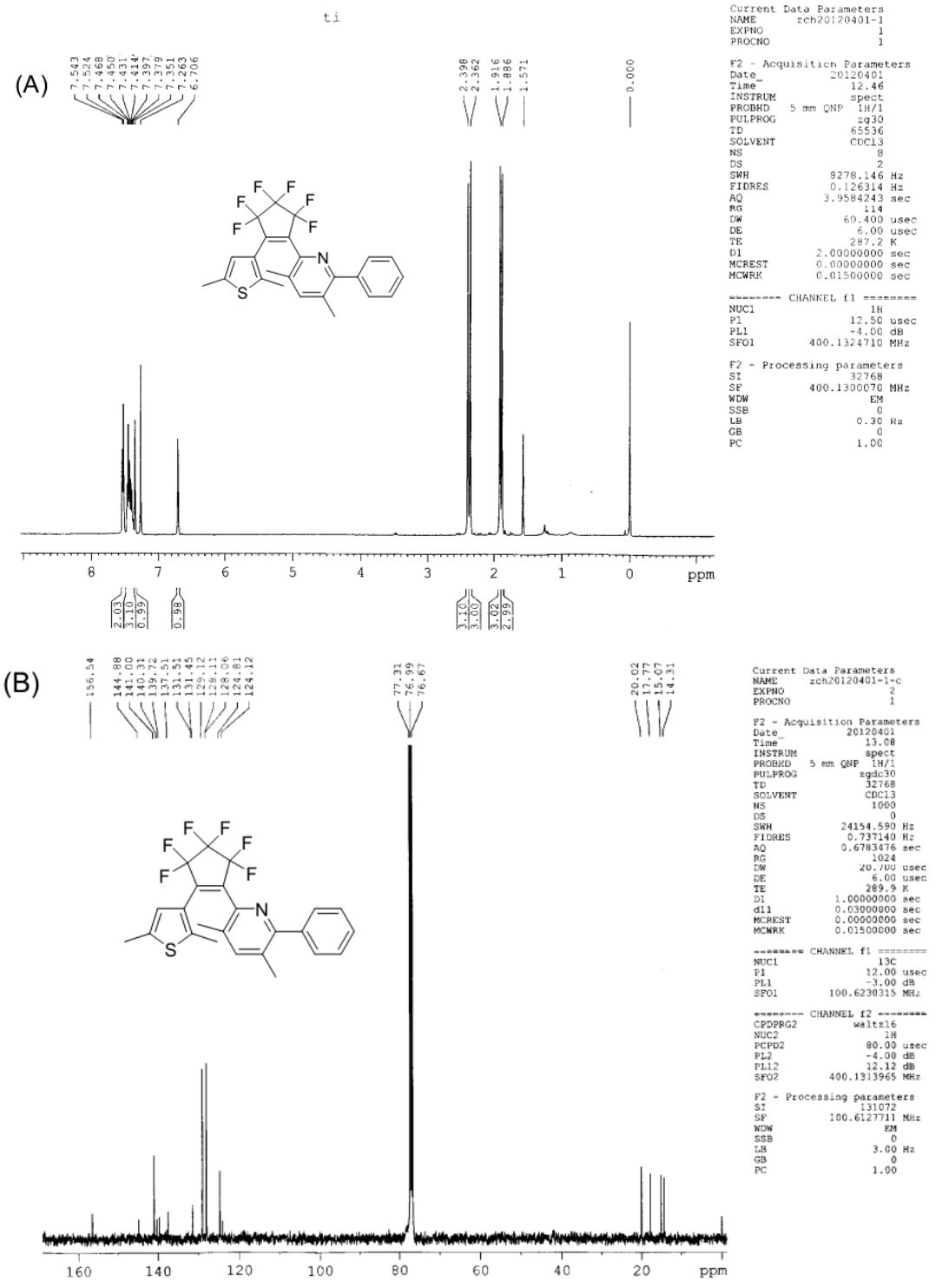


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **3o**.

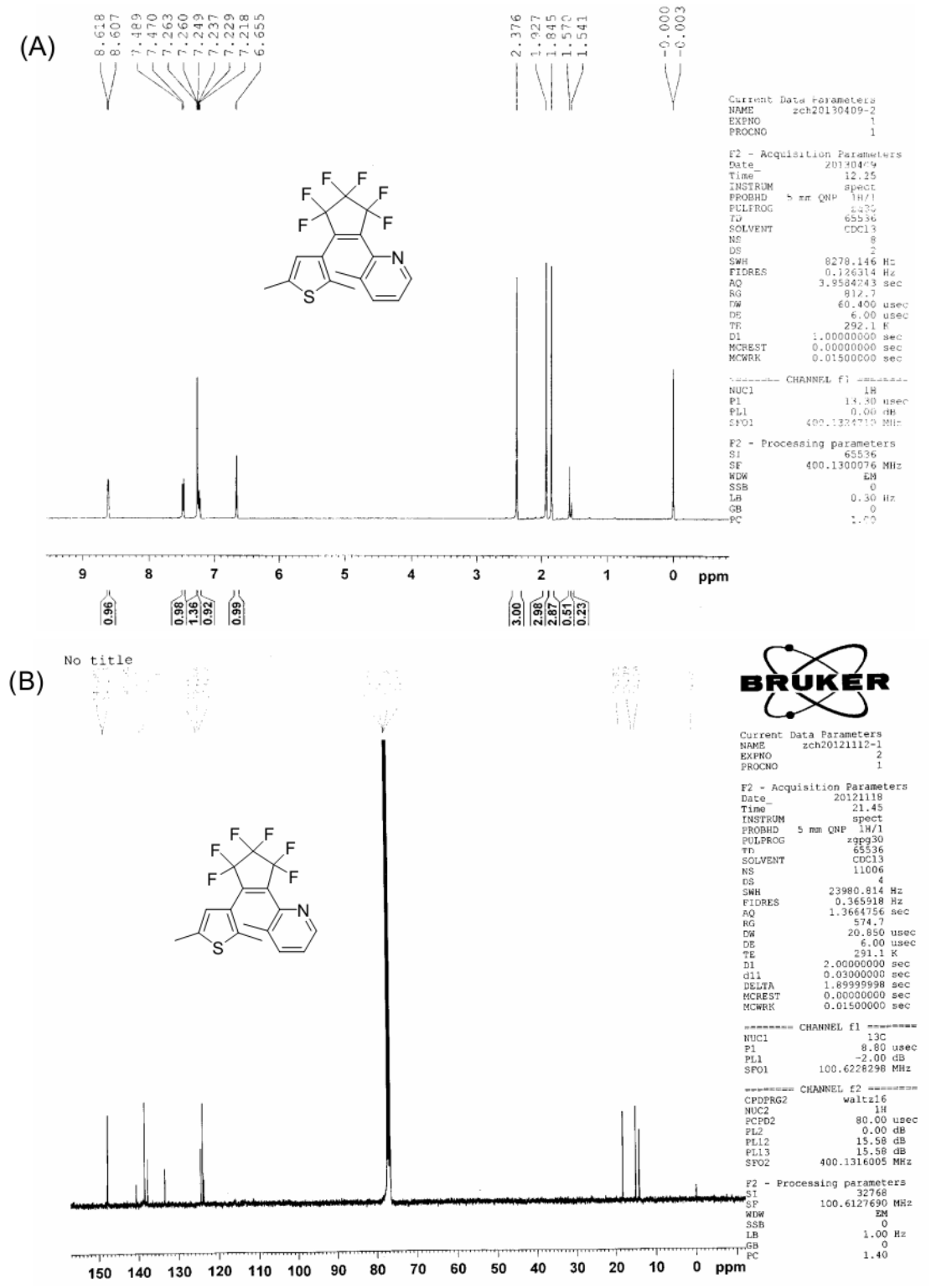


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of **4o**.