

Room-temperature Columnar Liquid Crystals Based on Tetrathiafulvalene

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Experimental section:

General. All reagents and solvents were purchased from commercially available sources and used without further purification. All the reactions were performed under an inert atmosphere of nitrogen. ¹H NMR spectra were recorded on a JNM-EX400 spectrometer in deuterated chloroform. Chemical shifts are quoted in parts per million (ppm) and referenced to tetramethylsilane. The ¹³C NMR spectra were recorded at 100 MHz on the same spectrometer in deuterated chloroform. Chemical shifts were defined relative to the ¹³C resonance shift of chloroform (77.0 ppm). Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-300E spectrometer in the region of 4000-400 cm⁻¹ region by using KBr pellets. The UV absorption was determined with a SCINCO UV-vis S-2100 spectrometer. Elemental analyses were carried out on a FISON EA-1108 Elemental Analyzer. High-resolution mass spectrometry was taken on a SD303 spectrometer. The phase transition behavior of the materials was examined by a differential scanning calorimetry (DSC) using a TA Instruments DSC 2010. The heating and cooling rate was 5 °C/min. The reported temperatures are onset temperatures of first cooling. The polarizing optical microscopic images were taken on a Nikon ECLIPSE E600POL polarizing optical microscope with a LINKAM LTS 350 hot stage. The 1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (Cu K α radiation) generator coupled to a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals of known crystal size in the high 2 θ -angle region (>15°) and silver behenate in the low 2 θ -angle region. The cyclic voltammetry measurements were performed by Versa STAT3 of Princeton Applied Research in a solution of Bu₄NBF₄ (0.1 M) in water-free dichloromethane with a scan rate of 50 mV/s at room temperature. A glass carbon electrode, a Ag/AgCl electrode and a platinum wire were used as a working electrode, a reference electrode and a counter electrode, respectively.

Materials:

Starting materials **1**, **2a-2d** and **4a-4d** were prepared according to the literatures.¹⁻³

General method to compound **3**:

Mixture of compound **1** (1.33 g, 5.0 mmol), 4-alkyloxy-benzoic acid (10.5 mmol), DMAP (1.2 g, 10.0 mmol), *p*-toluenesulfonic acid (0.19 g, 5.0 mmol), and DCC (2.38 g, 11.5 mmol) in dry CH₂Cl₂ (50 mL) was stirred at room temperature for 12 h. Solvent was removed by rotary evaporation. The yellow solid was obtained by column chromatography with mixture of petroleum ether and methylene chloride as an eluent.

Compound **3a**:

This compound was prepared according to the general procedure and obtained as yellow solid (1.60 g, 47.4%). ¹H-NMR (CDCl₃, δ): 8.25 (d, 4H), 7.87 (q, 2H), 7.55 (q, 2H), 7.05 (d, 4H), 4.10 (t, 4H), 1.85 (f, 4H), 1.51 (m, 4H), 1.45-1.27 (m, 8H), 0.93 (t, 6H). ¹³C-NMR: 210.98, 164.38, 163.20, 136.63, 132.84, 131.80, 127.67, 127.13, 121.49, 119.57, 114.75, 68.51, 31.53, 29.03, 25.64, 22.58, 14.02. UV (nm): 272, 330, 374. IR(KBr, cm⁻¹): 3067(w), 2945(m), 2871(m), 1918(w), 1741(s), 1606(s), 1575(m), 1508(s), 1467(w), 1427(w), 1399(w), 1369(w), 1313(w), 1250(s), 1155(s), 1071(s), 1039(s), 1018(s), 933(w), 849(m), 755(s), 691(m), 670(m), 628(w), 596(w), 507(w), 433(w). HRMS calcd for

$C_{37}H_{38}O_6S_3$ 674.18, found (M + H)⁺ 675.17. Anal. Calcd for $C_{37}H_{38}O_6S_3$: C, 65.9; H, 5.7; S, 14.3. Found: 66.1%, 5.8%, 14.4%.

Compound 3b:

This compound was prepared according to the general procedure, and obtained as yellow crystal (1.95 g, 53.4%). ¹H-NMR (CDCl₃, δ): 8.25 (d, 4H), 7.87 (q, 2H), 7.55 (q, 2H), 7.05 (d, 4H), 4.10 (t, 4H), 1.86 (f, 4H), 1.50 (m, 4H), 1.45-1.24 (m, 16H) 0.91 (t, 6H). ¹³C-NMR: 210.98, 164.38, 163.20, 136.63, 132.84, 131.81, 127.66, 127.13, 121.49, 119.57, 114.75, 68.52, 31.80, 29.31, 29.22, 29.05, 25.97, 22.65, 14.06. UV (nm): 273, 330, 373. IR(KBr, cm⁻¹): 3064(w), 2926(s), 2852(s), 1918(w), 1739(s), 1600(s), 1579(s), 1505(m), 1473(m), 1420(w), 1399(w), 1367(w), 1314(w), 1250(s), 1165(s), 1069(s), 1037(s), 1005(s), 920(w), 889(w), 847(s), 761(s), 687(m), 666(m), 634(w), 593(w), 574(w), 506(w). HRMS calcd for $C_{37}H_{38}O_6S_3$ 730.25, found (M + H)⁺ 731.15. Anal. Calcd for $C_{41}H_{46}O_6S_3$: C, 67.4; H, 6.3; S, 13.2. Found: 67.7%, 6.5%, 13.3%.

Compound 3c:

This compound was prepared according to the general procedure, and obtained as yellow solid (2.29 g, 58.2%). ¹H-NMR (CDCl₃, δ): 8.25 (d, 4H), 7.87 (q, 2H), 7.55 (q, 2H), 7.05 (d, 4H), 4.09 (t, 4H), 1.85 (f, 4H), 1.50 (m, 4H), 1.44-1.21 (m, 24H), 0.89 (t, 6H). ¹³C-NMR: 210.98, 164.39, 163.20, 136.64, 132.85, 131.82, 127.67, 127.14, 121.50, 119.58, 114.75, 68.53, 31.90, 29.56, 29.35, 29.31, 29.07, 25.97, 22.68, 14.11. UV (nm): 273, 330, 373. IR(KBr, cm⁻¹): 3069(w), 2920(m), 2856(m), 1922(w), 1742(s), 1603(s), 1581(m), 1507(m), 1465(w), 1422(w), 1369(w), 1316(w), 1250(s), 1163(s), 1068(s), 1035(s), 1003(s), 919(w), 887(w), 844(m), 760(s), 674(w), 632(w), 602(w), 572(w), 505(m), 447(w). HRMS calcd for $C_{45}H_{54}O_6S_3$ 786.31, found (M + H)⁺ 787.15. Anal. Calcd for $C_{45}H_{54}O_6S_3$: C, 68.7; H, 6.9; S, 12.2. Found: 68.9%, 7.1%, 12.3%.

Compound 3d:

This compound was prepared according to the general procedure, and obtained as yellow solid (2.50g 74.1%). ¹H-NMR (CDCl₃, δ): 8.25 (d, 4H), 7.87 (q, 2H), 7.55 (q, 2H), 7.05 (d, 4H), 4.09 (t, 4H), 1.85 (f, 4H), 1.50 (m, 4H), 1.45-1.20 (m, 32H), 0.89 (t, 6H). ¹³C-NMR: 210.96, 164.38, 163.19, 136.63, 132.83, 131.81, 127.66, 127.13, 121.50, 119.57, 114.76, 68.52, 31.91, 29.65, 29.63, 29.59, 29.55, 29.34, 29.06, 25.97, 22.68, 14.11. UV (nm): 272, 330, 373. IR(KBr, cm⁻¹): 3070(w), 2920(m), 2855(m), 1922(w), 1741(s), 1601(s), 1580(m), 1506(m), 1464(w), 1421(w), 1368(w), 1315(w), 1250(s), 1163(s), 1068(s), 1035(s), 1003(s), 961(w), 918(w), 887(w), 845(m), 760(s), 696(w), 674(m), 632(w), 602(w), 572(w), 505(m), 438(w). HRMS calcd for $C_{49}H_{62}O_6S_3$ 842.37, found (M + H)⁺ 843.39. Anal. Calcd for $C_{49}H_{62}O_6S_3$: C, 69.8; H, 7.4; S, 11.4. Found: 70.1%, 7.6%, 11.7%.

General method to compound 5:

Compound **3** (0.57 mmol) and compound **4**, 4,5-bis-hexylsulfanyl-[1,3]dithiolan-2-one (0.50 g, 1.42 mmol), were added to 25 mL triethylphosphate, and the mixture was heated to 120 °C for 4 h. After the solution was cooled, and the precipitate was filtered, column chromatography with mixture of PE and MC as the eluant gave orange solid.

Compound 5a:

This compound was prepared according to the general procedure, and obtained as dark orange solid (0.18 g, 31.4%). ¹H-NMR (CDCl₃, δ): 8.28 (m, 4H), 7.69 (m, 2H), 7.42 (m, 2H), 7.05 (m, 4H), 4.09 (t, 4H), 2.78 (t, 4H), 1.85 (m, 4H), 1.69-1.18 (m, 28H), 1.02-0.79 (m, 12H). ¹³C-NMR: 164.12, 163.21, 137.42, 132.80, 129.56, 127.70, 127.11, 126.79, 120.96, 120.18, 114.61, 68.46, 36.33, 31.53, 31.28, 29.66, 29.04, 28.17, 25.65, 22.59, 22.51, 14.01, 13.99. UV (nm): 263, 303, 319, 376. IR(KBr, cm⁻¹): 3064(w), 2920(s), 2857(s), 1731(s), 1607(s), 1576(s), 1509(s), 1466(s), 1414(w), 1393(w),

1365(w), 1311(w), 1247(s), 1152(s), 1078(s), 1046(s), 1003(s), 844(m), 759(s). HRMS calcd for $C_{52}H_{64}O_6S_6$ 976.30, found (M)⁺ 976.09. Anal. Calcd for $C_{52}H_{64}O_6S_6$: C, 63.9; H, 6.6; S, 19.7. Found: 64.6%, 6.9%, 19.8%.

Compound 5b:

This compound was prepared according to the general procedure, and obtained as orange solid (0.17 g, 28.5%). ¹H-NMR (CDCl₃, δ): 8.28 (m, 4H), 7.69 (m, 2H), 7.42 (m, 2H), 7.05 (m, 4H), 4.09 (t, 4H), 2.78 (t, 4H), 1.86 (m, 4H), 1.67-1.20 (m, 36H), 0.98-0.82 (m, 12H). ¹³C-NMR: 164.12, 163.21, 137.41, 132.80, 129.56, 127.69, 127.10, 126.79, 120.96, 120.17, 114.61, 68.47, 36.33, 31.81, 31.28, 29.67, 29.32, 29.23, 29.09, 28.18, 25.99, 22.66, 22.52, 14.09, 14.00. UV (nm): 262, 303, 320, 391. IR(KBr, cm⁻¹): 3061(w), 2923(s), 2849(s), 1735(s), 1608(s), 1576(s), 1513(s), 1470(s), 1417(w), 1396(w), 1364(w), 1311(w), 1248(s), 1152(s), 1078(s), 1046(s), 1004(s), 845(m), 760(s). HRMS calcd for $C_{56}H_{72}O_6S_6$ 1032.37, found (M)⁺ 1032.29. Anal. Calcd for $C_{56}H_{72}O_6S_6$: C, 65.1; H, 7.0; S, 18.6. Found: 65.6%, 7.3%, 18.4%.

Compound 5c:

This compound was prepared according to the general procedure, and obtained as yellow soft solid (0.21 g, 33.8%). ¹H-NMR (CDCl₃, δ): 8.20(m, 4H), 7.62(m, 2H), 7.35 (m, 2H), 6.98 (m, 4H), 4.02 (t, 4H), 2.71 (t, 4H), 1.78 (m, 4H), 1.60-1.12 (m, 44H), 0.90-0.72 (m, 12H). ¹³C-NMR: 164.12, 163.21, 137.41, 132.80, 129.56, 127.70, 127.10, 126.79, 120.96, 120.17, 114.61, 68.46, 36.33, 31.89, 31.27, 29.66, 29.56, 29.55, 29.35, 29.31, 29.09, 28.17, 25.98, 22.68, 22.52, 14.11, 14.00. UV (uv): 262, 302, 320, 388. IR(KBr, cm⁻¹): 3066(w), 2928(s), 2854(s), 1740(s), 1603(s), 1507(s), 1464(s), 1422(w), 1390(w), 1369(w), 1316(w), 1252(s), 1152(s), 1072(s), 1040(s), 1008(s), 849(m), 754(s). HRMS calcd for $C_{60}H_{80}O_6S_6$ 1088.43, found (M)⁺ 1088.29. Anal. Calcd for $C_{60}H_{80}O_6S_6$: C, 66.1; H, 7.4; S, 17.7. Found: 66.4%, 7.6%, 17.6%.

Compound 5d:

This compound was prepared according to the general procedure, and obtained as soft yellow solid (0.40 g, 67.0%). ¹H-NMR (CDCl₃, δ): 8.27 (m, 4H), 7.69 (m, 2H), 7.41 (m, 2H), 7.05 (m, 4H), 4.09 (t, 4H), 2.78 (t, 4H), 1.85 (m, 4H), 1.66-1.20 (m, 52H), 0.97-0.80 (m, 12H). ¹³C-NMR: 164.13, 163.22, 137.43, 132.81, 129.57, 127.71, 127.12, 126.80, 120.96, 120.19, 114.62, 68.48, 36.34, 31.92, 31.29, 29.66, 29.63, 29.60, 29.57, 29.37, 29.35, 29.09, 28.18, 25.99, 22.69, 22.52, 14.11, 14.00. UV (nm): 263, 302, 320, 386. IR(KBr, cm⁻¹): 3065(w), 2927(s), 2853(s), 1739(s), 1601(s), 1506(s), 1463(s), 1421(w), 1389(w), 1368(w), 1315(w), 1252(s), 1156(s), 1071(s), 1039(s), 1007(s), 849(m), 753(s). HRMS calcd for $C_{62}H_{88}O_6S_6$ 1144.49, found (M)⁺ 1144.24. Anal. Calcd for $C_{62}H_{88}O_6S_6$: C, 67.1; H, 7.7; S, 16.8. Found: 67.5%, 8.0%, 16.9%.

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- (1) Dumur, F.; Gautier, N.; Gallego-Planas, N.; Sahin, Y.; Levillain, E.; Mercier, N.; Hudhomme, P.; Masino, M.; Girlando, A.; Lloveras, V.; Vidal-Gancedo, J.; Veciana, J.; Rovira, C. *J. Org. Chem.* **2004**, *69*, 2164-2177.
 - (2) Schnurpfeil, G.; Harder, A.; Schröder, H.; Wöhrle, D.; Hartwig, A.; Hennemann, O-D. *Macromol. Chem. phys.* **2001**, *202*, 180-187.
 - (3) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mork, P.; Kristensen, G. J.; Becher, J. *Synthesis*, **1996**, 407-418.

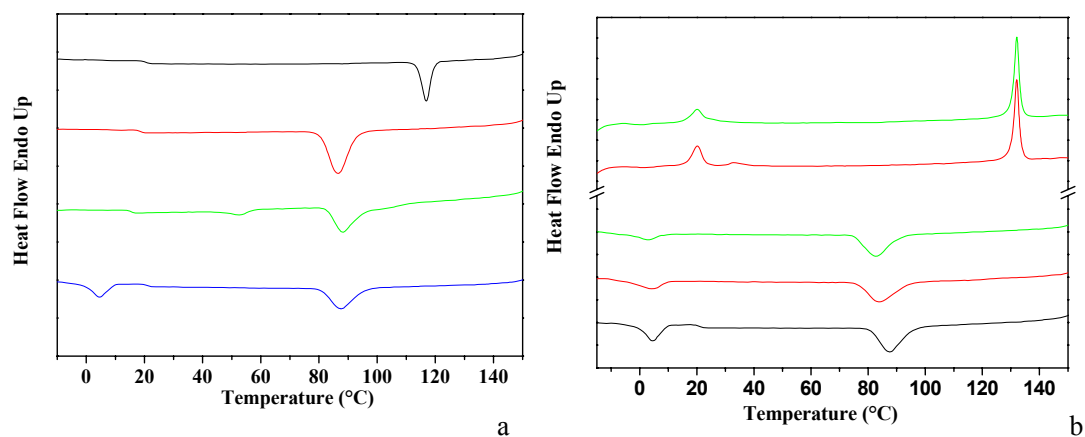


Figure S1. (a) DSC trace of first cooling of compound **5a-5d** (cooling rate: 5 °C/min), Black line is **5a**, red line is **5b**, green line is **5c**, blue line is **5d**; (b) DSC trace of **5d** (5 °C/min), Black line is first cooling, red line is second heating and cooling, green line is third cycle.

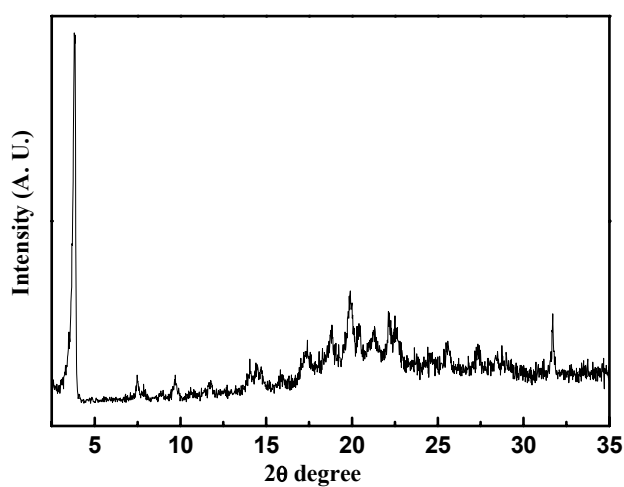


Figure S2. 1D WAXD of **5d** at 95°C.

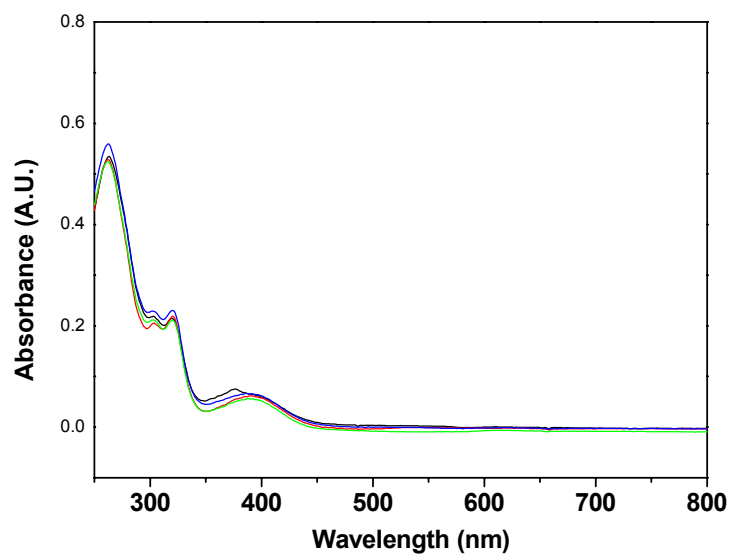


Figure S3. UV absorption spectrum of compound **5a-5d** in CHCl₃. Black line is **5a**, red line is **5b**, green line is **5c**, blue line is **5d**.

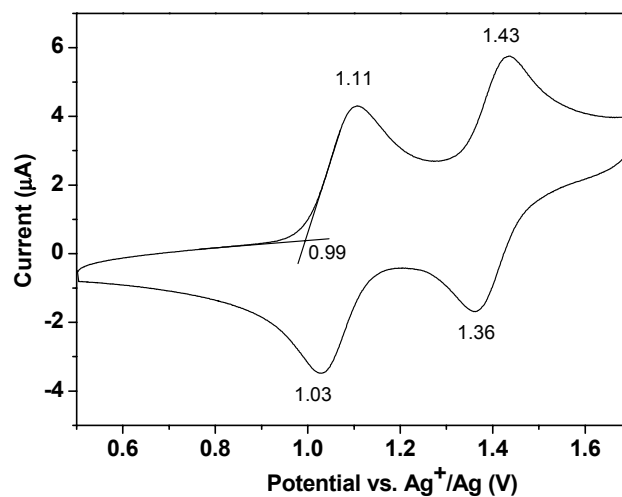


Figure S4. CV of compound 5a

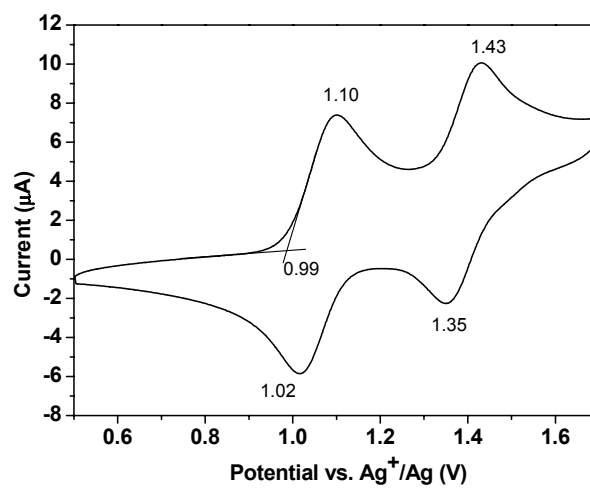


Figure S5. CV of compound 5b

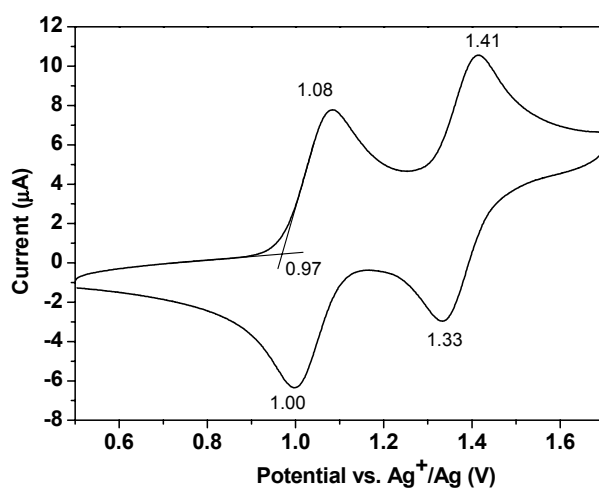


Figure S6. CV of compound **5c**

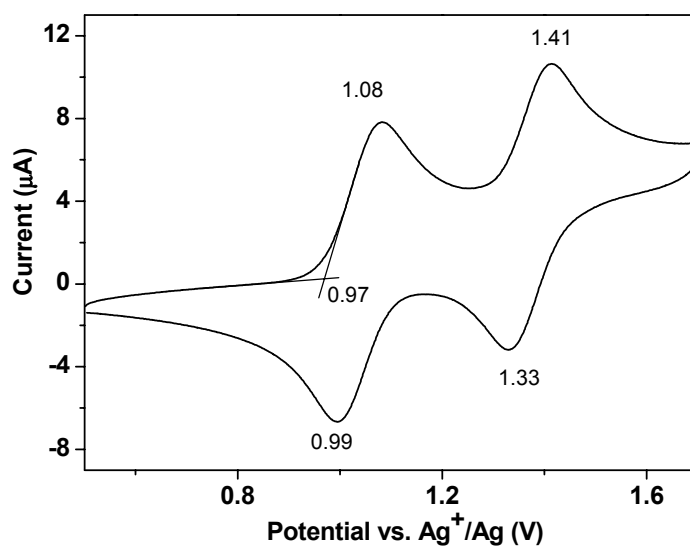


Figure S7. CV of compound **5d**

Compounds **5a-5d** show similar cyclic voltammograms, which means two reversible one electron oxidation processes, corresponding to the formation of cation and dication of TTF moieties.

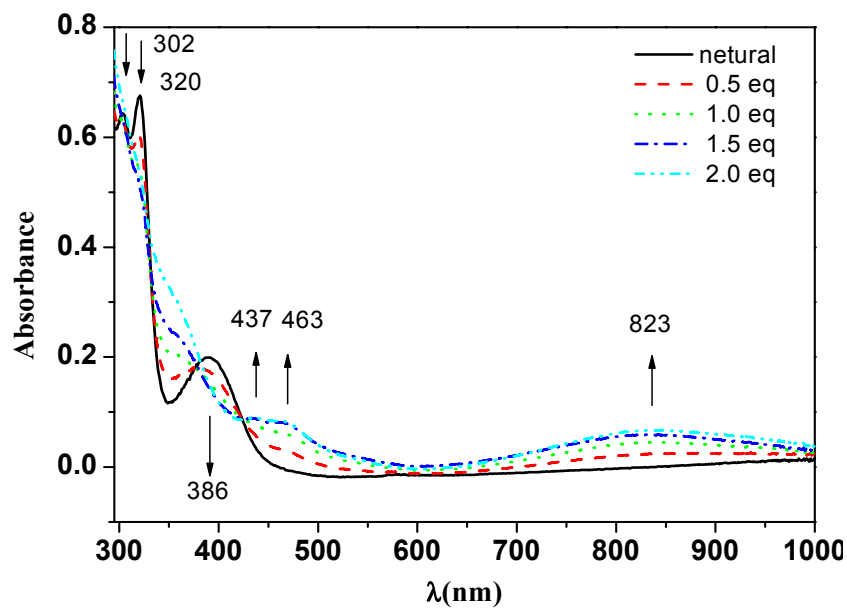


Figure S8. UV-vis absorption spectral change of compound **5d** (2×10^{-5} M) in dichloromethane solutions with addition of FeCl₃

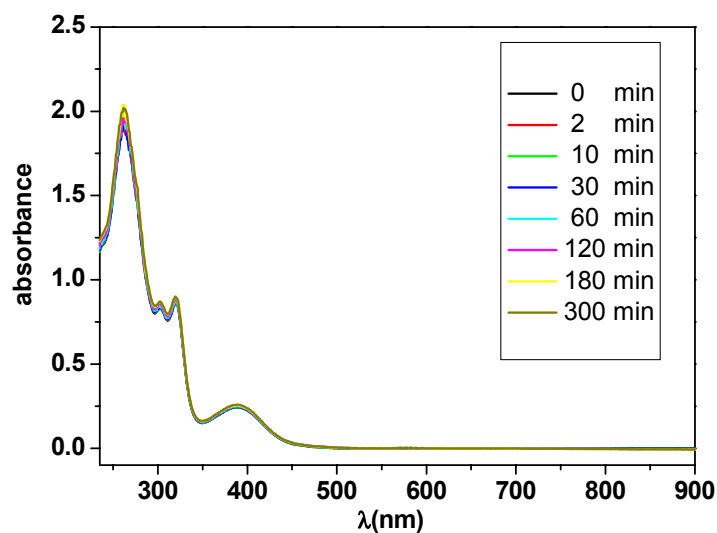


Figure S9. UV spectrum of **5d** in MC solution exposed to atmosphere for different period of time. They show same absorption spectrum without any absorption of **5d**⁺ and π -dimer of **5d** dications at 437, 463 or 823nm. The small variation is due to the change of concentration.