

## *Supplementary Information*

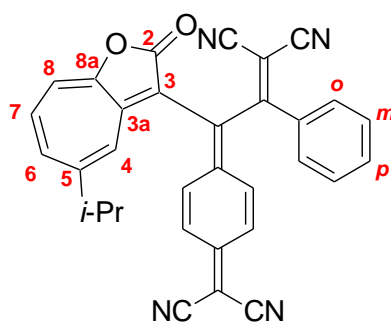
### ➤ *Contents*

1. Experimental of **10–18**.
2. UV/Vis spectra and continuous change in the visible spectra of **10–18**.
3. Cyclic voltammograms of **10–18**.
4. Theoretical calculations of **10'** and **12'**.

### ➤ *General*

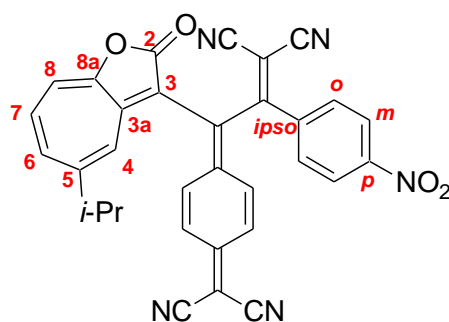
Melting points were determined with a Yanagimoto MPS3 micro melting apparatus and are uncorrected. Mass spectra were obtained with a JEOL HX-110, a Hitachi M-2500, or a Bruker APEX II instrument, usually at 70 eV. IR and UV/Vis spectra were measured with a Shimadzu FTIR-8100M and Shimadzu UV-2550 spectrophotometer, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a JEOL ECA500 at 500 MHz and 125 MHz or a Bruker AVANCE400 at 400 MHz and 100 MHz, respectively. Gel permeation chromatography (GPC) purification was performed with a TSKgel G2000H<sub>6</sub> with  $\text{CHCl}_3$  as an eluent. Voltammetry measurements were carried out with a BAS 100B/W electrochemical workstation equipped with Pt working and auxiliary electrodes and a reference electrode formed from  $\text{Ag}/\text{AgNO}_3$  (0.01 M) in acetonitrile containing tetrabutylammonium perchlorate (0.1 M). Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

## Compound (10)



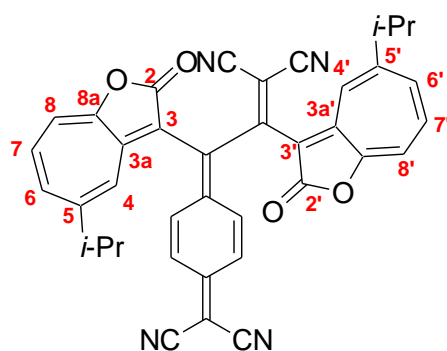
To a solution of **1** (73 mg, 0.25 mmol) in ethyl acetate (5 mL) was added TCNQ (76 mg, 0.37 mmol). The resulting mixture was refluxed for 4 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with ethyl acetate and Bio-Beads<sup>®</sup> with CH<sub>2</sub>Cl<sub>2</sub> to give **10** (119 mg, 91%) as dark blue crystals. m.p. 151.0–154.0 °C; IR (KBr disk):  $\nu_{\max}$  = 3058 (w), 2963 (w), 2926 (w), 2869 (w), 2211 (s, C≡N), 1748 (s, C=O), 1713 (w), 1653 (w), 1586 (m), 1559 (w), 1509 (m), 1474 (s), 1412 (s), 1314 (m), 1271 (s), 1246 (m), 1221 (w), 1192 (m), 841 (w), 799 (w), 768 (w), 758 (w), 743 (w), 714 (w), 693 (w), 658 (w), 604 (w), 469 (w), 419 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 271 (4.44), 306 (4.19), 374 (4.27), 430 sh (4.20), 615 nm (4.33); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 268 (4.47), 301 (4.23), 362 (4.30), 430 sh (4.22), 588 nm (4.35); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 7.66 (dd, 2H,  $J$  = 7.2, 1.6 Hz, *o*-Ph), 7.55 (dd, 1H,  $J$  = 7.2, 1.6 Hz, *p*-Ph), 7.47 (dd, 2H,  $J$  = 7.2, 7.2 Hz, *m*-Ph), 7.40 (dd, 1H,  $J$  = 10.8, 9.2 Hz, 7-H), 7.30 (dd, 1H,  $J$  = 9.2, 0.8 Hz, 8-H), 7.26 (s, 1H, 4-H), 7.25–7.19 (m, 3H, 6-H and H of DCNQ), 7.13 (dd, 1H,  $J$  = 9.6, 1.6 Hz, H of DCNQ), 7.03 (dd, 1H,  $J$  = 9.6, 1.6 Hz, H of DCNQ), 2.91 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr), 1.25 ppm (d, 6H,  $J$  = 6.8 Hz, *i*Pr); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 171.34 (C of *ipso*-Ph), 165.46 (C-2), 162.44 (C-5), 158.81 (C-3a or 8a), 153.51 (C of DCNQ), 150.08 (C-3a or 8a), 141.02 (C=C(CN)<sub>2</sub>), 136.10 (C-7), 135.92 (C of DCNQ), 135.63 (C of DCNQ), 134.86 (C of DCNQ), 134.21 (C of DCNQ), 133.44 (C of DCNQ), 133.19 (C of *p*-Ph), 129.78 (C of *o*-Ph), 129.42 (C of *m*-Ph), 126.01 (C-6), 125.14 (C-4), 118.19 (C-8), 113.38 (CN), 113.31 (CN), 112.83 (CN), 112.52 (CN), 105.31 (C-3), 87.62 (C(CN)<sub>2</sub>), 78.48 (C(CN)<sub>2</sub>), 39.48 (*i*Pr), 23.59 ppm (*i*Pr); HRMS (ESI): Calcd for [C<sub>32</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub> + Na]<sup>+</sup> 515.1478. Found: 515.1477; elemental analysis calcd (%) for C<sub>32</sub>H<sub>20</sub>N<sub>4</sub>O<sub>2</sub>·1/4H<sub>2</sub>O: C, 77.33; H, 4.16; N, 11.27. Found: C, 77.38; H, 4.17; N, 11.37.

## Compound (11)



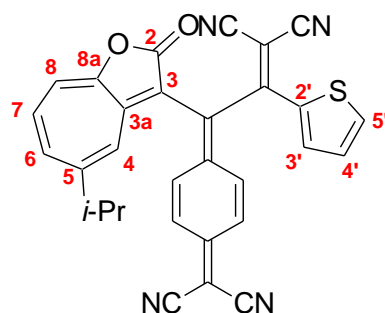
The procedure used for the preparation of **10** was adopted here. The reaction of **2** (83 mg, 0.25 mmol) with TCNQ (76 mg, 0.37 mmol) in refluxing ethyl acetate (5 mL) for 24 h afforded **11** (121 mg, 90%) as dark blue crystals. m.p. 117.0–119.0 °C; IR (KBr disk):  $\nu_{\max}$  = 2965 (w), 2926 (w), 2854 (w), 2211 (m), 1747 (m), 1600 (m), 1587 (m), 1521 (m), 1472 (s), 1414 (s), 1349 (m), 1315 (m), 1272 (s), 1247 (m), 1192 (m), 1148 (w), 1114 (w), 1064 (w), 1043 (w), 1015 (w), 974 (w), 949 (w), 908 (w), 863 (m), 848 (m), 800 (m), 766 (m), 759 (m), 744 (m), 715  $\text{cm}^{-1}$  (m); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 272 (4.53), 312 (4.31), 381 (4.37), 457 sh (4.15), 626 nm (4.33); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 270 (4.52), 312 (4.28), 378 (4.38), 457 sh (4.11), 597 nm (4.32);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.30 (d, 2H,  $J$  = 8.5 Hz,  $m$ -Ph), 7.85 (d, 2H,  $J$  = 8.5 Hz,  $o$ -Ph), 7.48 (dd, 1H,  $J$  = 11.0, 9.5 Hz, 7-H), 7.57 (d, 1H,  $J$  = 9.5 Hz, 8-H), 7.29–7.25 (m, 4H, 4,6-H and H of DCNQ), 7.10 (dd, 1H,  $J$  = 9.5, 1.0 Hz, H of DCNQ), 7.03 (d, 1H,  $J$  = 9.5 Hz, H of DCNQ), 2.92 (sept, 1H,  $J$  = 7.0 Hz,  $i$ Pr), 1.25 ppm (d, 6H,  $J$  = 7.0 Hz,  $i$ Pr);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 169.12 (C of  $ipso$ -Ph), 165.60 (C-2), 163.16 (C-5), 158.95 (C-3a or 8a), 153.02 (C of DCNQ), 150.14 (C-3a or 8a), 149.79 (C of  $p$ -Ph), 140.40 (C of DCNQ), 139.50 ( $\text{C}=\text{C}(\text{CN})_2$ ), 136.54 (C-7), 136.26 (C of DCNQ), 135.36 (C of DCNQ), 133.79 (C of DCNQ), 132.64 (C of DCNQ), 130.91 (C of  $o$ -Ph), 126.60 (C of DCNQ), 126.56 (C-6), 125.27 (C-4), 124.39 (C of  $m$ -Ph), 118.83 (C-8), 113.16 (CN), 113.08 (CN), 112.05 (CN), 111.75 (CN), 104.67 (C-3), 90.67 ( $\text{C}(\text{CN})_2$ ), 79.60 ( $\text{C}(\text{CN})_2$ ), 39.59 ( $i$ Pr), 23.67 ppm ( $i$ Pr); HRMS (FAB): Calcd for  $[\text{C}_{32}\text{H}_{19}\text{N}_5\text{O}_4 + \text{H}]^+$  538.1515. Found: 538.1520; elemental analysis calcd (%) for  $\text{C}_{32}\text{H}_{19}\text{N}_5\text{O}_4$ : C, 71.50; H, 3.56; N, 13.03. Found: C, 71.38; H, 3.72; N, 12.96.

## Compound (12)



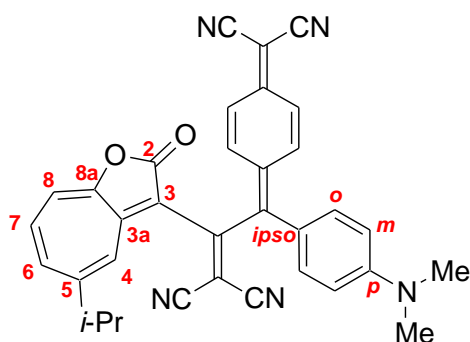
The procedure used for the preparation of **10** was adopted here. The reaction of **3** (47 mg, 0.12 mmol) with TCNQ (48 mg, 0.24 mmol) in refluxing ethyl acetate (5 mL) for 24 h afforded **12** (66 mg, 92%) as dark blue crystals. m.p. 206.0–208.0 °C; IR (KBr disk):  $\nu_{\max}$  = 2962 (w), 2869 (w), 2209 (m, C≡N), 1750 (s, C=O), 1586 (m), 1515 (s), 1474 (s), 1402 (s), 1314 (m), 1272 (s), 1245 (m), 1233 (m), 1190 (m), 1149 (w), 1045 (w), 938 (w), 841 (w), 800 (w), 761 (w), 711  $\text{cm}^{-1}$  (w); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 267 (4.69), 304 sh (4.29), 372 sh (4.37), 449 (4.68), 624 nm (4.49); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 259 (4.73), 302 sh (4.33), 363 (4.40), 446 (4.73), 590 nm (4.49);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 7.69 (br s, 1H, 4-H), 7.53 (dd, 1H,  $J$  = 10.8, 9.2 Hz, 7-H), 7.45–7.30 (m, 6H, 6, 8, 4', 6', 7', 8'-H), 7.25–7.19 (m, 3H, H of DCNQ), 7.09 (d, 1H,  $J$  = 9.2 Hz, H of DCNQ), 3.18 (br s, 1H, *i*Pr), 2.89 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr), 1.44 (br s, 6H, *i*Pr), 1.22 ppm (d, 6H,  $J$  = 6.8 Hz, *i*Pr); Low solubility hampered the measurement of  $^{13}\text{C}$  NMR. HRMS (ESI): Calcd for  $[\text{C}_{38}\text{H}_{26}\text{N}_4\text{O}_4 + \text{Na}]^+$  625.1846. Found: 625.1842; elemental analysis calcd (%) for  $\text{C}_{38}\text{H}_{26}\text{N}_4\text{O}_4 \cdot 1/2\text{H}_2\text{O}$ : C, 74.62; H, 4.45; N, 9.16. Found: C, 74.46; H, 4.59; N, 9.16.

## Compound (13)



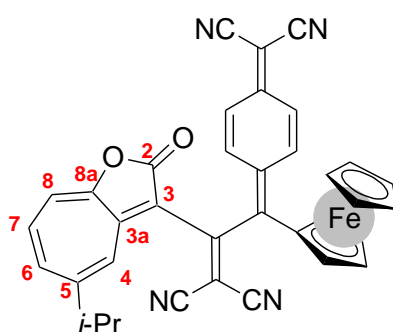
The procedure used for the preparation of **10** was adopted here. The reaction of **4** (78 mg, 0.26 mmol) with TCNQ (80 mg, 0.39 mmol) in refluxing ethyl acetate (5 mL) for 6 h afforded **13** (119 mg, 91%) as dark blue crystals. m.p. 158.5–161.5 °C; IR (KBr disk):  $\nu_{\max}$  = 3154 (w), 3102 (w), 2963 (w), 2872 (w), 2211 (s, C≡N), 1750 (s, C=O), 1601 (m), 1584 (m), 1512 (s), 1472 (s), 1406 (s), 1364 (s), 1347 (m), 1314 (m), 1271 (s), 1244 (m), 1192 (s), 970 (w), 939 (w), 841 (m), 795 (w), 764 (m), 714 (m), 662 (m), 642 (w), 467  $\text{cm}^{-1}$  (w); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 236 (4.41), 270 (4.46), 344 sh (4.48), 368 (4.53), 440 sh (4.19), 607 nm (4.48); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 267 (4.43), 362 (4.48), 437 sh (4.08), 585 nm (4.39);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 8.04 (dd, 1H,  $J$  = 4.0, 0.8 Hz, 3'-H of Th), 7.86 (dd, 1H,  $J$  = 5.2, 0.8 Hz, 5'-H of Th), 7.45 (dd, 1H,  $J$  = 10.8, 9.2 Hz, 7-H), 7.37 (dd, 1H,  $J$  = 9.2, 1.2 Hz, 8-H), 7.37 (d, 1H,  $J$  = 1.2 Hz, 4-H), 7.27 (dd, 1H,  $J$  = 5.2, 4.0 Hz, 4'-H of Th), 7.26 (ddd, 1H,  $J$  = 10.8, 1.2, 1.2 Hz, 6-H), 7.24 (dd, 1H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 7.19 (dd, 1H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 7.16 (dd, 1H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 6.99 (dd, 1H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 2.91 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr), 1.23 ppm (d, 6H,  $J$  = 6.8 Hz, *i*Pr);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 165.15 (C-2), 162.65 (C-5), 161.53 ( $\text{C}=\text{C}(\text{CN})_2$ ), 158.97 (C-3a or 8a), 153.79 (C of DCNQ), 149.88 (C-3a or 8a), 140.63 (C of DCNQ), 138.11 (C-2' of Th), 137.23 (C-5' of Th), 136.31 (C-4' of Th), 136.22 (C-7), 135.82 (C-3' of Th), 133.90 (C of DCNQ), 133.81 (C of DCNQ), 133.36 (C of DCNQ), 129.84 (C-6), 125.78 (C-4), 125.72 (C of DCNQ), 125.57 (C of DCNQ), 118.38 (C-8), 113.48 (CN), 113.39 (CN), 112.91 (CN), 104.86 (C-3), 80.70 ( $\text{C}(\text{CN})_2$ ), 77.96 ( $\text{C}(\text{CN})_2$ ), 39.46 (*i*Pr), 23.56 ppm (*i*Pr); HRMS (ESI): Calcd for  $[\text{C}_{30}\text{H}_{18}\text{N}_4\text{O}_2\text{S} + \text{Na}]^+$  521.1043. Found: 521.1042; elemental analysis calcd (%) for  $\text{C}_{30}\text{H}_{18}\text{N}_4\text{O}_2\text{S} \cdot 1/3\text{H}_2\text{O}$ : C, 71.41; H, 3.73; N, 11.10. Found: C, 71.45; H, 3.86; N, 11.18.

## Compound (14)



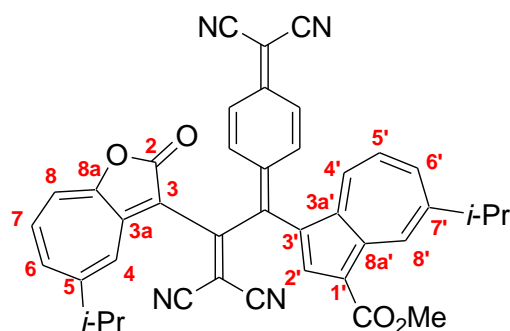
The procedure used for the preparation of **10** was adopted here. The reaction of **5** (83 mg, 0.25 mmol) with TCNQ (82 mg, 0.40 mmol) in refluxing ethyl acetate (5 mL) for 2 h afforded **14** (117 mg, 87%) as dark purple crystals. m.p. 206.0–210.0 °C; IR (KBr disk):  $\nu_{\max}$  = 2966 (w), 2193 (m, C≡N), 1760 (m, C=O), 1612 (w), 1578 (s), 1519 (w), 1477 (m), 1392 (m), 1365 (s), 1348 (s), 1322 (m), 1275 (m), 1231 (w), 1210 (w), 1167 (s), 1130 (m), 1066 (w), 1050 (w), 942 (w), 908 (w), 836 (w), 798 (w), 762 (w), 744 (w), 730 (w), 718  $\text{cm}^{-1}$  (w); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 254 (4.38), 267 (4.37), 344 (4.16), 429 (4.34), 496 (4.43), 718 nm (4.46); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 254 (4.40), 265 sh (4.39), 343 (4.13), 424 (4.34), 480 (4.41), 657 nm (4.46);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 7.51 (dd, 1H,  $J$  = 9.6, 9.6 Hz, 7-H), 7.44 (s, 1H, 4-H), 7.41 (m, 2H, 6-H and H of DCNQ), 7.32 (d, 1H,  $J$  = 9.6 Hz, 8-H), 7.29–7.25 (m, 3H, *o*-Ph and H of DCNQ), 7.18 (dd, 1H,  $J$  = 9.6, 1.2 Hz, H of DCNQ), 7.09 (dd, 1H,  $J$  = 9.6, 1.2 Hz, H of DCNQ), 6.70 (d, 2H,  $J$  = 9.2 Hz, *m*-Ph), 3.13 (s, 6H,  $\text{NMe}_2$ ), 2.98 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr), 1.25 ppm (d, 6H,  $J$  = 6.8 Hz, *i*Pr);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 163.64 (C-2), 163.46 (C-5), 163.23 (C-3a or 8a), 159.04 (C-3a or 8a), 153.98 ( $\text{C}=\text{C}(\text{CN})_2$ ), 153.06 (C of *ipso*-Ph), 151.94 (C of DCNQ), 149.11 (C of DCNQ), 137.04 (C-8), 136.42 (C-7), 136.34 (C of DCNQ), 135.10 (C of *m*-Ph), 134.29 (C of DCNQ), 133.34 (C of DCNQ), 126.36 (C-4), 125.33 (C of DCNQ), 124.85 (C of DCNQ), 124.47 (C of *p*-Ph), 119.53 (C-6), 114.89 (CN), 113.01 (CN), 112.77 (CN), 112.38 (C of *o*-Ph), 104.37 (C-3), 87.24 ( $\text{C}(\text{CN})_2$ ), 71.30 ( $\text{C}(\text{CN})_2$ ), 40.18 ( $\text{NMe}_2$ ), 39.83 (*i*Pr), 23.61 ppm (*i*Pr); HRMS (FAB): Calcd for  $[\text{C}_{34}\text{H}_{25}\text{N}_5\text{O}_2 + \text{H}]^+$  536.2087. Found: 536.2086; elemental analysis calcd (%) for  $\text{C}_{34}\text{H}_{25}\text{N}_5\text{O}_2$ : C, 76.24; H, 4.70; N, 13.08. Found: C, 76.12; H, 4.74; N, 13.01.

## Compound (15)



The procedure used for the preparation of **10** was adopted here. The reaction of **6** (105 mg, 0.27 mmol) with TCNQ (80 mg, 0.39 mmol) in refluxing ethyl acetate (5 mL) for 13 h afforded **15** (156 mg, 98%) as dark blue crystals. m.p. 175.0–180.0 °C; IR (KBr disk):  $\nu_{\max}$  = 3093 (w), 3085 (w), 3069 (w), 3060 (w), 2962 (w), 2872 (w), 2210 (s, C≡N), 1750 (s, C=O), 1601 (w), 1585 (s), 1512 (s), 1472 (s), 1438 (s), 1412 (s), 1313 (s), 1272 (s), 1245 (s), 1191 (s), 1107 (m), 1040 (m), 1003 (m), 930 (m), 840 (w), 796 (m), 742 (w), 712 (m), 668 (m), 498 (w), 426  $\text{cm}^{-1}$  (w); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 267 (4.46), 332 sh (4.35), 361 (4.37), 406 sh (4.31), 590 nm (4.40); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 265 (4.47), 324 sh (4.29), 358 (4.42), 394 sh (4.32), 573 nm (4.36);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 7.55 (br s, 1H, 4-H), 7.39 (dd, 1H,  $J$  = 10.8, 9.2 Hz, 7-H), 7.32 (dd, 1H,  $J$  = 9.2, 0.8 Hz, 8-H), 7.28–7.22 (m, 3H, 6-H and H of DCNQ), 7.12 (dd, 1H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 7.10 (dd, 1H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 4.99 (br s, 1H, H of Fc), 4.87 (br s, 1H, H of Fc), 4.82 (br s, 1H, H of Fc), 4.76 (br s, 1H, H of Fc), 4.40 (s, 5H, H of Cp), 2.88 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr), 1.24 ppm (d, 6H,  $J$  = 6.8 Hz, *i*Pr);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}}$  = 165.42 (C-2), 162.11 (C-4), 158.68 (C-8a), 154.07 (C-3a), 149.99 (C-6), 140.91 ( $\text{C}=\text{C}(\text{CN})_2$ ), 135.96, 135.81 (C-7), 134.44 (C of DCNQ), 134.08 (C of DCNQ), 133.30 (C of DCNQ), 131.20 (C-4), 125.65 (C of DCNQ), 125.36 (C of DCNQ), 125.33 (C of DCNQ), 117.89 (C-8), 114.54 (CN), 114.18 (CN), 113.54 (CN), 113.53 (CN), 104.90 (C-3), 78.60 ( $\text{C}(\text{CN})_2$ ), 77.64 ( $\text{C}(\text{CN})_2$ ), 74.76 (C of Fc), 74.32 (C of Fc), 72.74 (C of Fc), 72.11 (C of Fc), 71.98 (C of Cp), 39.43 (*i*Pr), 23.64 (*i*Pr), 23.39 ppm (*i*Pr); HRMS (ESI): Calcd for  $[\text{C}_{36}\text{H}_{24}\text{FeN}_4\text{O}_2 + \text{Na}]^+$  623.1141. Found: 623.1144; elemental analysis calcd (%) for  $\text{C}_{36}\text{H}_{24}\text{FeN}_4\text{O}_2 \cdot 1/2\text{H}_2\text{O}$ : C, 70.95; H, 4.13; N, 9.19. Found: C, 70.91; H, 4.19; N, 9.38.

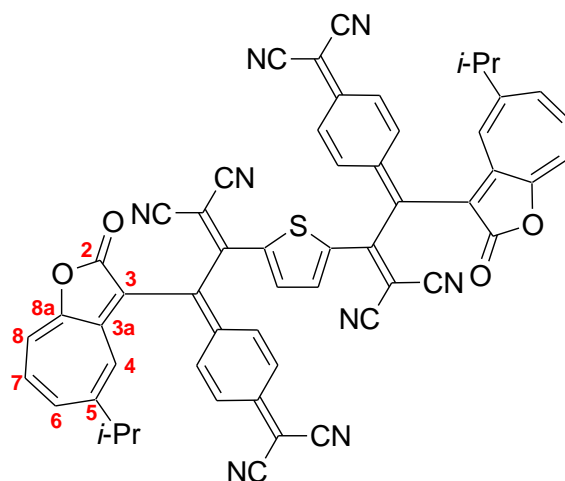
## Compound (16)



The procedure used for the preparation of **10** was adopted here. The reaction of **7** (110 mg, 0.25 mmol) with TCNQ (82 mg, 0.40 mmol) in refluxing ethyl acetate (5 mL) for 3 h afforded **16** (156 mg, 97%) as greenish blue crystals. m.p. 176.0–179.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (KBr disk):  $\nu_{\max}$  = 2964 (w), 2207 (m, C≡N), 1756 (m, C=O), 1698 (m, C=O), 1588 (m), 1506 (m), 1473 (s), 1441 (s), 1420 (s), 1399 (s), 1378 (m), 1315 (w), 1275 (m), 1233 (m), 1213 (s), 1190 (s), 1130 (w), 1057 (w), 932 (w), 897 (w), 842 (w), 806 (w), 778 (w), 718 cm<sup>-1</sup> (m); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 241 (4.62), 273 sh (4.52), 294 sh (4.48), 431 (4.46), 653 nm (4.35); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 243 (4.14), 294 (4.49), 426 (4.47), 604 nm (4.31); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 9.84 (d, 1H,  $J$  = 1.6 Hz, 4'-H of Az), 8.35 (d, 1H,  $J$  = 10.0 Hz, 8'-H of Az), 8.22 (s, 1H, 2'-H of Az), 7.97 (d, 1H,  $J$  = 10.0 Hz, 6'-H of Az), 7.66 (t, 1H,  $J$  = 10.0 Hz, 7'-H of Az), 7.51 (dd, 1H,  $J$  = 10.8, 9.6 Hz, 7-H), 7.49 (s, 1H, 4-H), 7.36–7.31 (m, 4H, 6,8-H and H of DCNQ), 7.23 (dd, 1H,  $J$  = 10.4, 1.6 Hz, H of DCNQ), 7.13 (dd, 1H,  $J$  = 10.4, 1.6 Hz, H of DCNQ), 3.91 (s, 3H, CO<sub>2</sub>Me), 3.28 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr), 3.07 (sept, 1H,  $J$  = 6.8 Hz, *i*Pr of Az), 1.43 (d, 6H,  $J$  = 6.8 Hz, *i*Pr of Az), 1.35 (d, 6H,  $J$  = 6.8 Hz, *i*Pr) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 164.71 (C-3a), 164.12 (C-5), 163.71 (C-2), 163.47 (CO<sub>2</sub>Me), 159.03 (C-8a), 154.79 (C-5' of Az), 153.84 (C=C(CN)<sub>2</sub>), 149.00 (C of DCNQ), 145.43 (C-1' of Az), 144.98 (C-8a' of Az), 144.06 (C-2' of Az), 141.65 (C-6' of Az), 139.92 (C-4' of Az), 137.08 (C-8' of Az), 136.95 (C-7), 136.70 (C of DCNQ), 136.32 (C of DCNQ), 135.84 (C of DCNQ), 133.97 (C-8), 131.24 (C-7' of Az), 126.83 (C of DCNQ), 126.13 (C-4), 125.59 (C of DCNQ), 119.51 (C-6), 118.33 (CN), 114.26 (CN), 113.09 (CN), 112.71 (CN), 103.95 (C-3), 86.36 (C(CN)<sub>2</sub>), 74.55 (C(CN)<sub>2</sub>), 51.44 (CO<sub>2</sub>Me), 40.02 (*i*Pr), 39.34 (*i*Pr of Az), 24.45 (*i*Pr of Az), 23.64 ppm (*i*Pr); HRMS (FAB): Calcd for [C<sub>41</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>]<sup>+</sup> 642.2267. Found: 642.2266; elemental analysis calcd (%) for C<sub>41</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>: C, 76.62; H, 4.70; N, 8.72. Found: C, 76.45; H, 4.86; N, 8.49.

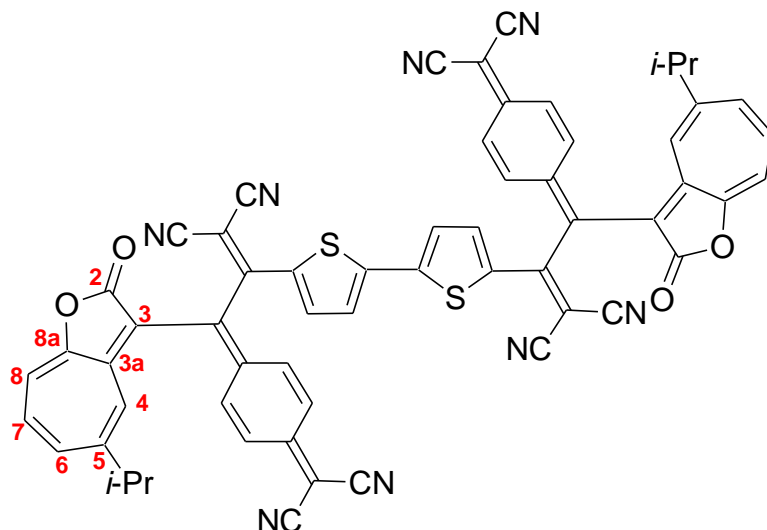


## Compound (17)

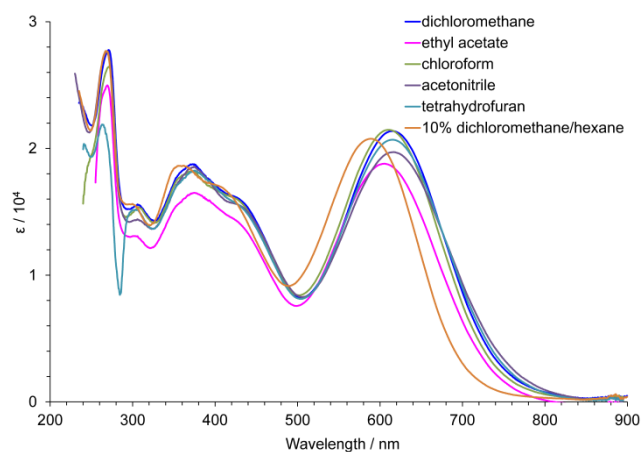


The procedure used for the preparation of **10** was adopted here. The reaction of **8** (126 mg, 0.25 mmol) with TCNQ (204 mg, 1.00 mmol) in refluxing ethyl acetate (5 mL) for 48 h afforded **17** (210 mg, 92%) as dark blue crystals. m.p. 211.0–215.0 °C (decomp.); IR (KBr disk):  $\nu_{\max}$  = 2980 (w), 2965 (w), 2211 (s, C≡N), 1757 (m, C=O), 1602 (m), 1587 (m), 1514 (m), 1472 (s), 1416 (s), 1314 (m), 1272 (s), 1247 (m), 1192 (m), 1145 (w), 1110 (w), 1064 (w), 1045 (w), 974 (w), 945 (w), 841 (m), 802 (m), 765 (m), 742 (m), 714  $\text{cm}^{-1}$  (m); UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\max}$  (log  $\epsilon$ ) = 269 (4.83), 350 sh (4.74), 407 (4.87), 597 nm (4.77); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 272 (4.58), 353 sh (4.50), 411 (4.60), 635 nm (4.53);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  = 7.95 (br s, 2H, H of Th), 7.51 (dd, 2H,  $J$  = 10.8, 9.6 Hz, 7-H), 7.42 (d, 2H,  $J$  = 9.6 Hz, 8-H), 7.33 (s, 2H, 4-H), 7.30 (d, 1H,  $J$  = 10.8 Hz, 6-H), 7.24–7.22 (m, 2H, H of DCNQ), 7.07 (d, 2H,  $J$  = 9.6 Hz, H of DCNQ), 6.95 (dd, 2H,  $J$  = 9.6 Hz, H of DCNQ), 2.93 (sept, 2H,  $J$  = 6.8 Hz, *i*Pr), 1.24 ppm (d, 12H,  $J$  = 6.8 Hz, *i*Pr); Low solubility hampered the measurement of  $^{13}\text{C}$  NMR. HRMS (FAB): Calcd for  $[\text{C}_{56}\text{H}_{32}\text{N}_8\text{O}_4\text{S} + \text{H}]^+$  913.2345. Found: 913.2347; elemental analysis calcd (%) for  $\text{C}_{56}\text{H}_{32}\text{N}_8\text{O}_4\text{S}$ : C, 73.67; H, 3.53; N, 12.27. Found: C, 73.48; H, 3.68; N, 12.20.

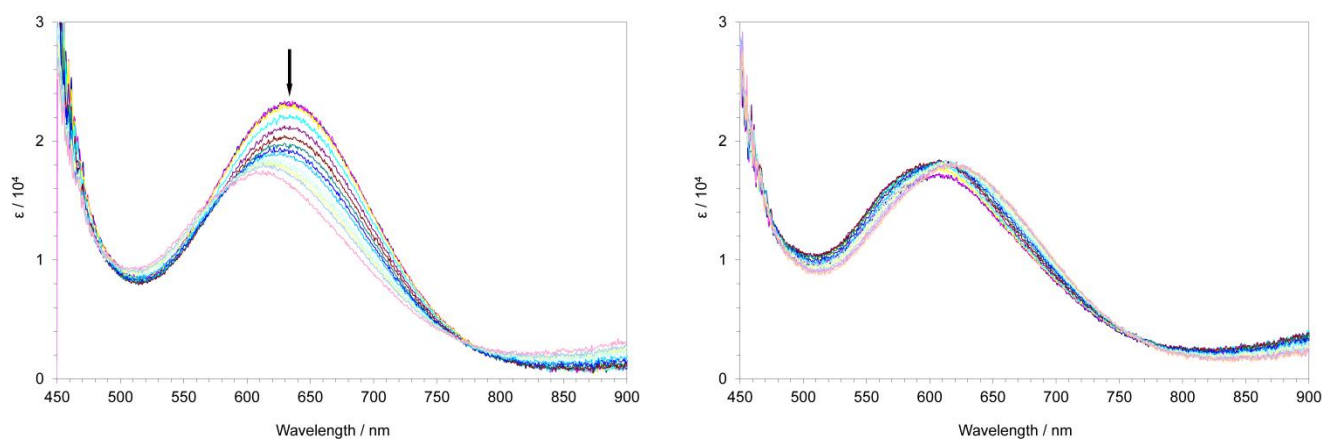
## Compound (18)



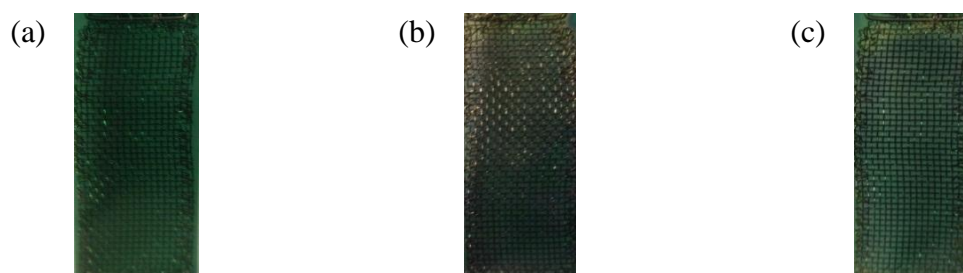
The procedure used for the preparation of **10** was adopted here. The reaction of **9** (147 mg, 0.25 mmol) with TCNQ (204 mg, 1.00 mmol) in refluxing ethyl acetate (5 mL) for 48 h afforded **18** (239 mg, 96%) as dark purple crystals. m.p. 237.0–240.0 °C (CH<sub>2</sub>Cl<sub>2</sub>/hexane); IR (KBr disk):  $\nu_{\max}$  = 2965 (w), 2210 (s, C≡N), 1750 (s, C=O), 1584 (m), 1512 (s), 1470 (s), 1416 (s), 1331 (w), 1314 (m), 1272 (s), 1245 (m), 1192 (m), 1061 (w), 1042 (w), 943 (w), 840 (m), 800 (w), 764 (w), 742 (w), 713 (w), 661 cm<sup>-1</sup> (w); UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 269 (4.72), 382 (4.64), 407 sh (4.66), 450 (4.71), 541 (4.72), 601 nm (4.70); UV/Vis (hexane):  $\lambda_{\max}$  (log  $\epsilon$ ) = 270 (4.60), 384 sh (4.51), 410 sh (4.54), 459 (4.58), 600 nm (4.59); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta_{\text{H}}$  = 7.89 (d, 2H,  $J$  = 1.2 Hz, 4-H), 7.48 (dd, 2H,  $J$  = 10.8, 9.6 Hz, 7-H), 7.42 (m, 6H, 8-H and H of Th), 7.29 (dd, 2H,  $J$  = 9.6, 1.2 Hz, 6-H), 7.24 (dd, 2H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 7.19 (dd, 2H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 7.13 (dd, 2H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 6.98 (dd, 2H,  $J$  = 9.6, 2.0 Hz, H of DCNQ), 2.92 (sept, 2H,  $J$  = 6.8 Hz, *i*Pr), 1.23 ppm (d, 12H,  $J$  = 6.8 Hz, *i*Pr); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta_{\text{C}}$  = 165.31 (C-5), 162.94 (C-2), 160.55 (C-8a), 159.01 (C of Th), 153.62 (C=C(CN)<sub>2</sub>), 150.00 (C-3a), 145.48 (C of Th), 140.07 (C of DCNQ), 139.21 (C of DCNQ), 137.04 (C of DCNQ), 136.50 (C-7), 136.35 (C-6), 133.61 (C of DCNQ), 133.47 (C of DCNQ), 133.11 (C of DCNQ), 128.30 (C of Th), 126.04 (C of DCNQ), 125.90 (C of Th), 118.65 (C-8), 113.41 (CN), 113.35 (CN), 113.27 (CN), 112.86 (CN), 104.72 (C-3), 80.80 (C(CN)<sub>2</sub>), 78.52 (C(CN)<sub>2</sub>), 39.50 (*i*Pr), 23.60 ppm (*i*Pr); HRMS (FAB): Calcd for [C<sub>60</sub>H<sub>34</sub>N<sub>8</sub>O<sub>4</sub>S<sub>2</sub> + H]<sup>+</sup> 995.2223. Found: 995.2203; elemental analysis calcd (%) for C<sub>60</sub>H<sub>34</sub>N<sub>8</sub>O<sub>4</sub>S<sub>2</sub>·H<sub>2</sub>O: C, 71.13; H, 3.58; N, 11.06. Found: C, 71.07; H, 3.62; N, 11.01.



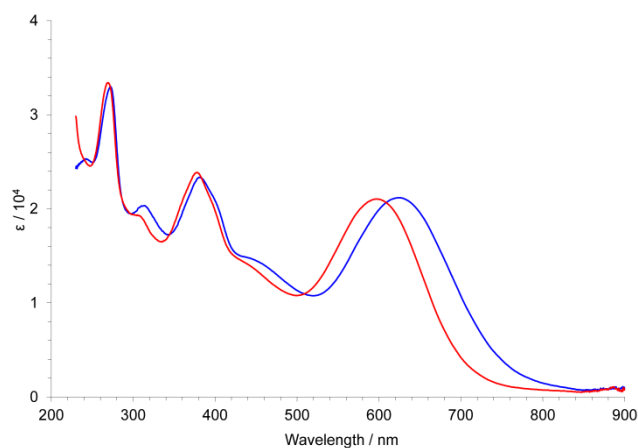
**Figure S-1.** UV/Vis spectrum of **10** in each solvent.



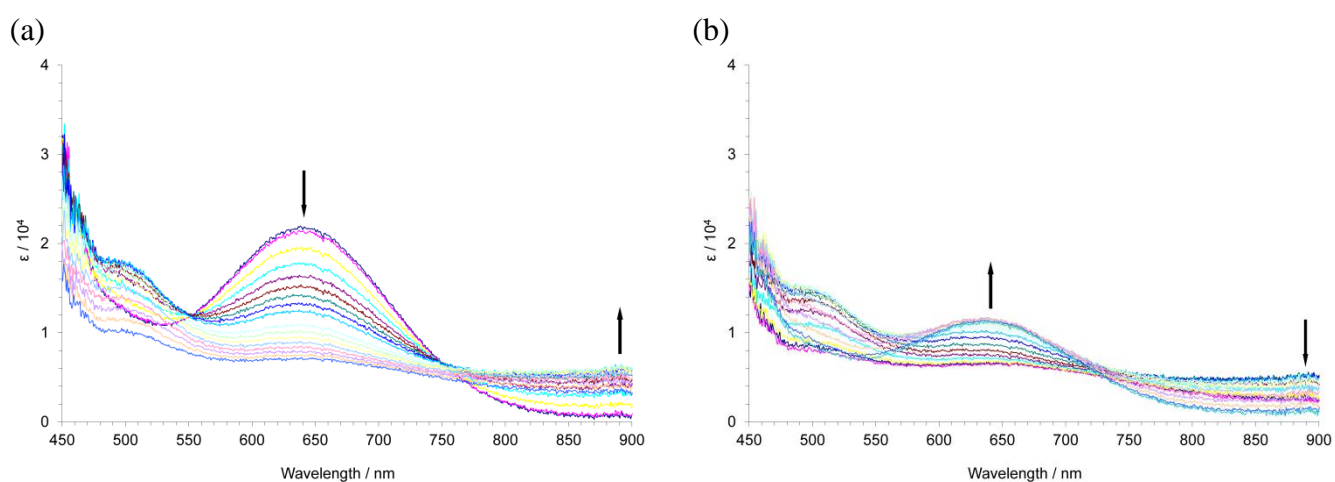
**Figure S-2.** Continuous change in the visible spectrum of **10**: (a) constant-current electrochemical reduction (50 uA) and (b) reverse oxidation of the reduced species (50 uA) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.



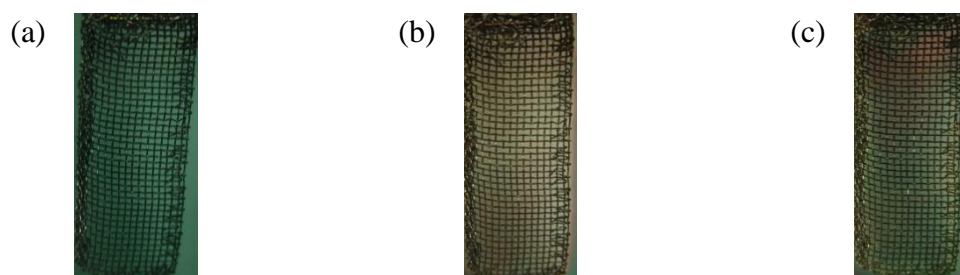
**Figure S-3.** Color changes of **10** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50 uA): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.



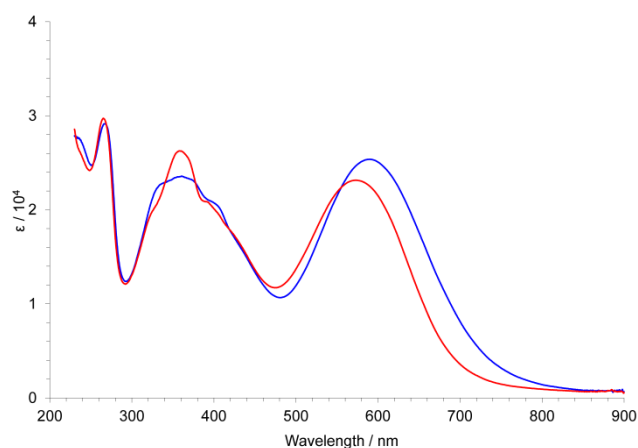
**Figure S-4.** UV/Vis spectrum of **11** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).



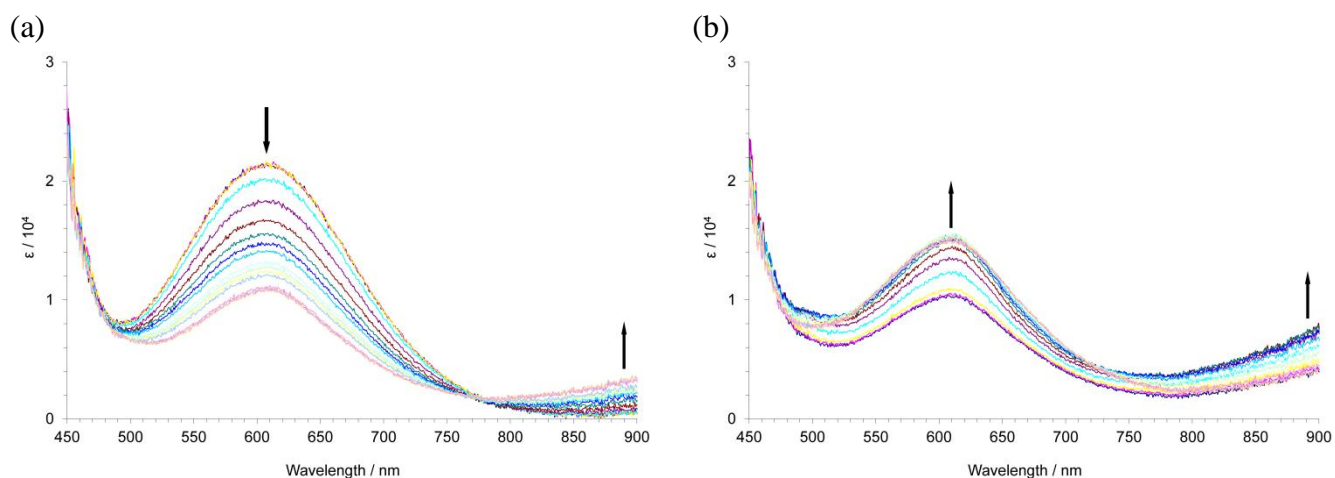
**Figure S-5.** Continuous change in the visible spectrum of **11**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.



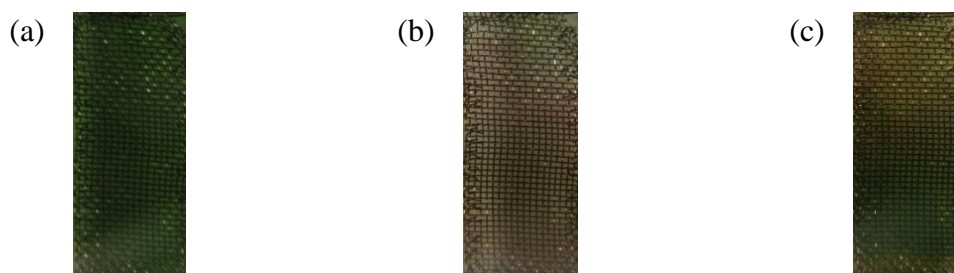
**Figure S-6.** Color changes of **11** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.



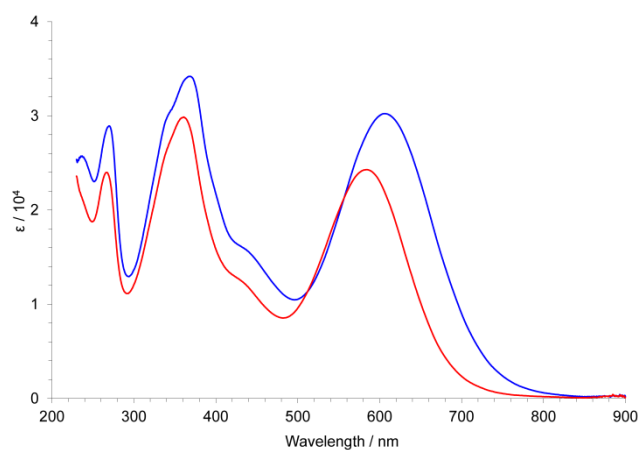
**Figure S-7.** UV/Vis spectrum of **12** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).



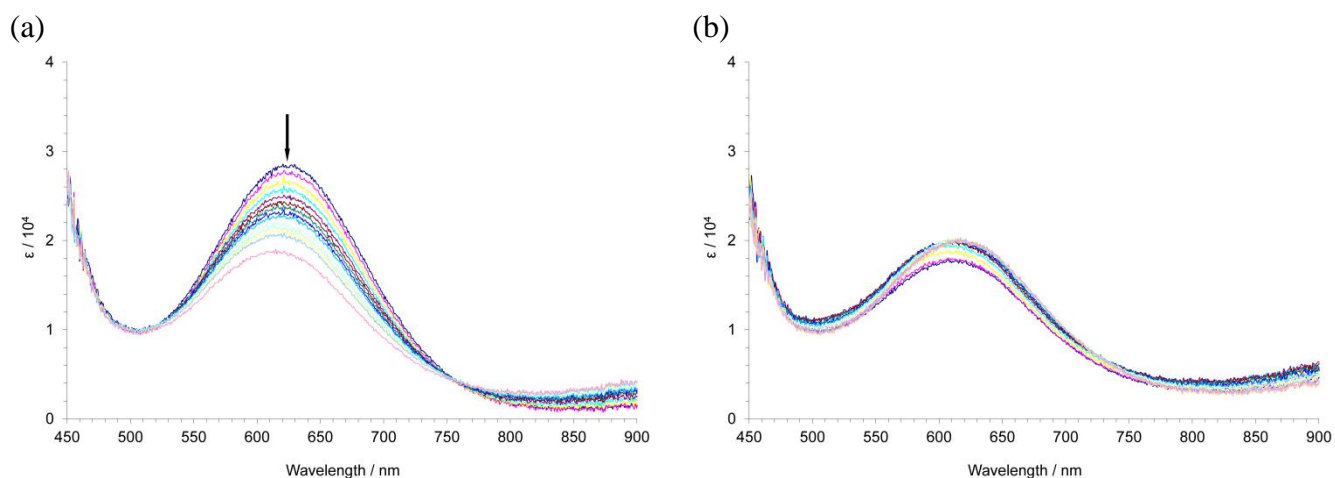
**Figure S-8.** Continuous change in the visible spectrum of **12**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.



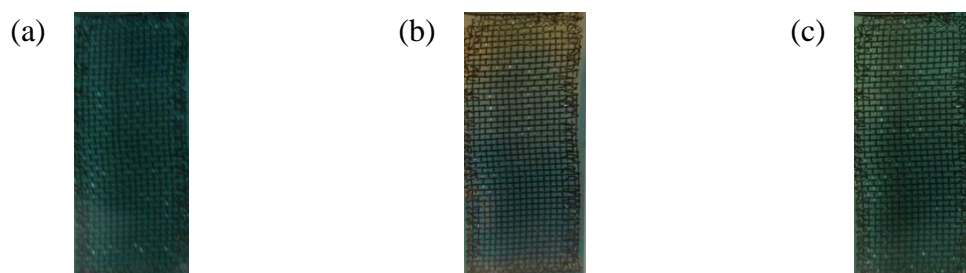
**Figure S-9.** Color changes of **12** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.



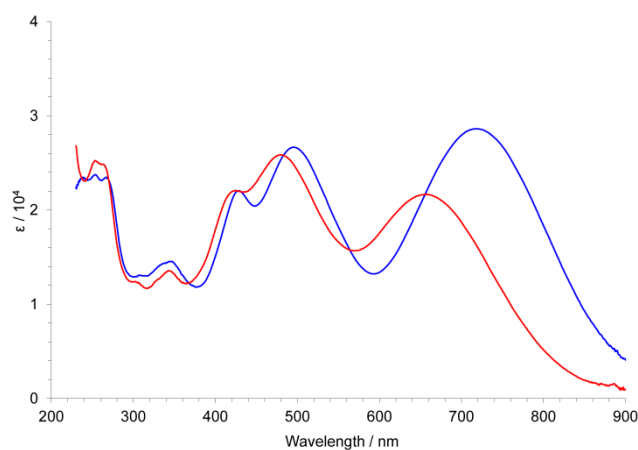
**Figure S-10.** UV/Vis spectrum of **13** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).



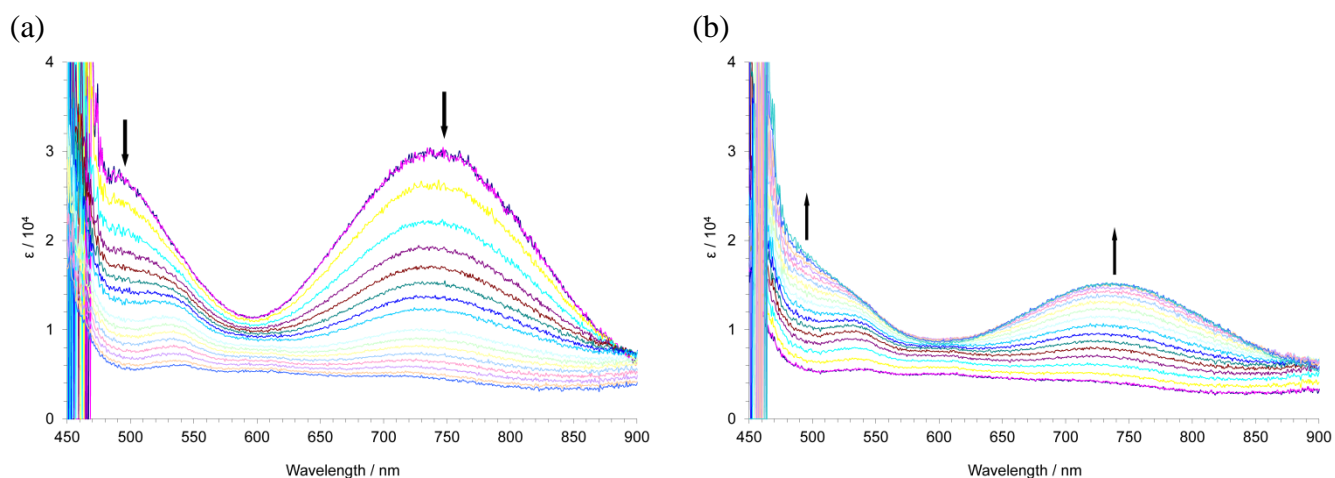
**Figure S-11.** Continuous change in the visible spectrum of **13**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.



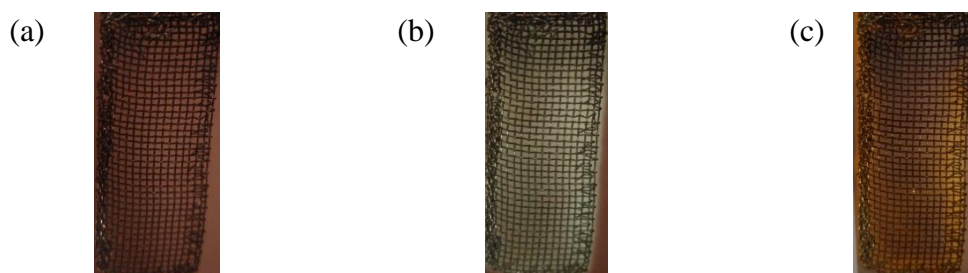
**Figure S-12.** Color changes of **13** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.



**Figure S-13.** UV/Vis spectrum of **14** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).

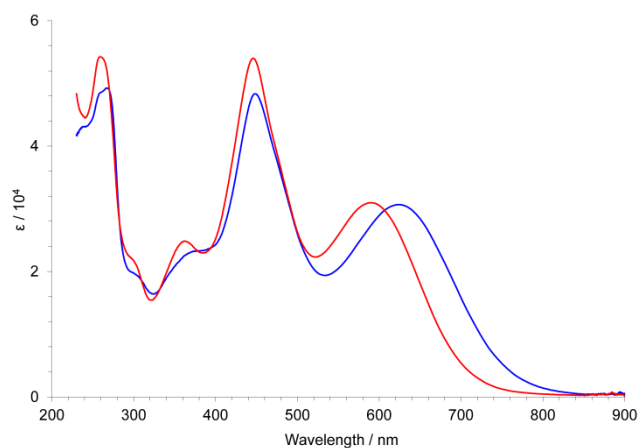


**Figure S-14.** Continuous change in the visible spectrum of **14**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.

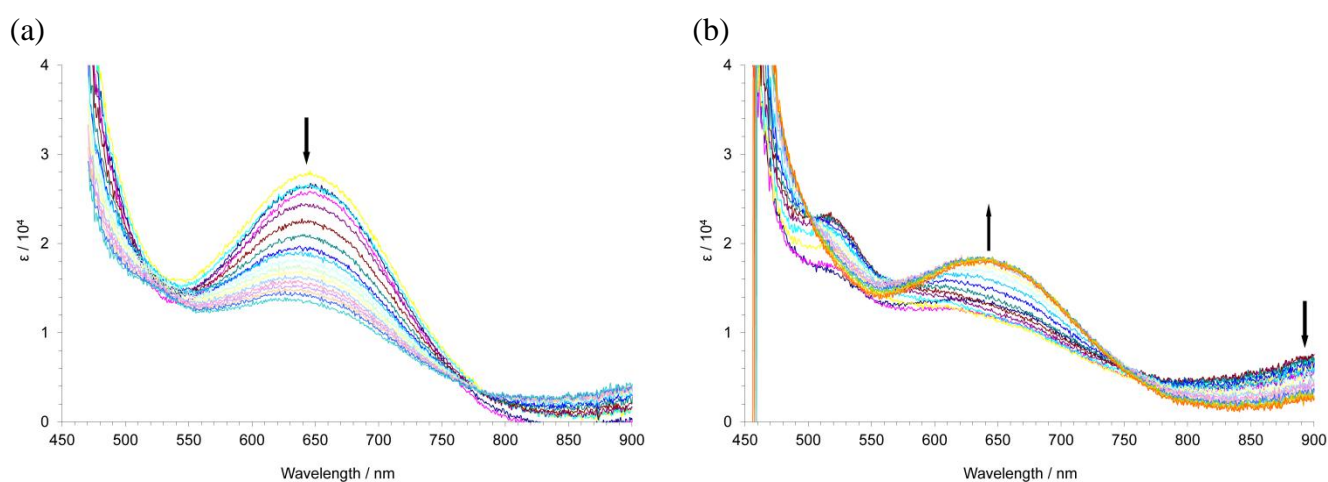


**Figure S-15.** Color changes of **14** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.

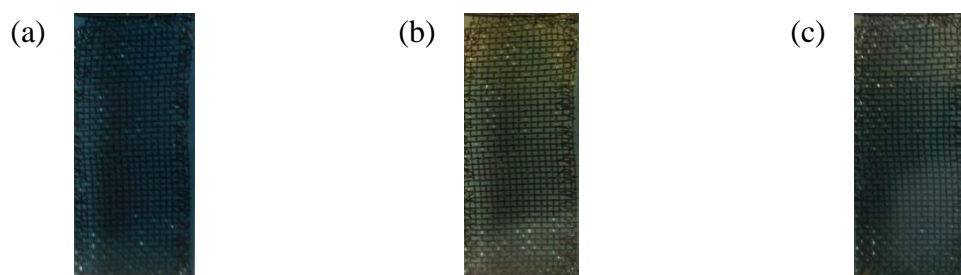




**Figure S-16.** UV/Vis spectrum of **15** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).

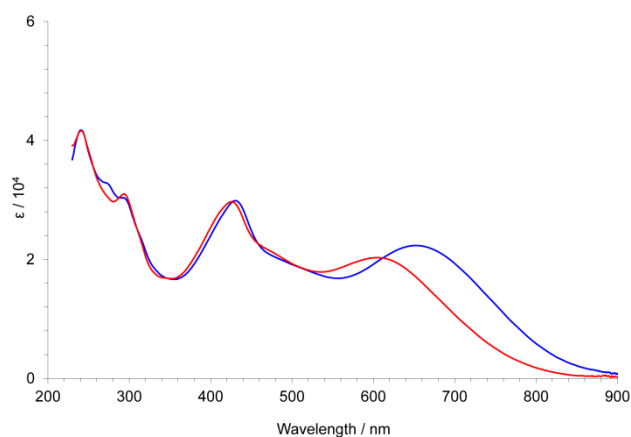


**Figure S-17.** Continuous change in the visible spectrum of **15**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.

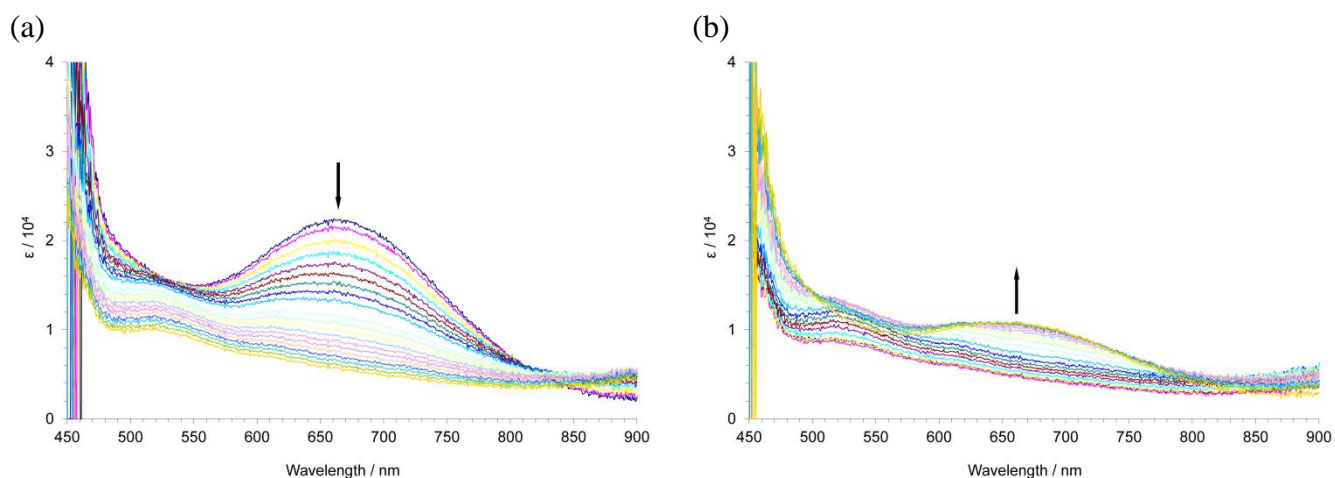


**Figure S-18.** Color changes of **15** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.

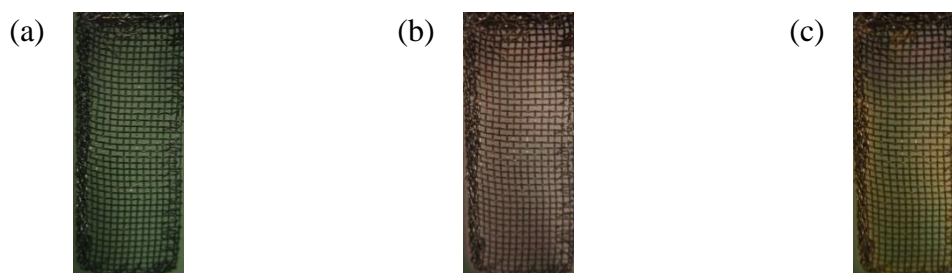




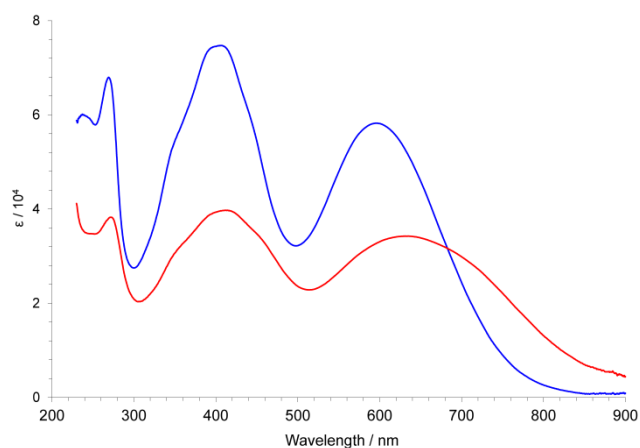
**Figure S-19.** UV/Vis spectrum of **16** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).



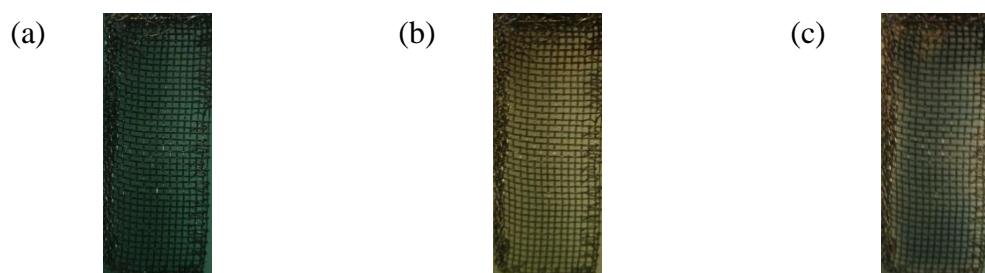
**Figure S-20.** Continuous change in the visible spectrum of **16**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.



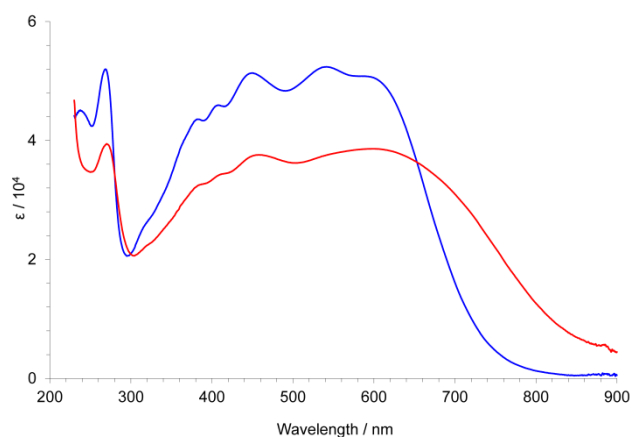
**Figure S-21.** Color changes of **16** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.



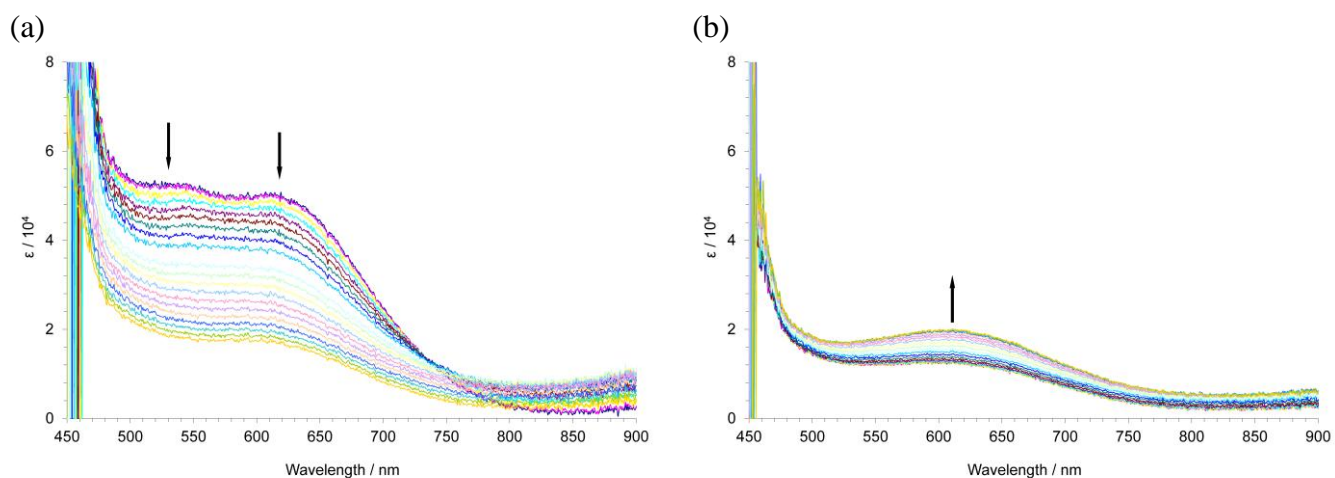
**Figure S-22.** UV/Vis spectrum of **17** in CH<sub>2</sub>Cl<sub>2</sub> (blue line) and 10% CH<sub>2</sub>Cl<sub>2</sub>/hexane (red line).



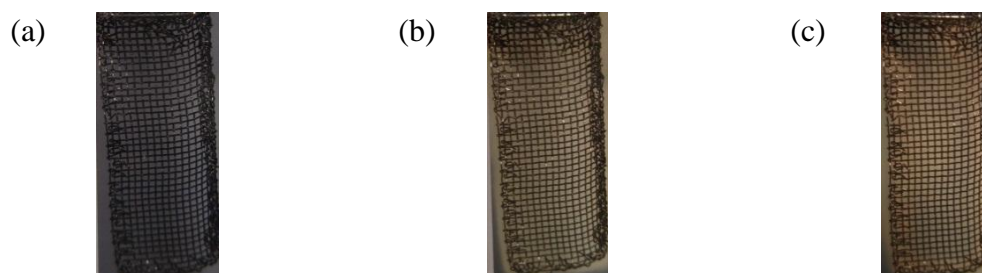
**Figure S-23.** Color changes of **17** upon the electrochromic analysis in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M) upon (50 uA): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.



**Figure S-24.** UV/Vis spectrum of **18** in  $\text{CH}_2\text{Cl}_2$  (blue line) and 10%  $\text{CH}_2\text{Cl}_2$ /hexane (red line).



**Figure S-25.** Continuous change in the visible spectrum of **18**: (a) constant-current electrochemical reduction (50  $\mu\text{A}$ ) and (b) reverse oxidation of the reduced species (50  $\mu\text{A}$ ) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) at 30 sec intervals.

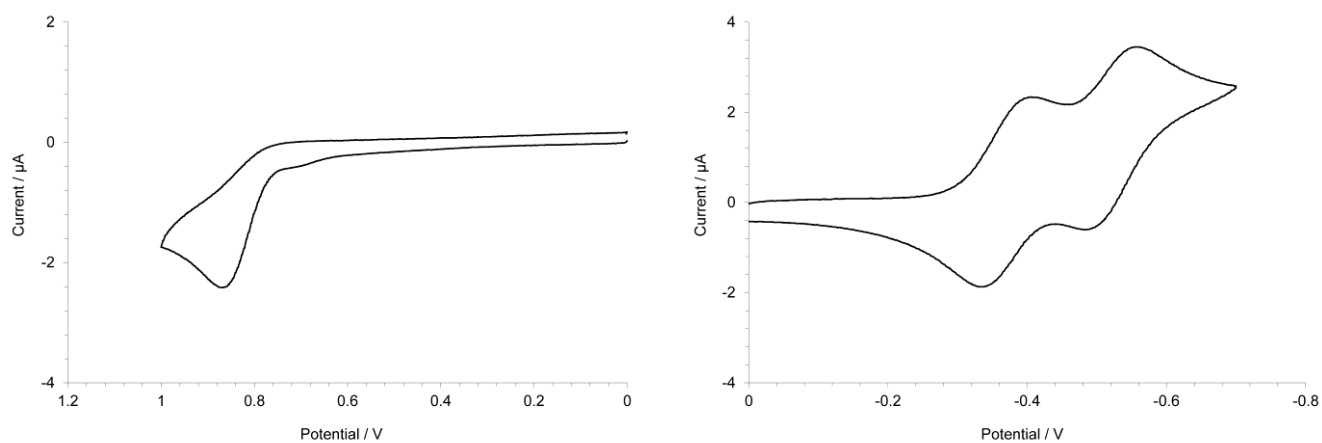


**Figure S-26.** Color changes of **18** upon the electrochromic analysis in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) upon (50  $\mu\text{A}$ ): (a) before electrochemical reduction, (b) after electrochemical reduction, and (c) after reverse electrochemical oxidation of the reduced species.

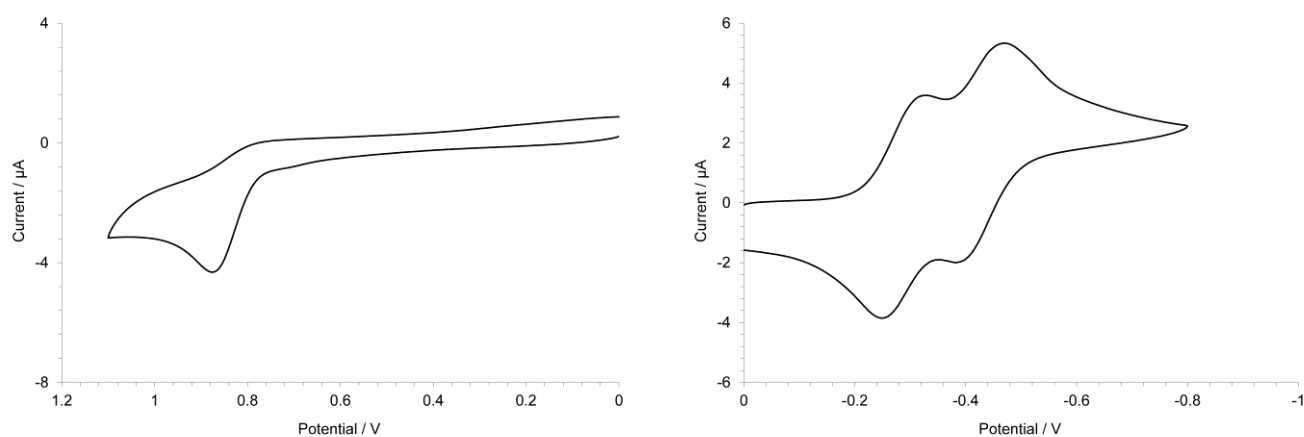
**Table S-1.** Redox potentials and band gap of DCNQ chromophores **10–18**.

Sample	Method	$E_1^{\text{ox}}$ [V]	$E_2^{\text{ox}}$ [V]	$E_1^{\text{red}}$ [V]	$E_2^{\text{red}}$ [V]	$E_3^{\text{red}}$ [V]	$E_4^{\text{red}}$ [V]	$E_1^{\text{ox}} - E_1^{\text{red}}$ [V]
<b>10</b>	CV			-0.37	-0.53			
	(DPV)	(+0.79)		(-0.35)	(-0.51)			(1.14)
<b>11</b>	CV			-0.29	-0.43			
	(DPV)	(+0.80)		(-0.27)	(-0.41)	(-1.46)	(-1.80)	(1.07)
<b>12</b>	CV			-0.38	-0.49			
	(DPV)	(+0.79)		(-0.36)	(-0.47)	(-1.92)		(1.15)
<b>13</b>	CV			-0.42	-0.50			
	(DPV)	(+0.78)		(-0.40)	(-0.48)			(1.18)
<b>14</b>	CV			-0.47	-0.58			
	(DPV)	(+0.74)	(+0.88)	(-0.45)	(-0.58)	(-1.73)		(1.19)
<b>15</b>	CV	+0.46		-0.49	-0.62			
	(DPV)	(+0.45)	(+0.82)	(-0.47)	(-0.60)			(0.92)
<b>16</b>	CV			-0.42	-0.57			
	(DPV)	(+0.69)		(-0.40)	(-0.55)	(-1.92)		(1.09)
<b>17</b>	CV			-0.26	-0.37	-0.52 (2e)		
	(DPV)	(+0.82)		(-0.24)	(-0.35)	(-0.50)	(-1.77)	(1.06)
<b>18</b>	CV			-0.50 (4e)				
	(DPV)	(+0.78)		(-0.36)	(-0.48)			(1.14)

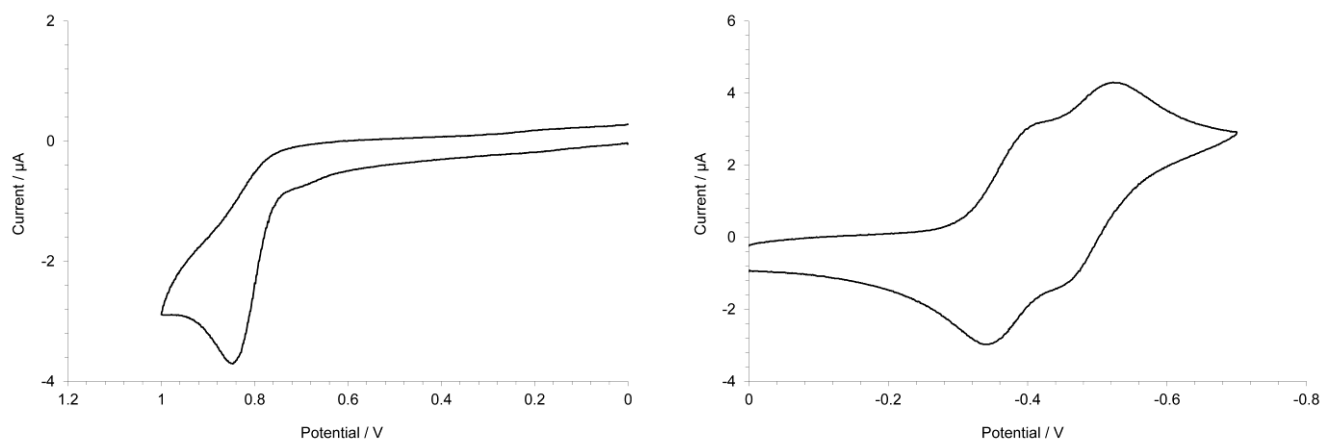
Redox potentials were measured by CV and DPV [V vs Ag/AgNO<sub>3</sub>, 1 mM in benzonitrile containing Et<sub>4</sub>NClO<sub>4</sub> (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs<sup>-1</sup>, and Fc/Fc<sup>+</sup> = +0.15 V]. In the case of reversible waves, redox potentials measured by CV are presented. The peak potentials measured by DPV are shown in parentheses.



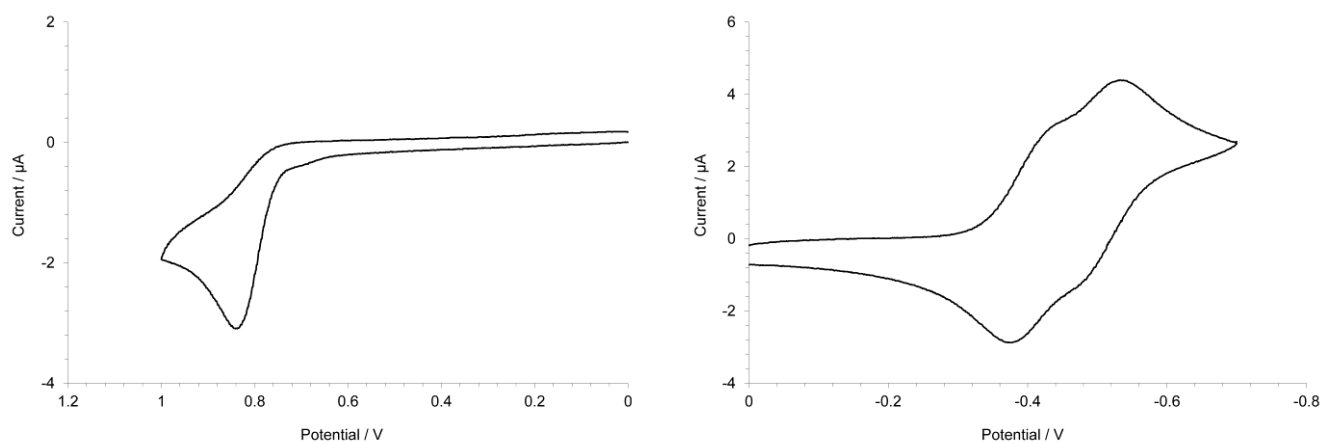
**Figure S-27.** Cyclic voltammograms of oxidation (left) and reduction (right) of **10** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate 100  $\text{mV s}^{-1}$ .



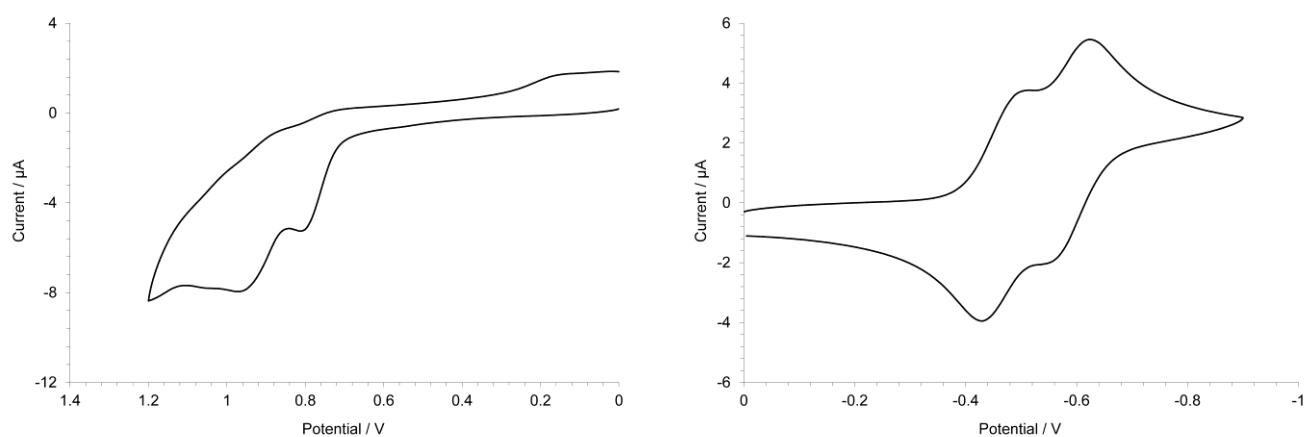
**Figure S-28.** Cyclic voltammograms of oxidation (left) and reduction (right) of **11** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate 100  $\text{mV s}^{-1}$ .



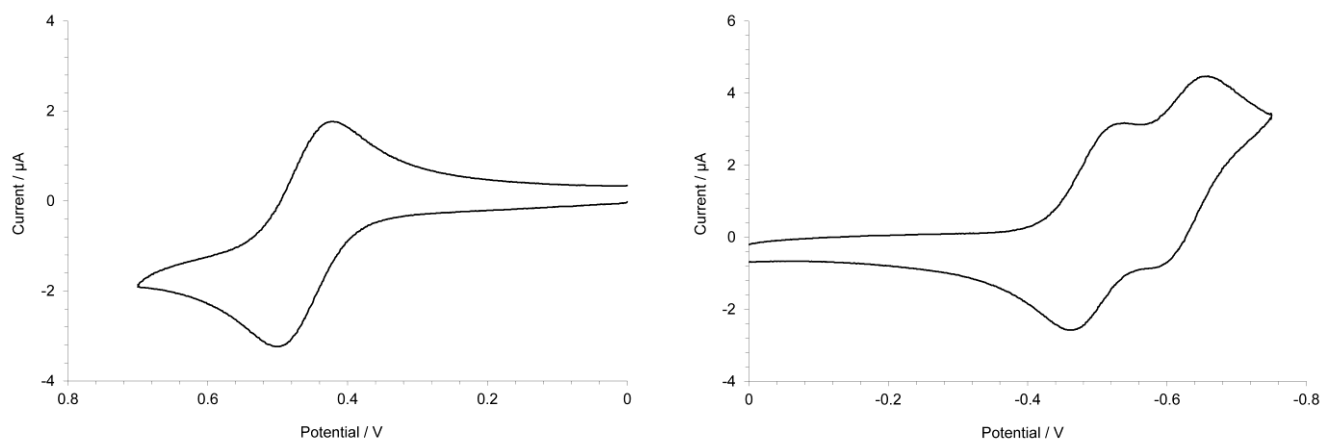
**Figure S-29.** Cyclic voltammograms of oxidation (left) and reduction (right) of **12** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate 100  $\text{mV s}^{-1}$ .



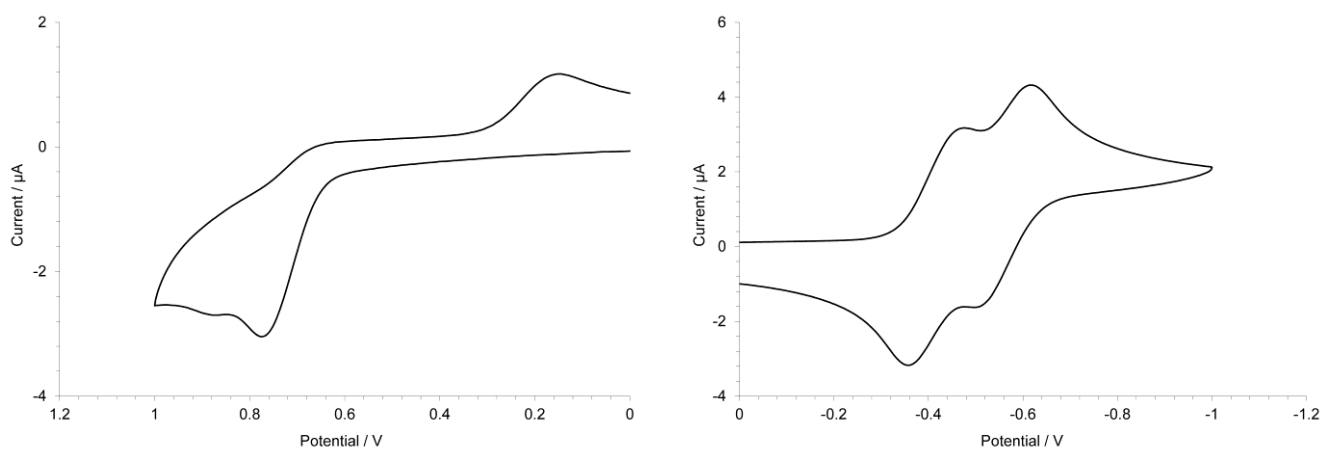
**Figure S-30.** Cyclic voltammograms of oxidation (left) and reduction (right) of **13** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate  $100 \text{ mV s}^{-1}$ .



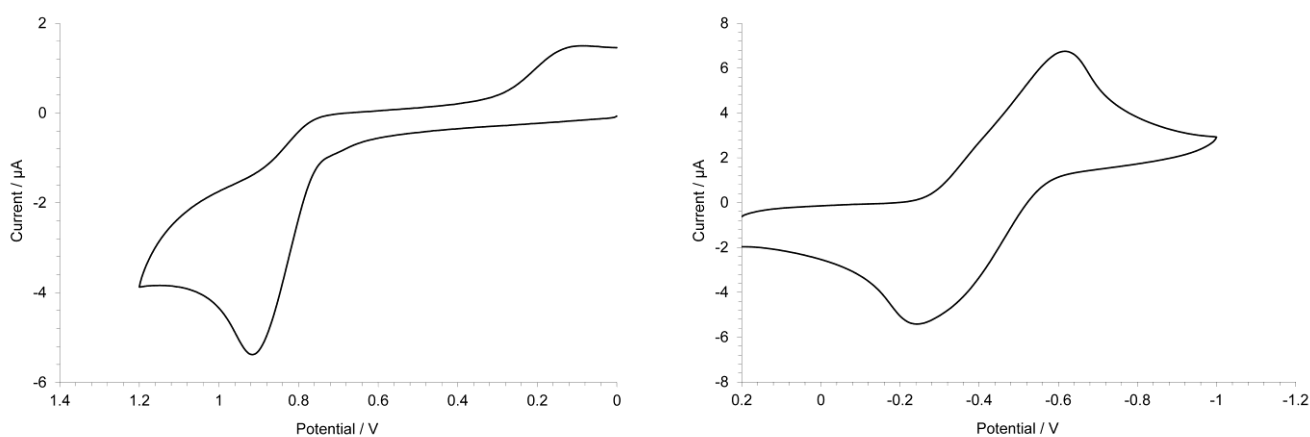
**Figure S-31.** Cyclic voltammograms of oxidation (left) and reduction (right) of **14** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate  $100 \text{ mV s}^{-1}$ .



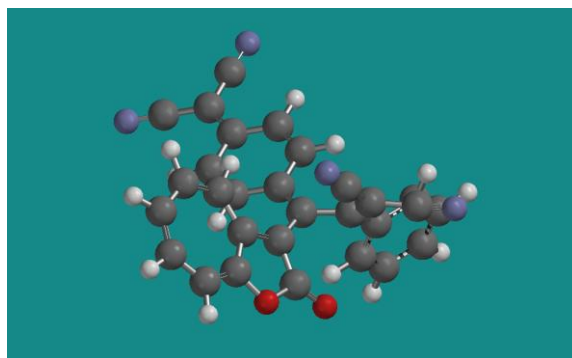
**Figure S-32.** Cyclic voltammograms of oxidation (left) and reduction (right) of **15** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate  $100 \text{ mV s}^{-1}$ .



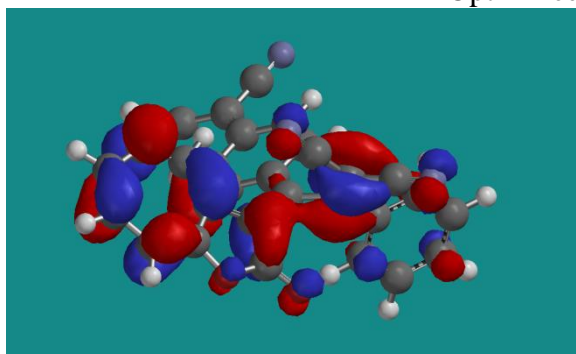
**Figure S-33.** Cyclic voltammograms of oxidation (left) and reduction (right) of **16** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate  $100 \text{ mV s}^{-1}$ .



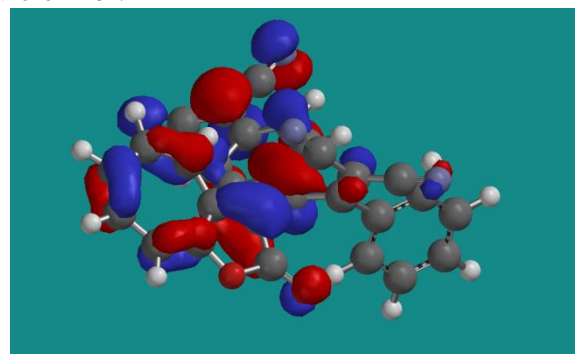
**Figure S-34.** Cyclic voltammograms of oxidation (left) and reduction (right) of **18** (1 mM) in benzonitrile containing  $\text{Et}_4\text{NClO}_4$  (0.1 M) as a supporting electrolyte; scan rate  $100 \text{ mV s}^{-1}$ .



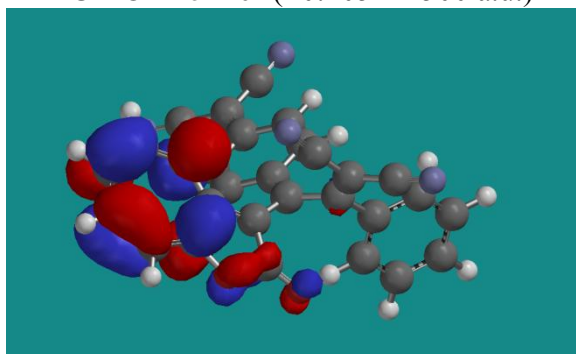
Optimized structure of **10'**.



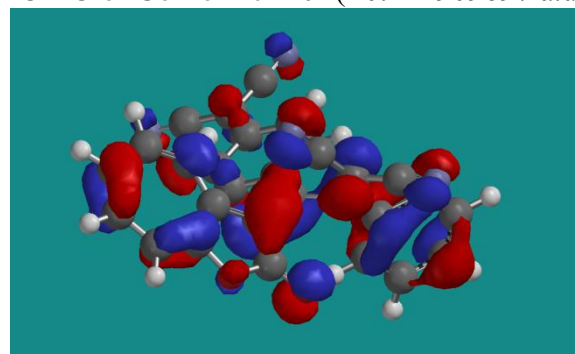
LUMO+2 of **10'** (-0.105244500 a.u.)



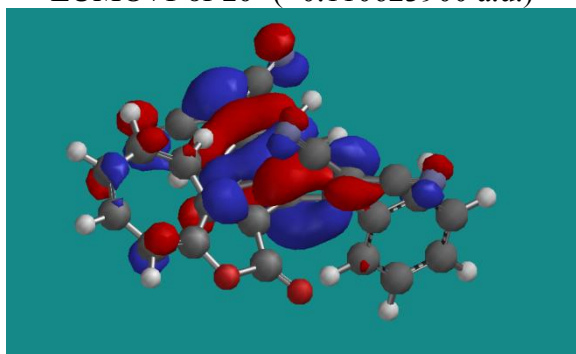
HOMO of Conformer **10'** (-0.222909697 a.u.)



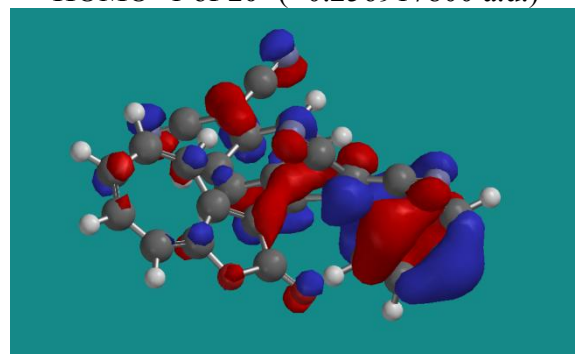
LUMO+1 of **10'** (-0.110623900 a.u.)



HOMO-1 of **10'** (-0.256917800 a.u.)



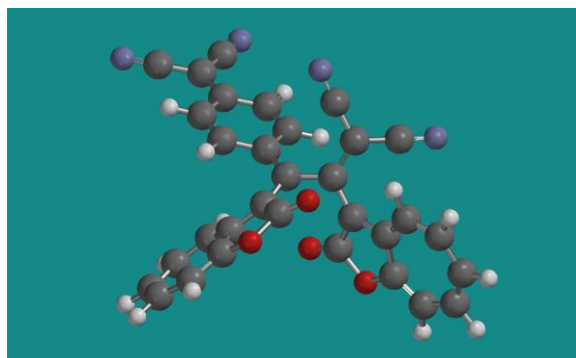
LUMO of **10'** (-0.146491641 a.u.)



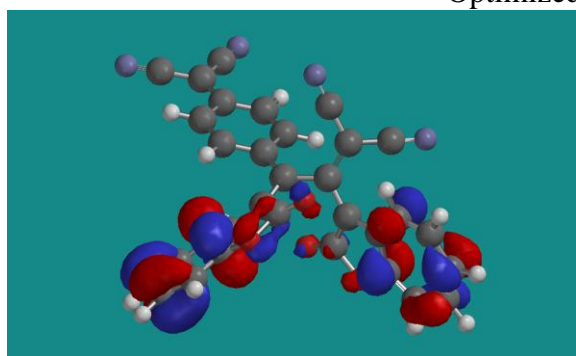
HOMO-2 of **10'** (-0.265238900 a.u.)

**Figure S-35.** Frontier Kohn-Sham orbitals and their energy levels of **10'** at the B3LYP/6-31G<sup>\*\*</sup> level.

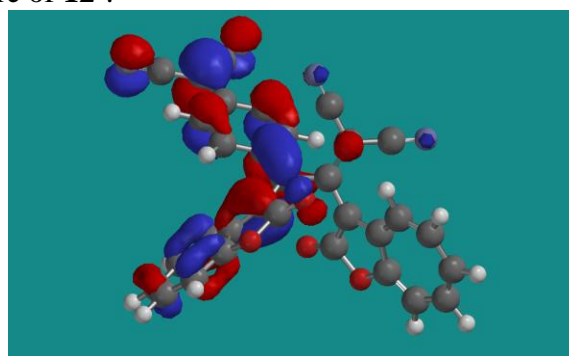




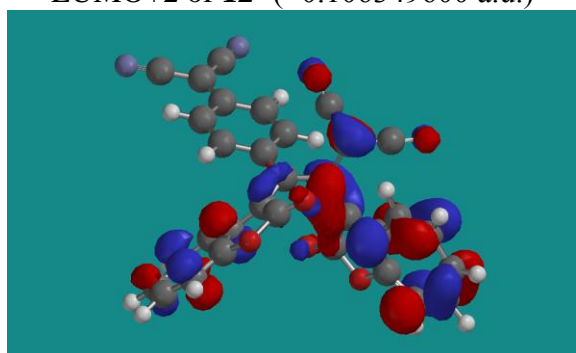
Optimized structure of **12'**.



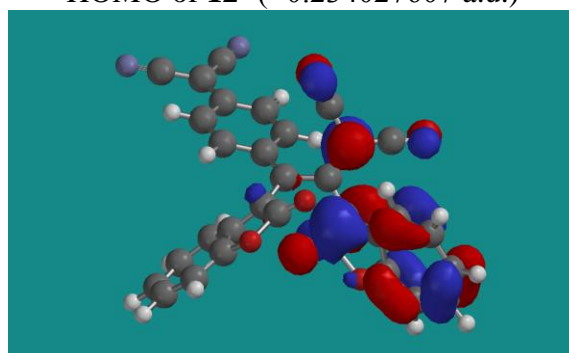
LUMO+2 of **12'** (-0.106349600 a.u.)



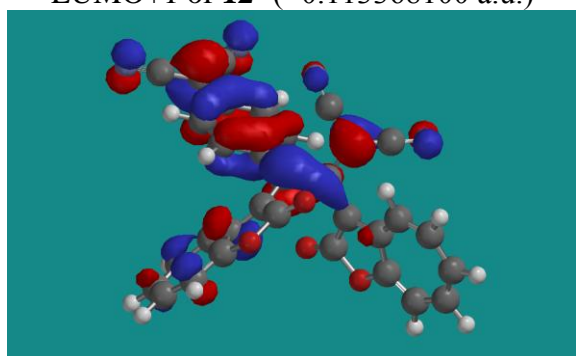
HOMO of **12'** (-0.234027607 a.u.)



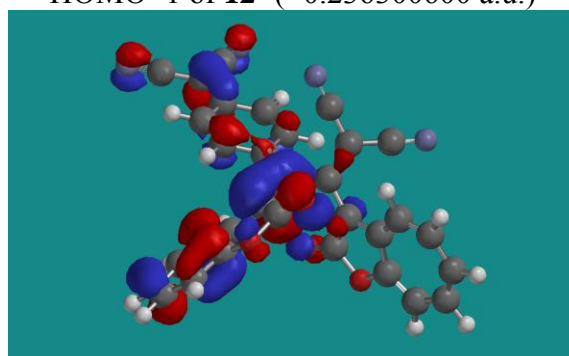
LUMO+1 of **12'** (-0.113368100 a.u.)



HOMO-1 of **12'** (-0.236300600 a.u.)



LUMO of **12'** (-0.124329969 a.u.)



HOMO-2 of **12'** (-0.276038100 a.u.)

**Figure S-36.** Frontier Kohn-Sham orbitals and their energy levels of **12'** at the B3LYP/6-31G\*\* level.