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. ¹H and ¹³C 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 G2000H₆ with CHCl₃ 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 Ag/AgNO₃ (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.
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® with CH$_2$Cl$_2$ to give 10 (119 mg, 91%) as dark blue crystals. m.p. 151.0–154.0 °C; IR (KBr disk): $\nu_{\text{max}}$ = 3058 (w), 2963 (w), 2926 (w), 2869 (w), 2211 (s, C≡N), 1748 (s, C=O), 1713 (w), 1653 (w), 1586 (m), 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), 419 cm$^{-1}$ (w); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 271 (4.44), 306 (4.19), 374 (4.27), 430 sh (4.20), 615 nm (4.33); UV/Vis (hexane): $\lambda_{\text{max}}$ (log $\varepsilon$) = 268 (4.47), 301 (4.23), 362 (4.30), 430 sh (4.22), 588 nm (4.35); $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H$ = 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, iPr), 1.25 ppm (d, 6H, J = 6.8 Hz, iPr); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C$ = 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)$_2$), 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)$_2$), 78.48 (C(CN)$_2$), 39.48 ppm (iPr); HRMS (ESI): Calcd for [C$_{32}$H$_{20}$N$_4$O$_2$ + Na]$^+$ 515.1478. Found: 515.1477; elemental analysis calcd (%) for C$_{32}$H$_{20}$N$_4$O$_2$·1/4H$_2$O: C, 77.33; H, 4.16; N, 11.27. Found: C, 77.38; H, 4.17; N, 11.37.
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): ν_{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 cm^{-1} (m); UV/Vis (CH_{2}Cl_{2}): λ_{max} (log ε) = 272 (4.53), 312 (4.31), 381 (4.37), 457 sh (4.15), 626 nm (4.33); UV/Vis (hexane): λ_{max} (log ε) = 270 (4.52), 312 (4.28), 378 (4.38), 457 sh (4.11), 597 nm (4.32); ^{1}H NMR (500 MHz, CDCl_{3}): δ_{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, iPr), 1.25 ppm (d, 6H, J = 7.0 Hz, iPr); ^{13}C NMR (125 MHz, CDCl_{3}): δ_{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 (C=C(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 (C=C(CN)_{2}), 79.60 (C=C(CN)_{2}), 39.59 (iPr), 23.67 ppm (iPr); HRMS (FAB): Calcd for [C_{32}H_{19}N_{5}O_{4} + H]^+ 538.1515. Found: 538.1520; elemental analysis calcd (%) for C_{32}H_{19}N_{5}O_{4}: C, 71.50; H, 3.56; N, 13.03. Found: C, 71.38; H, 3.72; N, 12.96.
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): ν_{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 cm^{-1} (w); UV/Vis (CH_{2}Cl_2): \lambda_{max} (\log \varepsilon) = 267 (4.69), 304 sh (4.29), 372 sh (4.37), 449 (4.68), 624 nm (4.49); UV/Vis (hexane): \lambda_{max} (\log \varepsilon) = 259 (4.73), 302 sh (4.33), 363 (4.40), 446 (4.73), 590 nm (4.49); \textsuperscript{1}H NMR (500 MHz, CDCl_3): \delta_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, iPr), 2.89 (sept, 1H, J = 6.8 Hz, iPr), 1.44 (br s, 6H, iPr), 1.22 ppm (d, 6H, J = 6.8 Hz, iPr); Low solubility hampered the measurement of \textsuperscript{13}C NMR. HRMS (ESI): Calcd for [C_{38}H_{25}N_4O_4 + Na]^+ 625.1846. Found: 625.1842; elemental analysis calcd (%) for C_{38}H_{25}N_4O_4 \cdot 1/2H_2O: C, 74.62; H, 4.45; N, 9.16. Found: C, 74.46; H, 4.59; N, 9.16.
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): $\nu_{\text{max}} = 3154$ (w), 3102 (w), 2963 (w), 2872 (w), 2211 (s, $\text{C} \equiv \text{N}$), 1750 (s, $\text{C} = \text{O}$), 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 cm$^{-1}$ (w); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}} \ (\log \varepsilon) =$ 236 (4.41), 270 (4.46), 344 sh (4.48), 368 (4.53), 440 sh (4.19), 607 nm (4.48); UV/Vis (hexane): $\lambda_{\text{max}} \ (\log \varepsilon) =$ 267 (4.43), 362 (4.48), 437 sh (4.08), 585 nm (4.39); $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 8.04$ (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, iPr), 1.23 ppm (d, 6H, $J = 6.8$ Hz, iPr); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C =$165.15 (C-2), 162.65 (C-5), 161.53 (C=CCN$_2$), 158.97 (C-3a or 8a), 153.79 (C of DCNQ), 149.88 (C-3a or 8a), 140.63 (C of DCNQ), 138.11 (C-2’ of Th), 137.23 (C-5’ of Th), 136.31 (C-4’ of Th), 136.22 (C-7), 135.82 (C-3’ of Th), 133.90 (C of DCNQ), 133.81 (C of DCNQ), 133.36 (C of DCNQ), 129.84 (C-6), 125.78 (C-4), 125.72 (C of DCNQ), 125.57 (C of DCNQ), 118.38 (C-8), 113.48 (CN), 113.39 (CN), 112.91 (CN), 104.86 (C-3), 80.70 (CCN$_2$), 77.96 (CCN$_2$), 39.46 (iPr), 23.56 ppm (iPr); HRMS (ESI): Calcd for [C$_{30}$H$_{18}$N$_4$O$_2$S + Na$^+$] 521.1043. Found: 521.1042; elemental analysis calcd (%): for C$_{30}$H$_{18}$N$_4$O$_2$S·1/3H$_2$O: C, 71.41; H, 3.73; N, 11.10. Found: C, 71.45; H, 3.86; N, 11.18.
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): ν_max = 2966 (w), 2193 (m, C≡N), 1760 (m, C=O), 1612 (w), 1578 (s), 1519 (w), 1578 (s), 1519 (w), 1477 (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 cm⁻¹ (w); UV/Vis (CH₂Cl₂): λ_max (log ε) = 254 (4.38), 267 (4.37), 344 (4.16), 429 (4.34), 496 (4.43), 718 nm (4.46); UV/Vis (hexane): λ_max (log ε) = 254 (4.40), 265 sh (4.39), 343 (4.13), 424 (4.34), 480 (4.41), 657 nm (4.46); ¹H NMR (500 MHz, CDCl₃): δ_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, NMe₂), 2.98 (sept, 1H, J = 6.8 Hz, iPr), 1.25 ppm (d, 6H, J = 6.8 Hz, iPr); ¹³C NMR (125 MHz, CDCl₃): δ_C = 163.64 (C-2), 163.46 (C-5), 163.23 (C-3a or 8a), 159.04 (C-3a or 8a), 153.98 (C=CN₂), 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 (C(CN)₂), 71.30 (C(CN)₂), 40.18 (NMe₂), 39.83 (iPr), 23.61 ppm (iPr); HRMS (FAB): Calcd for [C₃₄H₂₅N₅O₂ + H]⁺ 536.2087. Found: 536.2086; elemental analysis calcd (%) for C₃₄H₂₅N₅O₂: C, 76.24; H, 4.70; N, 13.08. Found: C, 76.12; H, 4.74; N, 13.01.
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): ν\text{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 cm\(^{-1}\) (w); UV/Vis (CH\(_2\)Cl\(_2\)): λ\text{max} (log ε) = 267 (4.46), 332 sh (4.35), 361 (4.37), 406 sh (4.31), 590 nm (4.40); UV/Vis (hexane): λ\text{max} (log ε) = 265 (4.47), 324 sh (4.29), 358 (4.42), 394 sh (4.32), 573 nm (4.36); \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ\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, \(\text{iPr}\)), 1.24 ppm (d, 6H, J = 6.8 Hz, \(\text{iPr}\)); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ\text{C} = 165.42 (C-2), 162.11 (C-4), 158.68 (C-8a), 154.07 (C-3a), 149.99 (C-6), 140.91 (C=C(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 (C(CN)\(_2\)), 77.64 (C(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 (\(\text{iPr}\)), 23.64 (\(\text{iPr}\)), 23.39 ppm (\(\text{iPr}\)); HRMS (ESI): Calcd for [C\(_{36}\)H\(_{24}\)FeN\(_4\)O\(_2\) + Na\(^+\)] 623.1141. Found: 623.1144; elemental analysis calcd (%) for C\(_{36}\)H\(_{24}\)FeN\(_4\)O\(_2\)·\(\frac{1}{2}\)H\(_2\)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$_2$Cl$_2$/hexane); IR (KBr disk): $v_{\text{max}} = 2964$ (w), 2207 (m, C=O), 1756 (m, C=O), 1698 (m, C=O), 1588 (m), 1506 (s), 1473 (s), 1441 (s), 1420 (s), 1339 (s), 1315 (m), 1275 (m), 1233 (m), 1213 (s), 1190 (s), 1130 (w), 1057 (w), 932 (w), 897 (w), 842 (w), 806 (w), 778 (w), 718 cm$^{-1}$ (m); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 241 (4.62), 273 sh (4.52), 294 sh (4.48), 431 (4.46), 653 nm (4.35); UV/Vis (hexane): $\lambda_{\text{max}}$ (log $\varepsilon$) = 234 (4.14), 294 (4.49), 426 (4.47), 604 nm (4.31); $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H = 9.84$ (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$_2$Me), 3.28 (sept, 1H, $J = 6.8$ Hz, iPr), 3.07 (sept, 1H, $J = 6.8$ Hz, iPr of Az), 1.43 (d, 6H, $J = 6.8$ Hz, iPr of Az), 1.35 (d, 6H, $J = 6.8$ Hz, iPr of Az); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C = 164.71$ (C-3a), 164.12 (C-5), 163.71 (C-2), 163.47 (CO$_2$Me), 159.03 (C-8a), 154.79 (C-5’ of Az), 153.84 ($\text{C=CCN}_2$), 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 ($\text{C(CN)}_2$), 74.55 ($\text{C(CN)}_2$), 51.44 (CO$_2$Me), 40.02 (iPr), 39.34 (iPr of Az), 24.45 (iPr of Az), 23.64 ppm (iPr); HRMS (FAB): Calcd for [C$_4$H$_3$O$_4$]$: 642.2267$. Found: 642.2266; elemental analysis calcd (%): C$_{41}$H$_{30}$N$_4$O$_4$: C, 76.62; H, 4.70; N, 8.72. Found: C, 76.45; H, 4.86; N, 8.49.
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): ν\text{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 cm\(^{-1}\) (m); UV/Vis (CH\(_2\)Cl\(_2\)): λ\text{max} (log ε) = 269 (4.83), 350 sh (4.74), 407 (4.87), 597 nm (4.77); UV/Vis (hexane): λ\text{max} (log ε) = 272 (4.58), 353 sh (4.50), 411 (4.60), 635 nm (4.53); \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ\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, iPr), 1.24 ppm (d, 12H, J = 6.8 Hz, iPr); Low solubility hampered the measurement of \(^{13}\)C NMR. HRMS (FAB): Calcd for [C\(_{56}\)H\(_{32}\)N\(_8\)O\(_4\)S + H]\(^+\) 913.2345. Found: 913.2347; elemental analysis calcd (%) for C\(_{56}\)H\(_{32}\)N\(_8\)O\(_4\)S: C, 73.67; H, 3.53; N, 12.27. Found: C, 73.48; H, 3.68; N, 12.20.
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$_2$Cl$_2$/hexane); IR (KBr disk): $\nu_{\text{max}}$ = 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), 764 (w), 742 (w), 713 (w), 661 cm$^{-1}$ (w); UV/Vis (CH$_2$Cl$_2$): $\lambda_{\text{max}}$ (log $\varepsilon$) = 269 (4.72), 382 (4.64), 407 sh (4.66), 450 (4.71), 541 (4.72), 601 nm (4.70); UV/Vis (hexane): $\lambda_{\text{max}}$ (log $\varepsilon$) = 270 (4.60), 384 sh (4.51), 410 sh (4.54), 459 (4.58), 600 nm (4.59); $^1$H NMR (500 MHz, CDCl$_3$): $\delta_H$ = 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, iPr), 1.23 ppm (d, 12H, $J = 6.8$ Hz, iPr); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta_C$ = 165.31 (C-5), 162.94 (C-2), 160.55 (C-8a), 159.01 (C of Th), 153.62 (C=C(CN)$_2$), 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)$_2$), 78.52 (C(CN)$_2$), 39.50 (iPr), 23.60 ppm (iPr); HRMS (FAB): Calcd for [C$_{60}$H$_{34}$N$_8$O$_4$S$_2$ + H]$^+$ 995.2223. Found: 995.2203; elemental analysis calcd (%) for C$_{60}$H$_{34}$N$_8$O$_4$S$_2$·H$_2$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 Et$_4$NClO$_4$ (0.1 M) at 30 sec intervals.

**Figure S-3.** Color changes of 10 upon the electrochromic analysis in benzonitrile containing Et$_4$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 CH₂Cl₂ (blue line) and 10% CH₂Cl₂/hexane (red line).

Figure S-5. Continuous change in the visible spectrum of 11: (a) constant-current electrochemical reduction (50 uA) and (b) reverse oxidation of the reduced species (50 uA) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.

Figure S-6. Color changes of 11 upon the electrochromic analysis in benzonitrile containing Et₄NClO₄ (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-7.** UV/Vis spectrum of 12 in CH$_2$Cl$_2$ (blue line) and 10% CH$_2$Cl$_2$/hexane (red line).

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

**Figure S-9.** Color changes of 12 upon the electrochromic analysis in benzonitrile containing Et$_4$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-10.** UV/Vis spectrum of 13 in CH$_2$Cl$_2$ (blue line) and 10% CH$_2$Cl$_2$/hexane (red line).

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

**Figure S-12.** Color changes of 13 upon the electrochromic analysis in benzonitrile containing Et$_4$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-13. UV/Vis spectrum of 14 in CH₂Cl₂ (blue line) and 10% CH₂Cl₂/hexane (red line).

Figure S-14. Continuous change in the visible spectrum of 14: (a) constant-current electrochemical reduction (50 uA) and (b) reverse oxidation of the reduced species (50 uA) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.

Figure S-15. Color changes of 14 upon the electrochromic analysis in benzonitrile containing Et₄NClO₄ (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-16.** UV/Vis spectrum of 15 in CH$_2$Cl$_2$ (blue line) and 10% CH$_2$Cl$_2$/hexane (red line).

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

**Figure S-18.** Color changes of 15 upon the electrochromic analysis in benzonitrile containing Et$_4$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-19.** UV/Vis spectrum of 16 in CH$_2$Cl$_2$ (blue line) and 10% CH$_2$Cl$_2$/hexane (red line).

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

**Figure S-21.** Color changes of 16 upon the electrochromic analysis in benzonitrile containing Et$_4$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-22. UV/Vis spectrum of 17 in CH$_2$Cl$_2$ (blue line) and 10% CH$_2$Cl$_2$/hexane (red line).

Figure S-23. Color changes of 17 upon the electrochromic analysis in benzonitrile containing Et$_4$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-24.** UV/Vis spectrum of 18 in CH₂Cl₂ (blue line) and 10% CH₂Cl₂/hexane (red line).

**Figure S-25.** Continuous change in the visible spectrum of 18: (a) constant-current electrochemical reduction (50 uA) and (b) reverse oxidation of the reduced species (50 uA) in benzonitrile containing Et₄NClO₄ (0.1 M) at 30 sec intervals.

**Figure S-26.** Color changes of 18 upon the electrochromic analysis in benzonitrile containing Et₄NClO₄ (0.1 M) upon (50 uA): (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.

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<th>Sample</th>
<th>Method</th>
<th>$E_{1}^{\text{ox}}$ [V]</th>
<th>$E_{2}^{\text{ox}}$ [V]</th>
<th>$E_{1}^{\text{red}}$ [V]</th>
<th>$E_{2}^{\text{red}}$ [V]</th>
<th>$E_{3}^{\text{red}}$ [V]</th>
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<td>(DPV)</td>
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<td>11</td>
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Redox potentials were measured by CV and DPV [V vs Ag/AgNO$_3$, 1 mM in benzonitrile containing Et$_4$NClO$_4$ (0.1 M), Pt electrode (internal diameter: 1.6 mm), scan rate = 100 mVs$^{-1}$, and Fc/Fc+ = +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 Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate 100 mV s⁻¹.

Figure S-28. Cyclic voltammograms of oxidation (left) and reduction (right) of 11 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate 100 mV s⁻¹.

Figure S-29. Cyclic voltammograms of oxidation (left) and reduction (right) of 12 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate 100 mV s⁻¹.
Figure S-30. Cyclic voltammograms of oxidation (left) and reduction (right) of 13 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate 100 mV s⁻¹.

Figure S-31. Cyclic voltammograms of oxidation (left) and reduction (right) of 14 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate 100 mV s⁻¹.

Figure S-32. Cyclic voltammograms of oxidation (left) and reduction (right) of 15 (1 mM) in benzonitrile containing Et₄NClO₄ (0.1 M) as a supporting electrolyte; scan rate 100 mV s⁻¹.
Figure S-33. Cyclic voltammograms of oxidation (left) and reduction (right) of 16 (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate 100 mV s$^{-1}$.

Figure S-34. Cyclic voltammograms of oxidation (left) and reduction (right) of 18 (1 mM) in benzonitrile containing Et$_4$NClO$_4$ (0.1 M) as a supporting electrolyte; scan rate 100 mV s$^{-1}$. 
Optimized structure of $10'$.

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

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