Electronic supplementary information (ESI)

Synthesis of push–pull chromophores by the sequential [2 + 2] cycloaddition of 1-azulenylbutadiynes with tetracyanoethylene and tetrathiafulvalene

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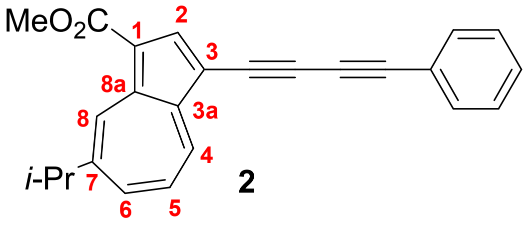
✧ Contents

✧ General

Melting points were determined with a Yanagimoto MPS3 micro melting apparatus and are uncorrected. High resolution mass spectra were obtained with a Bruker Daltonics APEX III instrument. IR and UV/Vis spectra were measured with JASCO FT/IR-4100 and Shimadzu UV-2550 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AVANCE 400 at 400 MHz and 100 MHz, or a JEOL ECA 500 at 500 MHz and 125 MHz, respectively. 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/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.

Methyl-7-isopropyl-3-(4-phenyl-buta-1,3-diynyl)-azulene-1-carboxylate (2)

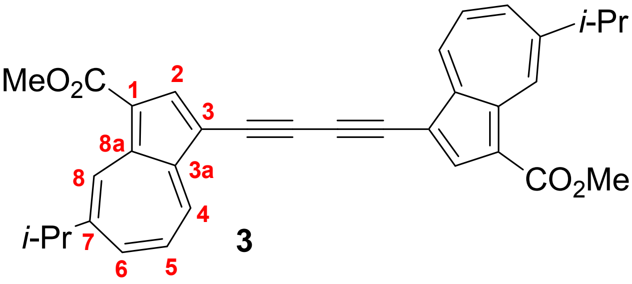


2

CuI (190 mg, 1.00 mmol) and tetramethylethylenediamine (116 mg, 1.00 mmol) in dichloromethane (3 mL) were added to a solution of **1** (252 mg, 1.00 mmol) and ethynylbenzene (510 mg, 5.00 mmol) in dichloromethane (20 mL). The resulting mixture was stirred at room temperature for 6 h under an air. The reaction mixture was poured into a 10% aqueous solution of NH_4Cl and was extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane as an eluent to give **2** (261 mg, 74%) as purple crystals and **3** (51 mg, 20%) as green needless.

M.p. 110.0−114.0 °C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.73 (s, 1H, 8-H), 8.64 (d, 1H, *J* = 10.0 Hz, 4-H), 8.44 (s, 1H, 2-H), 7.84 (d, 1H, *J* = 10.0 Hz, 6-H), 7.55 (d, 2H, *J* = 7.0 Hz, *o*-Ph), 7.54 (dd, 1H, *J* = 10.0, 10.0 Hz, 5-H), 7.58 (m, 3H, *m, p*-Ph), 3.95 (s, 3H, CO_2Me), 3.24 (sept, 1H, *J* = 6.5 Hz, *i*Pr), 1.43 (d, 6H, *J* = 6.5 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.18 (CO_2Me), 151.42 (C-7), 146.49 (C-3a or 8a), 143.76 (C-2), 141.48 (C-3a or 8a), 139.74 (C-6), 138.61 (C-8), 136.49 (C-4), 132.33 (*o*-Ph), 128.92 (*p*-Ph), 128.40 (*m*-Ph), 128.10 (C-5), 122.13 (*ipso*-Ph), 115.22 (C-1), 107.20 (C-3), 82.36 (C≡C), 78.00 (C≡C), 77.54 (C≡C), 74.61 (C≡C), 51.24 (CO_2Me), 39.28 (*i*Pr), 24.59 (*i*Pr) ppm; IR (KBr disk): ν_{max} = 2960 (w), 2205 (w), 2131 (w), 1693 (s), 1509 (m), 1489 (w), 1449 (s), 1415 (m), 1395 (w), 1373 (w), 1362 (w), 1334 (w), 1279 (w), 1211 (s), 1172 (m), 1117 (m), 1079 (m), 1065 (w), 1019 (w), 959 (w), 909 (w), 886 (w), 860 (w), 801 (w), 773 (m), 761 (m), 689 (m), 673 (m), 664 (m), 643 (m) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 244 (4.62), 278 (4.58), 286 sh (4.55), 314 (4.60), 324 sh (4.55), 356 (4.36), 398 (4.26), 414 sh (4.22), 562 (2.91), 610 sh (2.80) nm; HRMS (ESI): calcd for $C_{25}H_{20}O_2 + Na^+$ $[M + Na]^+$ 375.1361; found: 375.1356; Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 85.14; H, 5.79.

1,4-Di(7-isopropyl-1-methoxycarbonylazulen-3-yl)butadiyne (3)

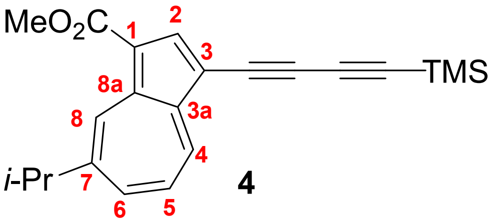


3

CuI (190 mg, 1.00 mmol) and tetramethylethylenediamine (116 mg, 1.00 mmol) in dichloromethane (3 mL) were added to a solution of **1** (252 mg, 1.00 mmol) in dichloromethane (10 mL). The resulting mixture was stirred at room temperature for 3 h under an air. The reaction mixture was poured into a 10% aqueous solution of NH_4Cl and was extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane as an eluent to give **3** (229 mg, 91%) as green needless.

M.p. 165.0−167.0 °C (AcOEt); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.73 (s, 2H, 8-H), 8.68 (d, 2H, *J* = 10.0 Hz, 4-H), 8.46 (s, 2H, 2-H), 7.83 (d, 2H, *J* = 10.0 Hz, 6-H), 7.54 (dd, 2H, *J* = 10.0, 10.0 Hz, 5-H), 3.96 (s, 6H, CO_2Me), 3.24 (sept, 2H, *J* = 6.5 Hz, *i*Pr), 1.43 (d, 12H, *J* = 6.5 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.23 (CO_2Me), 151.28 (C-7), 146.37 (C-3a or 8a), 143.68 (C-2), 141.47 (C-3a or 8a), 139.70 (C-6), 138.57 (C-8), 136.56 (C-4), 127.98 (C-5), 115.25 (C-1), 107.68 (C-3), 78.65 (C≡C), 78.25 (C≡C), 51.25 (CO_2Me), 39.28 (*i*Pr), 24.61 (*i*Pr) ppm; IR (KBr disk): ν_{max} = 2964 (w), 2126 (w), 1685 (s), 1524 (w), 1498 (w), 1437 (m), 1420 (m), 1397 (w), 1365 (w), 1310 (w), 1205 (s), 1194 (m), 1175 (s), 1137 (w), 1119 (m), 1072 (w), 1057 (w), 1037 (w), 959 (w), 916 (w), 879 (w), 869 (w), 806 (m), 777 (m), 757 (w), 677 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 246 (4.71), 296 (4.86), 328 (4.71), 344 (4.49), 396 sh (4.40), 420 (4.47), 450 sh (4.32), 570 (3.27) nm; HRMS (ESI): calcd for $C_{34}H_{30}O_4 + Na^+$ $[M + Na]^+$ 525.2042; found: 525.2036; Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.25; H, 6.02. Found: C, 81.11; H, 6.18.

Methyl 7-isopropyl-3-(4-trimethylsilanyl-buta-1,3-diynyl)-azulene-1-carboxylate (4)

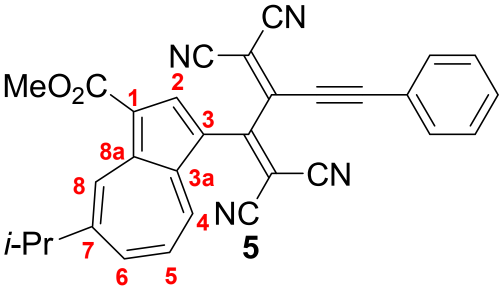


4

CuI (190 mg, 1.00 mmol) and tetramethylethylenediamine (116 mg, 1.00 mmol) in dichloromethane (3 mL) were added to a solution of **1** (252 mg, 1.00 mmol) and trimethylsilylacetylene (491 mg, 5.00 mmol) in dichloromethane (20 mL). The resulting mixture was stirred at room temperature for 12 h under an air. The reaction mixture was poured into a 10% aqueous solution of NH_4Cl and was extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane as an eluent to give **4** (262 mg, 76%) as purple oil and **3** (43 mg, 17%) as green needless.

^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 9.71 (s, 1H, 8-H), 8.57 (d, 1H, *J* = 10.0 Hz, 4-H), 8.38 (s, 1H, 2-H), 7.81 (d, 1H, *J* = 10.0 Hz, 6-H), 7.50 (dd, 1H, *J* = 10.0, 10.0 Hz, 5-H), 3.94 (s, 3H, CO_2Me), 3.21 (sept, 1H, *J* = 6.5 Hz, *i*Pr), 1.40 (d, 6H, *J* = 6.5 Hz, *i*Pr), 0.27 (s, 9H, TMS) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.06, 151.45, 146.73, 143.92, 141.42, 139.72, 138.58, 136.41, 128.09, 115.20, 106.69, 91.19, 88.58, 78.43, 72.78, 51.15, 39.21, 24.51, −0.29 ppm; IR (KBr disk): ν_{max} = 2961 (m), 2899 (w), 2870 (m), 2191 (m), 1679 (s), 1523 (w), 1508 (w), 1446 (s), 1425 (m), 1410 (m), 1371 (m), 1250 (m), 1217 (s), 1176 (w), 1163 (w), 1130 (m), 1091 (m), 1074 (m), 1020 (w), 951 (w), 910 (m), 860 (m), 843 (s), 802 (w), 775 (w), 760 (w), 669 (w), 638 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 (4.61), 266 (4.42), 300 (4.67), 330 (4.58), 392 (4.16), 410 (4.13), 560 (2.88), 604 sh (2.79), 674 sh (2.22) nm; HRMS (ESI): calcd for $C_{22}H_{24}O_2Si + Na^+$ $[M + Na]^+$ 371.1443; found: 371.1438; Anal. Calcd for $C_{22}H_{24}O_2Si$: C, 75.82; H, 6.94. Found: C, 75.72; H, 6.86.

Compound 5

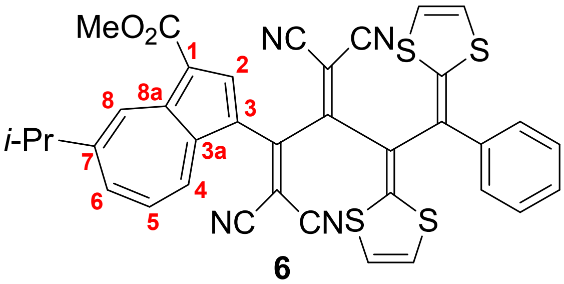


5

TCNE (96 mg, 0.75 mmol) was added to a solution of **2** (176 mg, 0.50 mmol) in ethyl acetate (5 mL). The resulting mixture was stirred at room temperature for 3 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (20 : 1) as an eluent and on Bio-Beads with CH_2Cl_2 as an eluent to give **5** (228 mg, 95%) as purple crystals.

M.p. 208.0–211.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 10.02 (s, 1H, 8-H), 8.52 (s, 1H, 2-H), 8.41 (d, 1H, J = 10.0 Hz, 4-H), 8.14 (d, 1H, J = 10.0 Hz, 6-H), 7.95 (dd, 1H, J = 10.0, 10.0 Hz, 5-H), 7.72 (d, 2H, J = 7.0 Hz, *o*-Ph), 7.58 (t, 1H, J = 7.0 Hz, *p*-Ph), 7.48 (t, 2H, J = 7.0 Hz, *m*-Ph), 3.98 (s, 3H, CO_2Me), 3.36 (sept, 1H, J = 6.5 Hz, *i*Pr), 1.48 (d, 6H, J = 6.5 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C =164.44 (CO_2Me), 156.86 (C-7), 156.78 ($\underline{C}$=C(CN)$_2$), 150.60 ($\underline{C}$=C(CN)$_2$), 145.99 (C-3a), 142.72 (C-2), 142.32 (C-6), 140.83 (C-8), 137.03 (C-4), 133.63 (*o*-Ph), 132.82 (*p*-Ph), 132.10 (C-5), 129.07 (*m*-Ph), 119.31 (*ipso*-Ph), 119.19 (C-1), 118.78 (C-3), 113.68 (CN), 112.27 (CN), 111.58 (CN), 109.95 (CN), 95.20 ($\underline{C}$(CN)$_2$), 85.87 ($\underline{C}$(CN)$_2$), 80.62 (C≡C), 51.73 (CO_2Me), 39.52 (*i*Pr), 24.50 (*i*Pr) ppm. The one signal of C≡C moiety was overlapped with signals of $CDCl_3$. IR (KBr disk): ν_{max} = 2962 (w), 2223 (w), 2190 (s), 1698 (s), 1541 (m), 1508 (s), 1445 (s), 1424 (s), 1375 (s), 1245 (w), 1217 (s), 1176 (m), 1159 (w), 1132 (w), 1109 (w), 1059 (m), 1016 (w), 997 (w), 932 (w), 895 (w), 877 (w), 848 (w), 810 (w), 776 (w), 760 (m), 726 (w), 713 (w), 688 (m), 652 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.53), 266 (4.47), 300 (4.58), 388 (4.47), 530 (3.93) nm; UV/Vis (10% CH_2Cl_2/hexane): λ_{max} (log ε) = 264 (4.47), 297 (4.58), 373 (4.43), 513 (3.87) nm; HRMS (ESI): calcd for $C_{31}H_{20}N_4O_2$ + Na$^+$ [M + Na]$^+$ 503.1484; found: 503.1478; Anal. Calcd for $C_{31}H_{20}N_4O_2$: C, 77.49; H, 4.20; N, 11.66. Found: C, 77.58; H, 4.37; N 11.70.

Compound 6

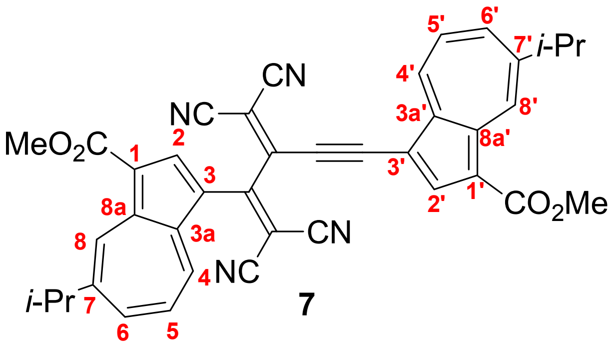


6

TTF (104 mg, 0.50 mmol) was added to a solution of **5** (120 mg, 0.25 mmol) in acetonotrile (10 mL). The resulting mixture was heated at reflux temperature for 24 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (20 : 1) as an eluent and on Bio-Beads with CH_2Cl_2 as an eluent to give **6** (158 mg, 92%) as red crystals.

M.p. 133.0−137.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (600 MHz, tetrachloroethane-*d*$_2$, 110 °C): δ_H = 9.96 (s, 1H, 8-H), 8.57 (br s, 2H, 2,4-H), 8.14 (d, 1H, *J* = 10.0 Hz, 6-H), 7.94 (br s, 1H, 5-H), 7.56 (br s, 2H, *o*-Ph), 7.41 (br s, 2H, *m*-Ph), 7.56 (br s, 1H, *p*-Ph), 7.01 (br s, 2H, dithiolylidene), 6.55−6.50 (m, 2H, dithiolylidene), 4.01 (s, 3H, CO_2Me), 3.36 (br s, 1H, *i*Pr), 1.54 (br s, 6H, *i*Pr) ppm; ^{13}C NMR (150 MHz, tetrachloroethane-*d*$_2$, 110 °C): δ_C = 171.31 (dithiolylidene), 164.41 (CO_2Me), 160.61 ($\underline{C}$=C(CN)$_2$), 157.27 ($\underline{C}$=C(CN)$_2$), 156.41 (C-7), 146.33 (dithiolylidene), 143.34 (C-2), 142.40 (C-3a), 141.67 (C-6), 139.97 (C-8), 138.34 (C-4), 136.22 (*ipso*-Ph), 131.74 (C-5), 128.77 (*m*-Ph), 127.24 (*o*-Ph), 126.45 (*o*-Ph), 125.45 (dithiolylidene), 119.73 (dithiolylidene), 119.58 (C-1), 118.53 (dithiolylidene), 117.84 (C-3), 115.56 (CN), 114.65 (CN), 114.27 (CN), 113.24 (CN), 81.41 ($\underline{C}$(CN)$_2$), 51.46 (CO_2Me), 39.31 (*i*Pr), 24.32 (*i*Pr) ppm. The one signal of C(CN)$_2$ moiety was overlapped with signals of $CDCl_3$.; IR (KBr disk): ν_{max} = 3084 (w), 2960 (w), 2203 (m), 1699 (m), 1497 (m), 1439 (m), 1417 (m), 1364 (s), 1213 (m), 1180 (m), 1135 (w), 1087 (w), 1051 (w), 1017 (w), 901 (w), 806 (w), 767 (w), 727 (m), 705 (w), 675 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 242 (4.52), 266 sh (4.46), 300 (4.35), 337 sh (4.31), 348 (4.32), 471 (4.52) nm; UV/Vis (10% CH_2Cl_2/hexane): λ_{max} (log ε) = 240 (4.52), 266 sh (4.43), 301 (4.34), 332 sh (4.30), 345 (4.31), 463 (4.48) nm; HRMS (ESI): calcd for $C_{37}H_{24}N_4O_2S_4$ + Na$^+$ [M + Na]$^+$ 707.0680; found: 707.0674; Anal. Calcd for $C_{37}H_{24}N_4O_2S_4$: C, 64.89; H, 3.53; N, 8.18. Found: C, 64.77; H, 3.67; N 8.11.

Compound 7



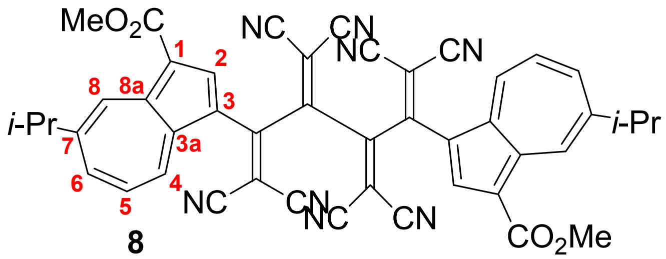
7

TCNE (96 mg, 0.75 mmol) was added to a solution of **3** (251 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was stirred at room temperature for 1 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (20 : 1) as an eluent and on Bio-Beads with CH_2Cl_2 as an eluent to give **7** (306 mg, 97%) as purple crystals.

M.p. 145.0−148.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 10.02 (s, 1H, 8-H), 9.88 (s, 1H, 8'-H), 8.85 (d, 1H, J = 10.0 Hz, 4-H), 8.60 (s, 2H, 2,2'-H), 8.48 (d, 1H, J = 10.0 Hz, 4'-H), 8.11 (d, 1H, J = 10.0 Hz, 6-H), 8.05 (d, 1H, J = 10.0 Hz, 6'-H), 7.93 (dd, 1H, J = 10.0, 10.0 Hz, 5-H), 7.83 (dd, 1H, J = 10.0, 10.0 Hz, 5'-H), 3.97 (s, 3H, CO_2Me), 3.96 (s, 3H, CO_2Me), 3.36−3.32 (m, 2H, *i*Pr), 1.48 (d, 6H, J = 6.5 Hz, *i*Pr), 1.47 (d, 6H, J = 6.5 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 164.61 (CO_2Me), 164.53 (CO_2Me), 157.91 ($\underline{C}$=C$(CN)_2$), 156.39 (C-7 or 7'), 155.78 (C-7 or 7'), 149.31 ($\underline{C}$=C$(CN)_2$), 148.18 (C-3a'), 145.94 (C-2 or 2'), 144.58 (C-8a), 143.00 (C-2 or 2'), 142.38 (C-3a), 142.08 (C-6), 141.57 (C-6'), 140.63 (C-8), 139.95 (C-8'), 137.71 (C-4), 137.05 (C-4'), 131.91 (C-5), 131.87 (C-5'), 119.75 (C-3 or 3'), 119.06 (C-1), 118.92 (C-1'), 118.80 (C-3 or 3'), 113.96 (CN), 113.59 (CN), 112.49 (CN), 111.10 (CN), 105.48 (C≡C), 96.08 ($\underline{C}(CN)_2$), 87.86 ($\underline{C}(CN)_2$), 80.51 (C≡C), 51.64 (CO_2Me), 51.56 (CO_2Me), 39.59 (*i*Pr), 39.47 (*i*Pr), 24.53 (*i*Pr), 24.49 (*i*Pr) ppm; IR (KBr disk): ν_{max} = 2961 (w), 2221 (w), 2131 (s), 1699 (m), 1489 (s), 1417 (s), 1364 (s), 1284 (w), 1212 (s), 1168 (m), 1134 (w), 1084 (w), 1058 (w), 895 (w), 808 (w), 777 (m), 729 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 (4.72), 272 sh (4.60), 300 (4.69), 347 sh (4.38), 394 (4.33), 545 (4.52) nm; UV/Vis (10% CH_2Cl_2/hexane): λ_{max} (log ε) = 264 sh (4.58), 299 (4.68), 339 sh (4.41), 392 (4.29), 515 (4.49) nm; HRMS (ESI): calcd for $C_{40}H_{30}N_4O_4$ + Na^+ $[M + Na]^+$ 653.2165; found: 653.2159; Anal. Calcd for $C_{40}H_{30}N_4O_4$: C, 76.17; H, 4.79; N, 8.88. Found: C, 76.05; H, 4.88; N 8.77.

Reaction of 7 with TCNE: TCNE (640 mg, 5.00 mmol) was added to a solution of **7** (630 mg, 1.00 mmol) in 1,1,2,2-tetrachloroethane (5 mL). The resulting mixture was heated at reflux temperature for 24 h under an Ar atmosphere. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (10 : 1) as an eluent and on Bio-Beads with CH_2Cl_2 as an eluent to give **8** (539 mg, 71%) as brown crystals and **9** (139 mg, 22%) as deep-blue crystals.

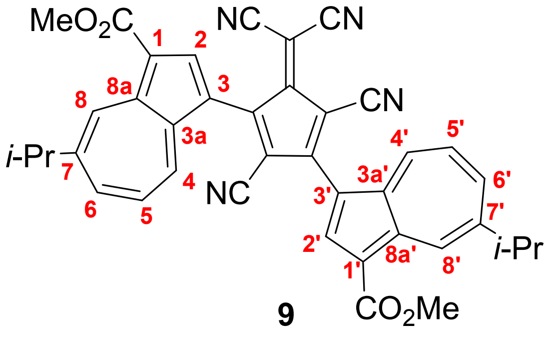
Compound 8



8

M.p. 165.0−168.0 °C (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz, CD_3CN, 80 °C): δ_H = 9.73 (br s, 2H, 8-H), 8.16 (d, 2H, J = 9.5 Hz, 4-H), 7.65 (br s, 6H, 5,6,7-H), 3.87 (br s, 6H, CO_2Me), 3.34 (br s, 2H, *i*Pr), 1.45 (d, 12H, J = 7.0 Hz, *i*Pr) ppm. Low solubility of the compound hampered a measurement of ^{13}C NMR. IR (KBr disk): ν_{max} = 2969 (w), 2221 (w), 1738 (m), 1704 (m), 1498 (m), 1441 (m), 1400 (m), 1297 (w), 1212 (s), 1180 (m), 1134 (w), 1090 (w), 1023 (w), 902 (w), 810 (w), 777 (m), 729 (w), 669 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 245 (4.71), 264 (4.72), 348 sh (4.35), 450 (4.40), 510 sh (4.19) nm; UV/Vis (10% CH_2Cl_2/hexane): λ_{max} (log ε) = 241 (4.71), 260 sh (4.67), 340 sh (4.34), 419 (4.25), 438 (4.24), 488 sh (4.17) nm; HRMS (FAB): calcd for $C_{46}H_{30}N_8O_4$ $[M]^+$ 758.2390; found: 758.2388; Anal. Calcd for $C_{46}H_{30}N_8O_4\cdot H_2O$: C, 71.12; H, 4.15; N, 14.43. Found: C, 71.09; H, 4.17; N 14.38.

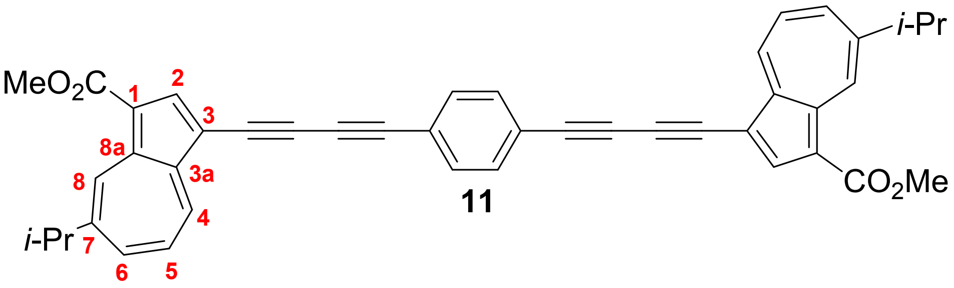
Compound 9



9

M.p. 180.0−182.0 °C ($CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ_H = 9.96 (s, 1H, 8-H), 9.88 (s, 1H, 8’-H), 8.46 (s, 1H, 2 or 2’-H), 8.46 (br s, 1H, 4-H), 7.88 (d, 1H, *J* = 10.0 Hz, 6-H), 7.75 (d, 1H, *J* = 10.0 Hz, 6’-H), 7.62 (d, 1H, *J* = 10.0 Hz, 4’-H), 7.45 (br s, 1H, 5-H), 7.04 (dd, 1H, *J* = 10.0, 10.0 Hz, 5’-H), 6.78 (s, 1H, 2 or 2’-H), 4.05 (s, 3H, CO_2Me), 3.98 (s, 3H, CO_2Me), 3.31 (sept, 1H, *J* = 6.5 Hz, *i*Pr), 3.20 (sept, 1H, *J* = 6.5 Hz, *i*Pr’), 1.49 (d, 6H, *J* = 6.5 Hz, *i*Pr), 1.41 (d, 3H, *J* = 6.5Hz, *i*Pr’), 1.40 (d, 3H, *J* = 6.5Hz, *i*Pr’) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.29 (CO_2Me), 163.91 (CO_2Me), 160.84 (C-5 of fulvene), 160.41 (C-2 or 4 of fulvene), 154.50 (C-7’), 151.99 (C-7), 145.32 (C-2 or 4 of fulvene), 144.24 (C-8a or 8a’), 143.19 (C-8a or 8a’), 142.85 (C-6’), 142.54 (C-8’), 141.74 (C-3a or 3a’), 140.93 (C-2 or 2’), 140.31 (C-6), 140.20 (C-3a or 3a’), 139.62 (C-8), 139.36 (C-4), 138.72 (C-4’), 136.25 (C-3 of fulvene), 130.51 (C-5), 128.77 (C-5’), 123.57 (C-3 or 3’), 122.03 (C-3 or 3’), 117.80 (C-2 or 2’), 117.50 (C-1’), 116.43 (C-1), 113.18 (CN), 112.72 (CN), 111.99 (CN), 111.93 (CN), 91.39 ($\underline{C}(CN)_2$), 80.20 (C-1 of fulvene), 52.29 (CO_2Me), 51.34 (CO_2Me), 39.30 (*i*Pr), 39.13 (*i*Pr), 24.56 (*i*Pr), 24.27 (*i*Pr) ppm; IR (KBr disk): ν_{max} = 2964 (w), 2219 (w), 1707 (m), 1693 (m), 1498 (m), 1449 (s), 1418 (s), 1379 (w), 1309 (w), 1286 (w), 1212 (s), 1175 (m), 1117 (w), 1080 (w), 1040 (w), 1011 (w), 915 (w), 851 (w), 810 (w), 795 (w), 777 (m), 762 (w), 735 (m), 724 (m), 696 (w), 647 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 243 (4.67), 300 (4.73), 349 (4.48), 394 sh (4.37), 542 sh (4.03), 583 (4.11), 808 (3.64); UV/Vis (10% CH_2Cl_2/hexane): λ_{max} (log ε) = 242 (4.68), 298 (4.72), 338 (4.49), 375 sh (4.40), 530 sh (4.04), 570 (4.11), 755 (3.50); HRMS (FAB): calcd for $C_{40}H_{30}N_4O_4$ $[M]^+$ 630.2267; found: 630.2278; Anal. Calcd for $C_{40}H_{30}N_4O_4$: C, 76.17; H, 4.79; N, 8.88. Found: C, 76.02; H, 4.97; N 8.74.

1,4-di(1-[7-isopropyl-1-methoxycarbonyl-3-azulenyl]butadiyne-4-yl)benzene (11)

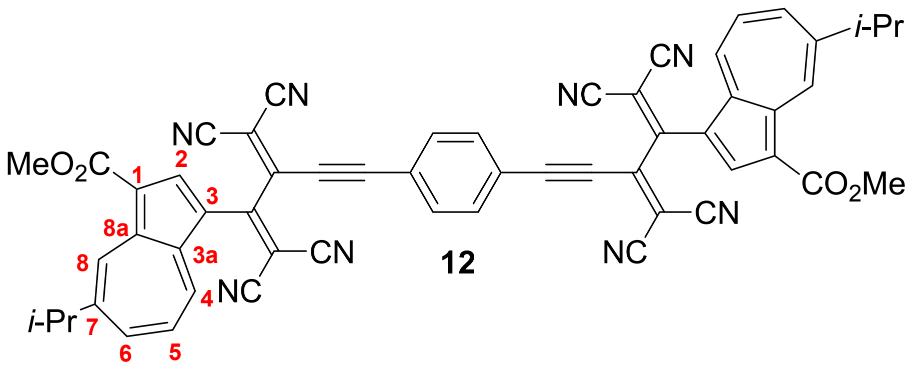


11

Potassium carbonate (414 mg, 3.00 mmol) was added to a solution of **4** (349 mg, 1.00 mmol) in methanol (20 mL). The resulting mixture was stirred at room temperature for 2 h. After an addition of diethyl ether and water to the reaction mixture, the organic layer was separated, dried with Na_2SO_4, and concentrated under reduced pressure up to 5 mL. 1,4-Diiodobenzene (165 mg, 0.50 mmol), CuI (19 mg, 0.10 mmol), triethylamine (10 mL), and THF (10 mL) were added to the solution of **10**. After an addition of $Pd(PPh_3)_4$ (58 mg, 0.050 mmol) to the degassed mixture, it was stirred at room temperature for 5 h. The reaction mixture was diluted with CH_2Cl_2, washed successively with 10% NH_4Cl and brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with dichloromethane to afford **11** (272 mg, 87%) as green crystals.

M.p. 207.0−209.0 °C ($CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 9.74 (s, 2H, 8-H), 8.64 (d, 2H, J = 10.0 Hz, 4-H), 8.45 (s, 2H, 2-H), 7.85 (d, 2H, J = 10.0 Hz, 6-H), 7.55 (dd, 2H, J = 10.0, 10.0 Hz, 5-H), 7.51 (s, 4H, Ph), 3.96 (s, 6H, CO_2Me), 3.25 (sept, 2H, J = 6.5 Hz, *i*Pr), 1.43 (d, 12H, J = 6.5 Hz, *i*Pr) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ_C = 165.17 (CO_2Me), 151.61 (C-7), 146.60 (C-3a or 8a), 143.88 (C-2), 141.61 (C-3a or 8a), 139.81 (C-6), 138.72 (C-8), 136.51 (C-4), 132.27 (Ph), 128.21 (C-5), 122.66 (*ipso*-Ph), 115.42 (C-1), 107.03 (C-3), 81.91 (C≡C), 79.11 (C≡C), 78.00 (C≡C), 77.31 (C≡C), 51.24 (CO_2Me), 39.28 (*i*Pr), 24.57 (*i*Pr) ppm; IR (KBr disk): ν_{max} = 2957 (m), 2868 (w), 2203 (m), 2137 (w), 1693 (s), 1597 (w), 1576 (w), 1523 (m), 1514 (m), 1448 (s), 1412 (m), 1396 (w), 1371 (w), 1284 (w), 1213 (s), 1172 (m), 1126 (m), 1078 (w), 1049 (w), 1012 (w), 962 (w), 906 (w), 887 (w), 835 (w), 804 (w), 777 (w), 673 (w), 578 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 (4.83), 294 (4.87), 308 sh (4.84), 324 (4.81), 358 sh (4.63), 384 (4.73), 412 (4.79), 432 (4.81), 558 (3.34), 606 sh (3.20), 684 sh (2.47) nm; HRMS (ESI): calcd for $C_{44}H_{34}O_4 + Na^+$ $[M + Na]^+$ 649.2355; found: 649.2349; Anal. Calcd for $C_{44}H_{34}O_4$: C, 84.32; H, 5.47. Found: C, 84.19; H, 5.47.

Compound 12



12

TCNE (256 mg, 2.00 mmol) was added to a solution of **11** (313 mg, 0.50 mmol) in ethyl acetate (10 mL). The resulting mixture was heated at reflux temperature for 6 h under an Ar atmosphere. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2/ethyl acetate (10 : 1) as an eluent and on Bio-Beads with CH_2Cl_2 as an eluent to give **12** (419 mg, 95%) as red crystals.

M.p. >300 °C (CH_2Cl_2/hexane); ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 10.05 (s, 2H, 8-H), 8.44 (d, 2H, *J* = 10.0 Hz, 4-H), 8.24 (s, 2H, 2-H), 8.20 (d, 2H, *J* = 10.0 Hz, 6-H), 8.03 (dd, 2H, *J* = 10.0, 10.0 Hz, 5-H), 7.92 (s, 4H, Ph), 3.97 (s, 6H, CO_2Me), 3.38 (sept, 2H, *J* = 6.5 Hz, *i*Pr), 1.48 (d, 12H, *J* = 6.5 Hz, *i*Pr) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 166.77 (CO_2Me), 164.21 ($\underline{C}$=C(CN)$_2$), 158.98 ($\underline{C}$=C(CN)$_2$), 157.80 (C-7), 146.58 (C-3a or 8a), 143.04 (C-6), 142.07 (C-3a or 8a), 141.99 (C-2), 141.18 (C-8), 137.75 (C-4), 136.40 (*ipso*-Ph), 132.69 (C-5), 130.65 (Ph), 120.00 (C-3), 118.41 (C-1), 113.32 (CN), 112.51 (CN), 111.18 (CN), 110.55 (CN), 90.83 ($\underline{C}$(CN)$_2$), 80.31 ($\underline{C}$(CN)$_2$), 77.20 (C≡C), 51.81 (CO_2Me), 39.57 (*i*Pr), 24.46 (*i*Pr) ppm. The one signal of C≡C moiety was overlapped with signals of $CDCl_3$.; IR (KBr disk): ν_{max} = 2964 (w), 2225 (w), 1693 (s), 1506 (s), 1439 (m), 1417 (s), 1365 (w), 1314 (w), 1239 (s), 1219 (s), 1183 (m), 1135 (w), 1047 (w), 887 (w), 808 (w), 781 (m), 738 (w), 693 (w) cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 264 (4.73), 299 (4.75), 332 (4.64), 443 (4.46), 544 sh (4.11) nm; UV/Vis (20% CH_2Cl_2/hexane): λ_{max} (log ε) = 262 (4.71), 297 (4.74), 331 (4.63), 438 (4.46), 544 sh (4.04) nm; HRMS (MALDI-TOF): calcd for $C_{56}H_{34}N_8O_4^+$ [M]$^+$ 882.2703; found: 882.4985; Anal. Calcd for $C_{56}H_{34}N_8O_4 \cdot H_2O$: C, 74.66; H, 4.03; N, 12.44. Found: C, 74.59; H, 4.11; N 12.38.

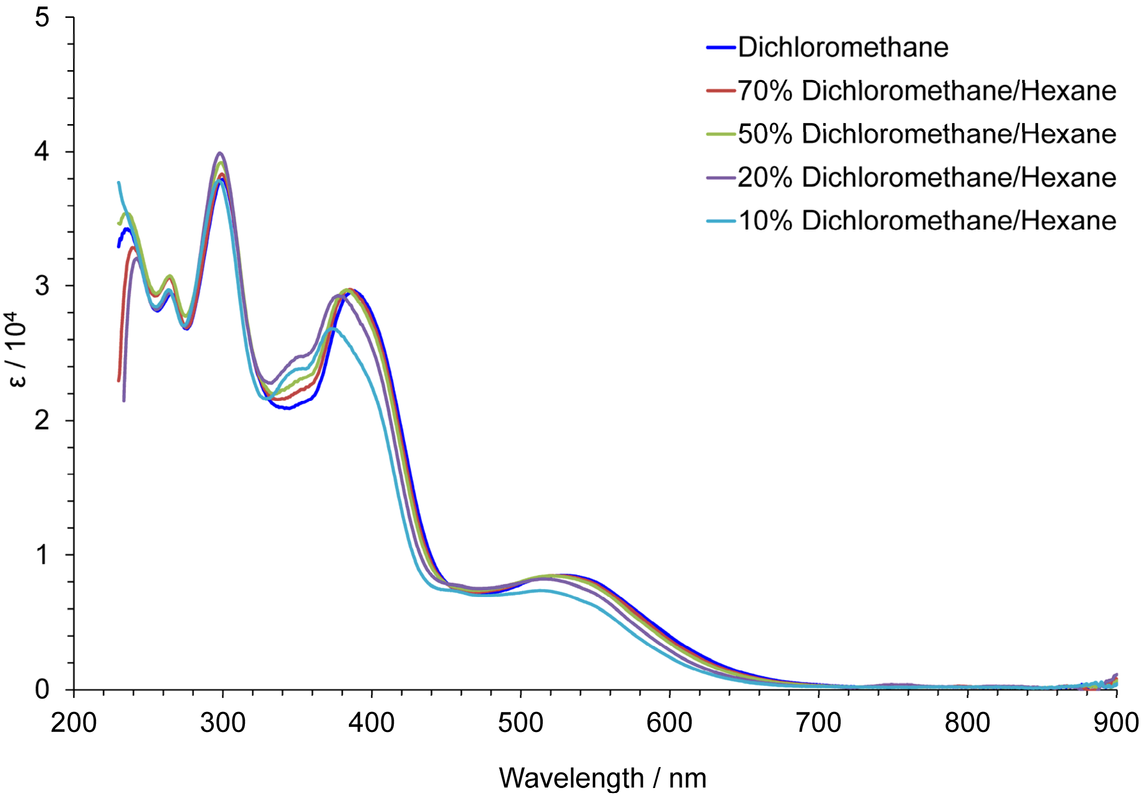


Figure S-1. UV/Vis spectra of **5** in dichloromethane and dichloromethane/hexane.

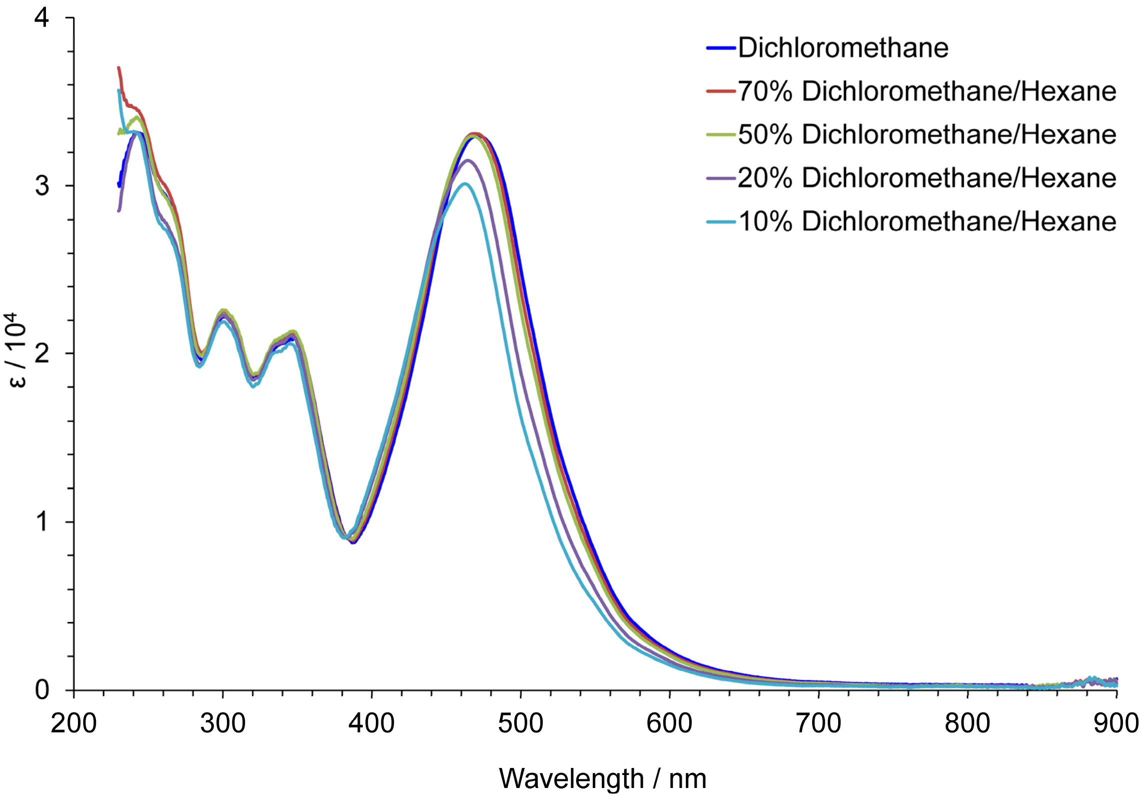


Figure S-2. UV/Vis spectra of **6** in dichloromethane and dichloromethane/hexane.

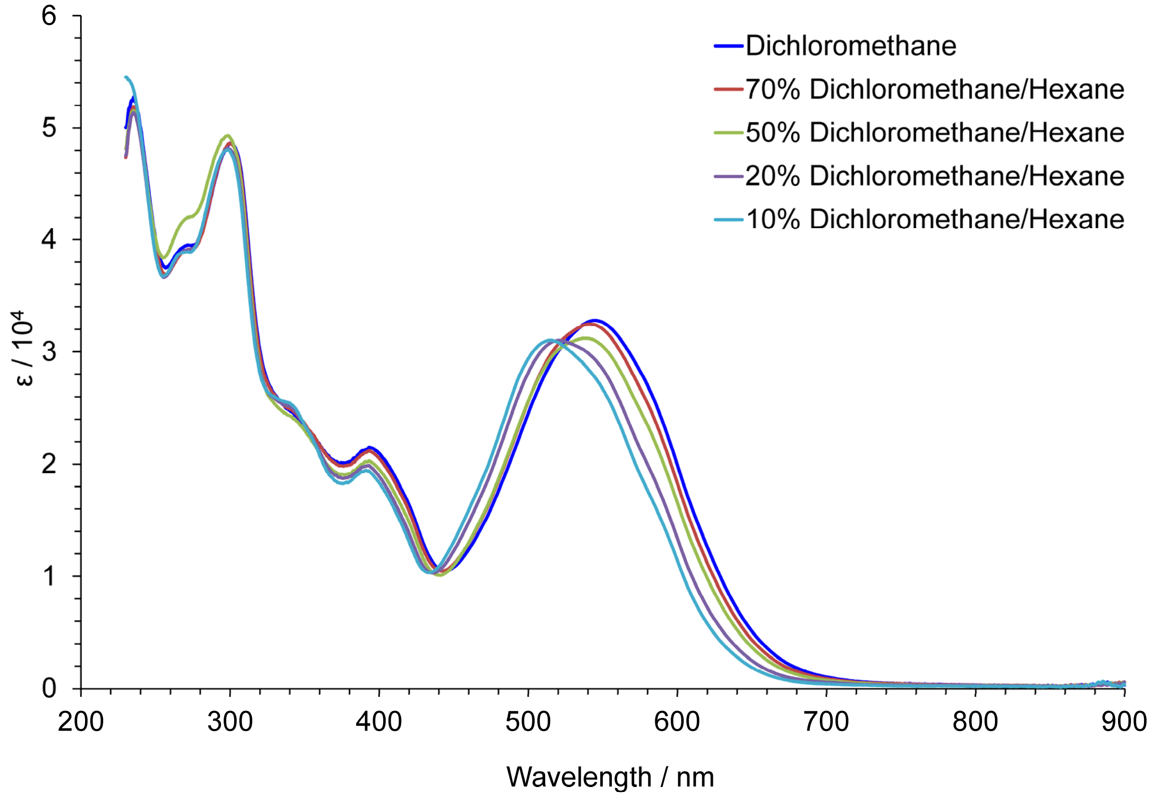


Figure S-3. UV/Vis spectra of **7** in dichloromethane and dichloromethane/hexane.

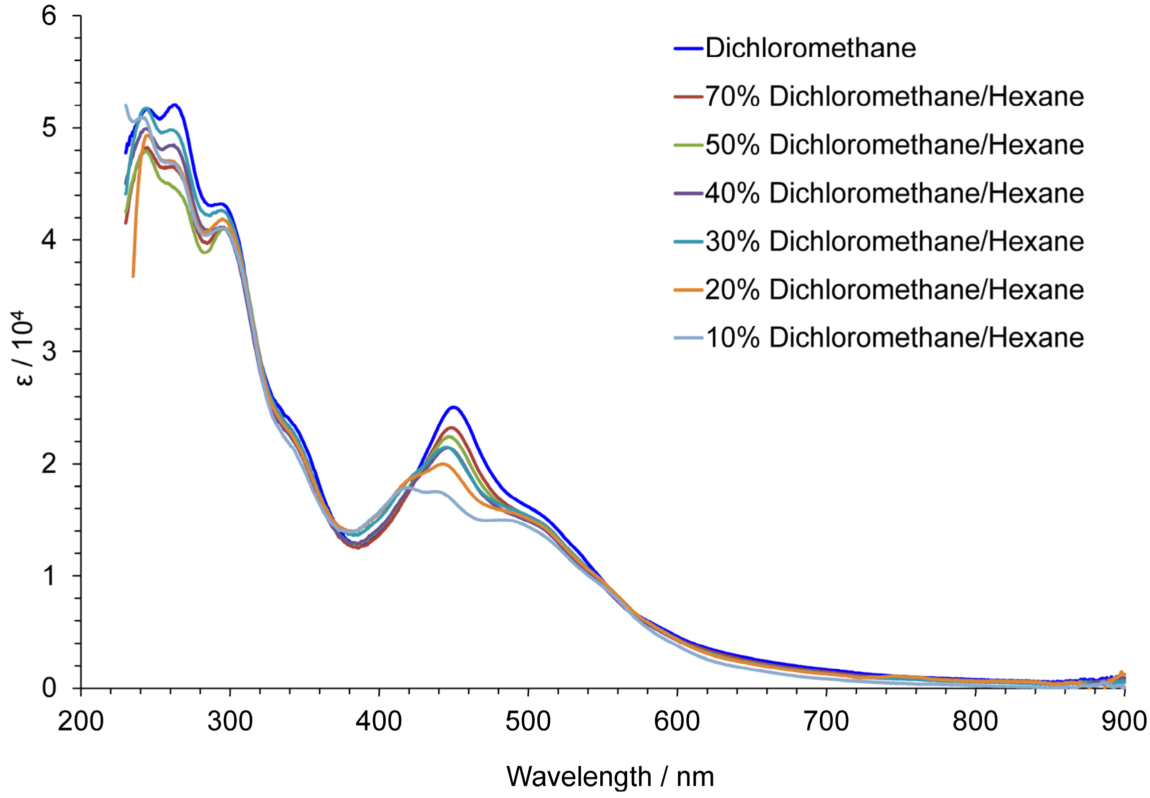


Figure S-4. UV/Vis spectra of **8** in dichloromethane and dichloromethane/hexane.

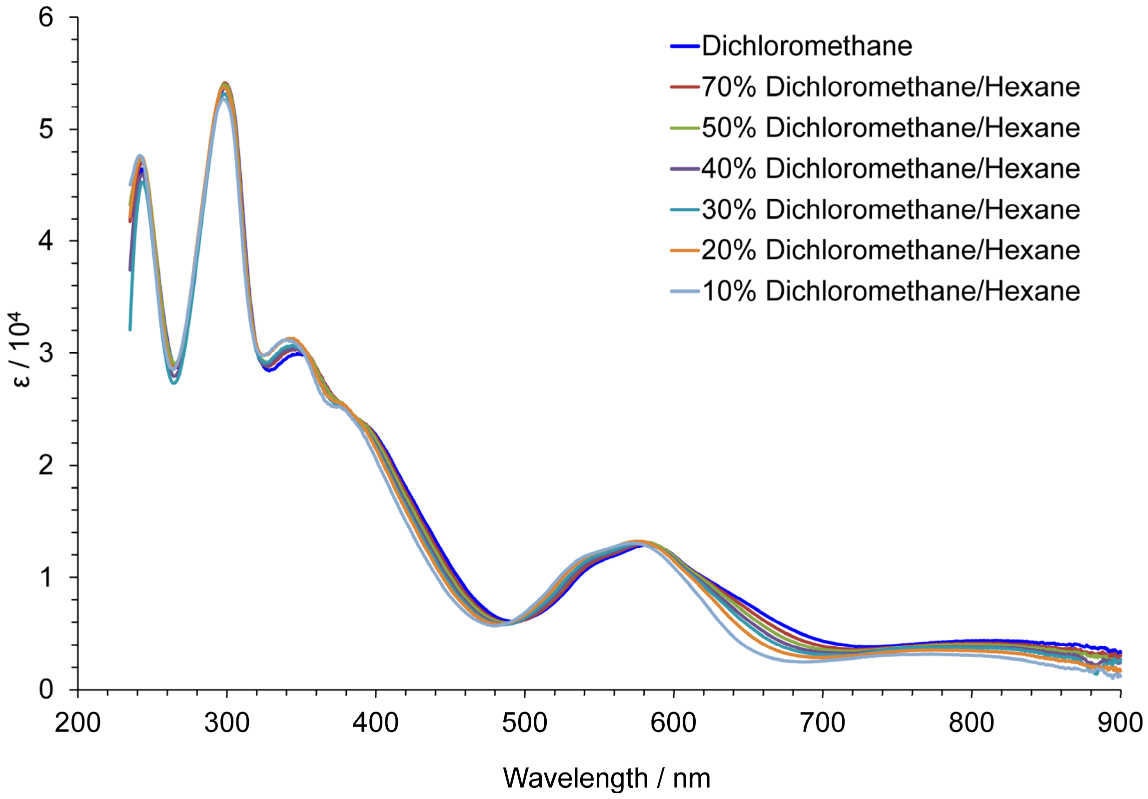


Figure S-5. UV/Vis spectra of **9** in dichloromethane and dichloromethane/hexane.

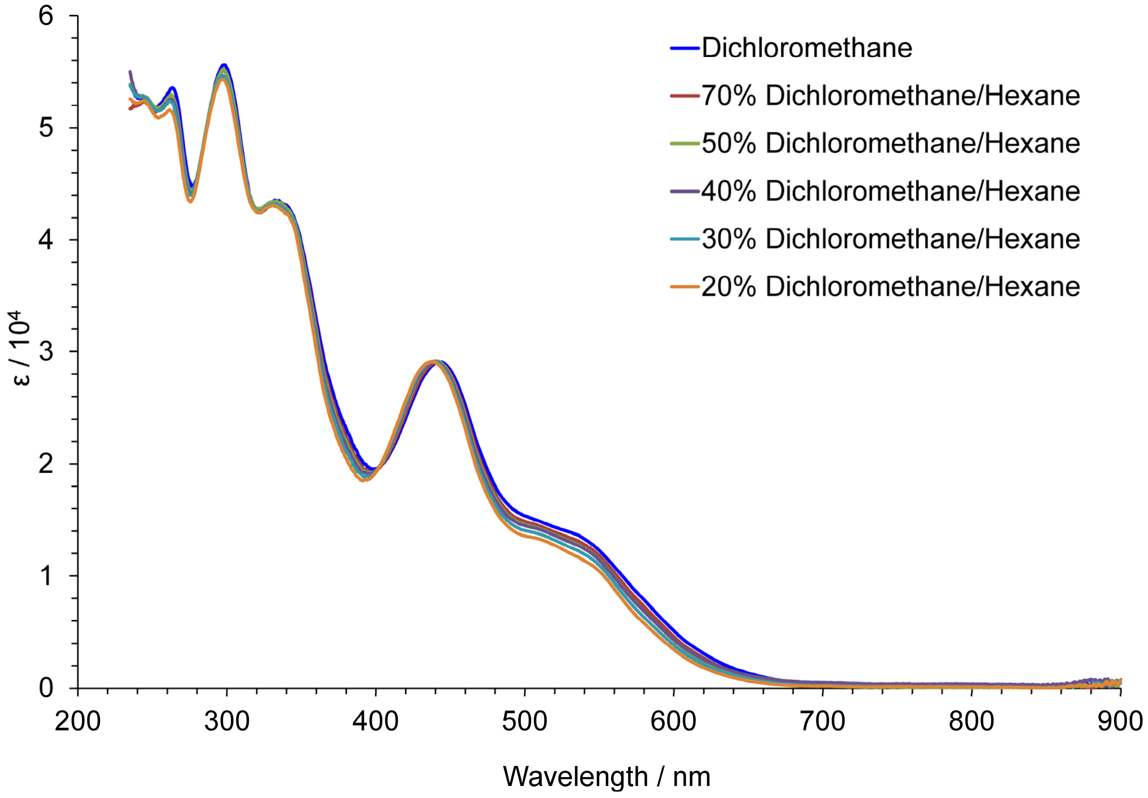


Figure S-6. UV/Vis spectra of **12** in dichloromethane and dichloromethane/hexane.

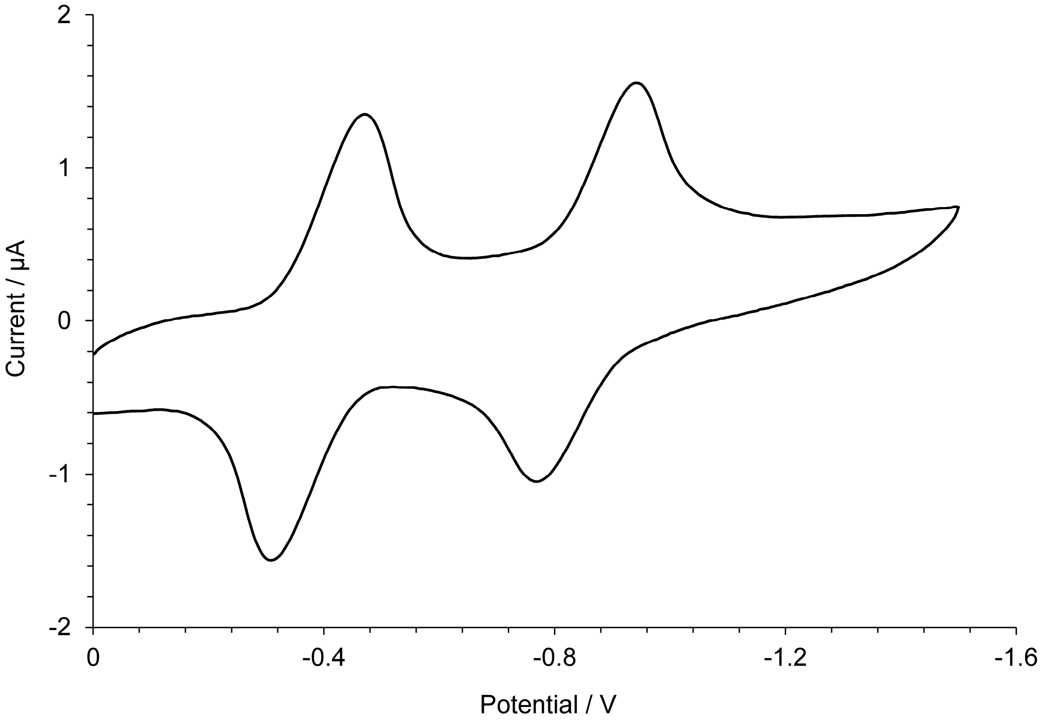


Figure S-7. Cyclic voltammogram of **5** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1}.

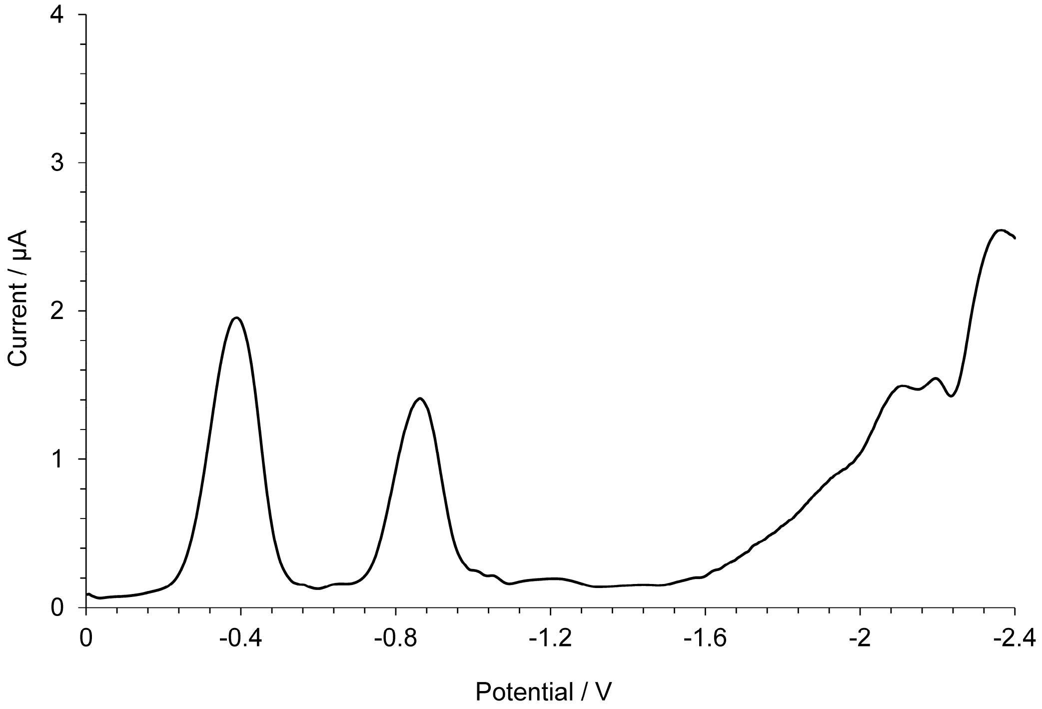


Figure S-8. Differential pulse voltammogram of **5** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 10 mVs^{-1}.

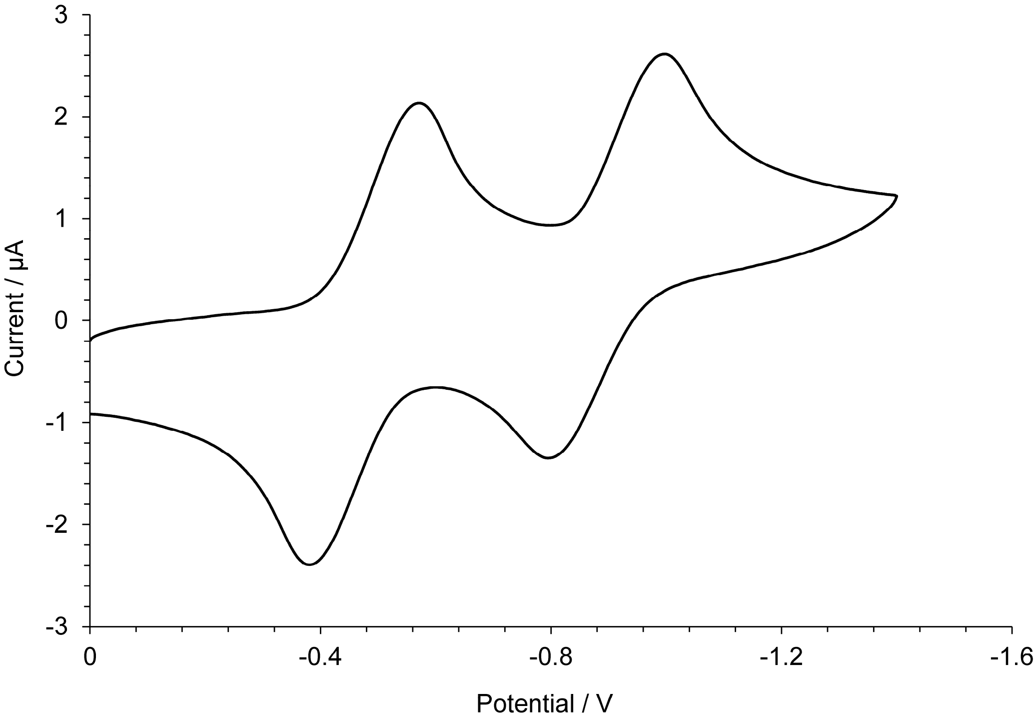


Figure S-9. Cyclic voltammogram of **7** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1}.

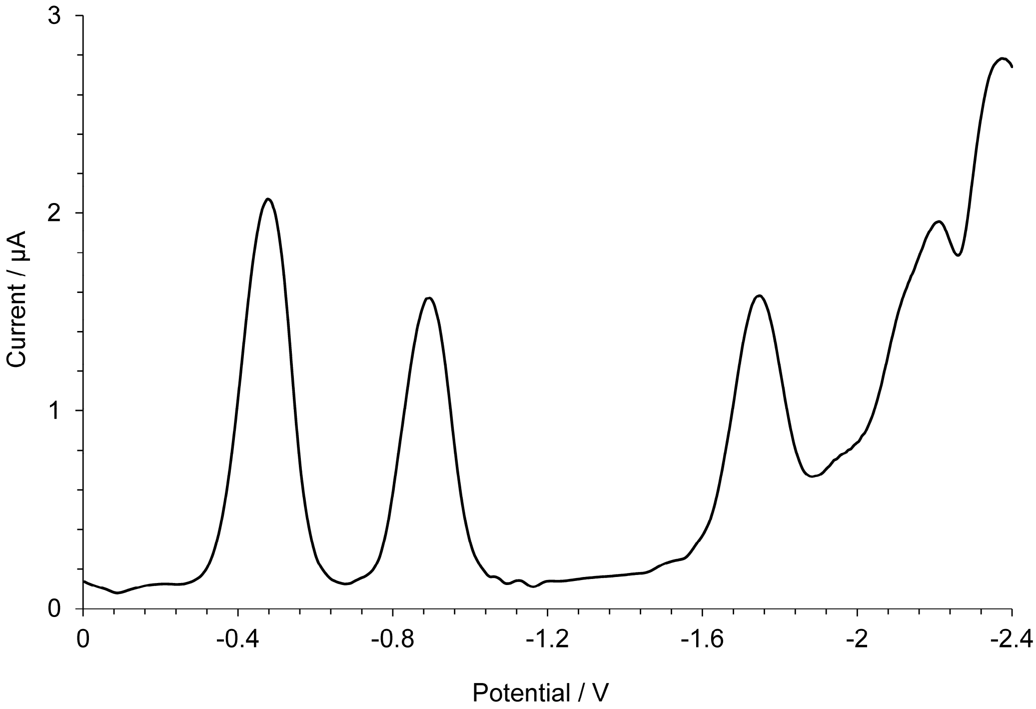


Figure S-10. Differential pulse voltammogram of **7** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 10 mVs^{-1}.

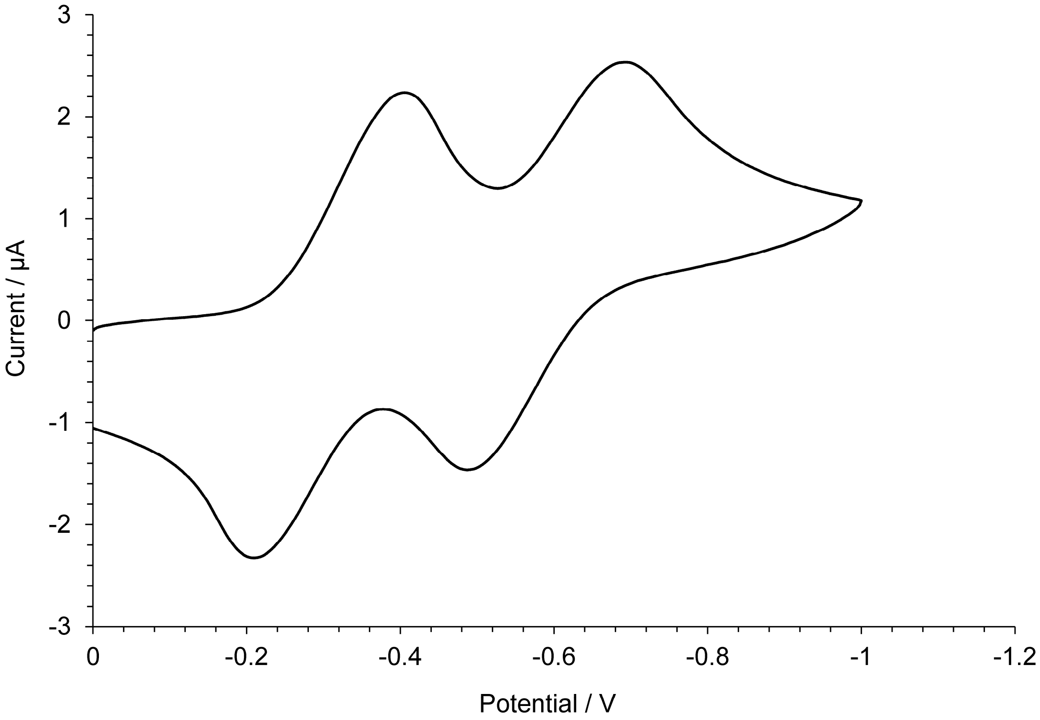


Figure S-11. Cyclic voltammogram of **9** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 100 mVs^{-1}.

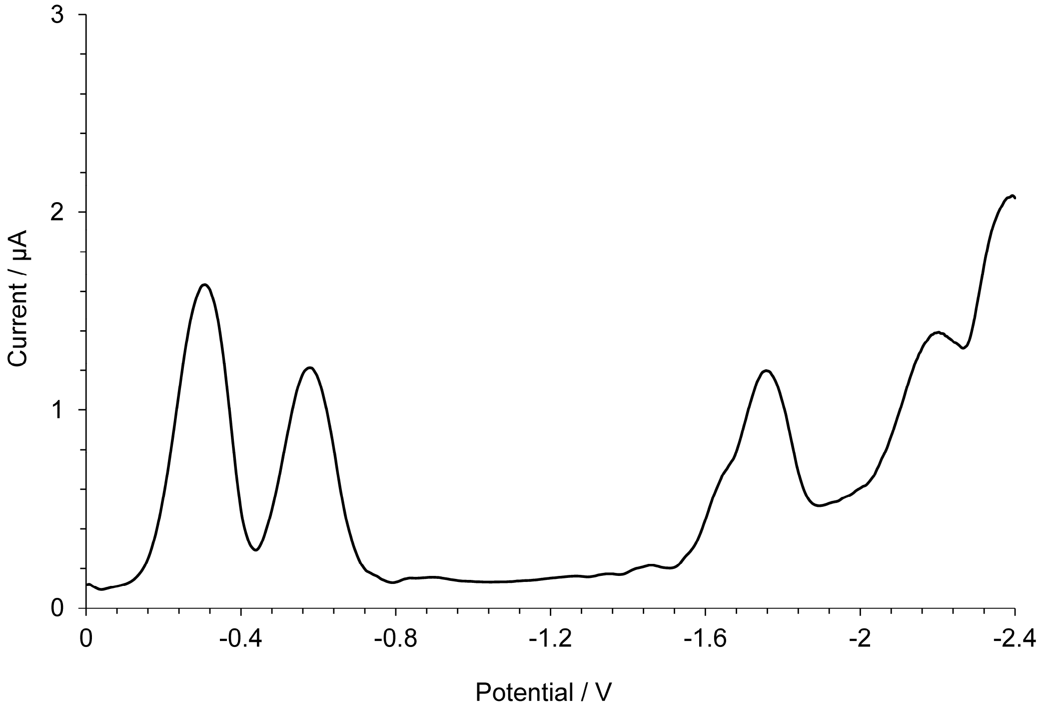
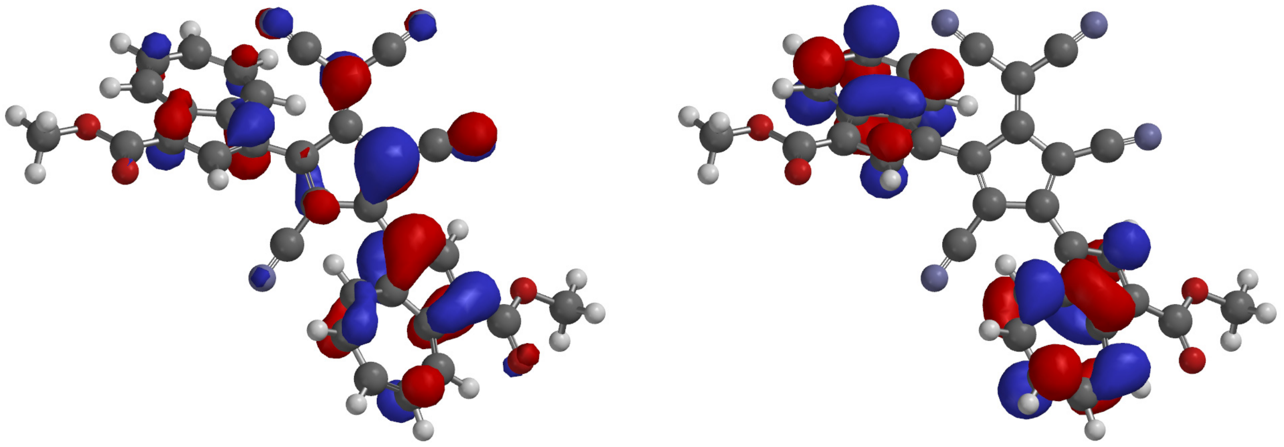
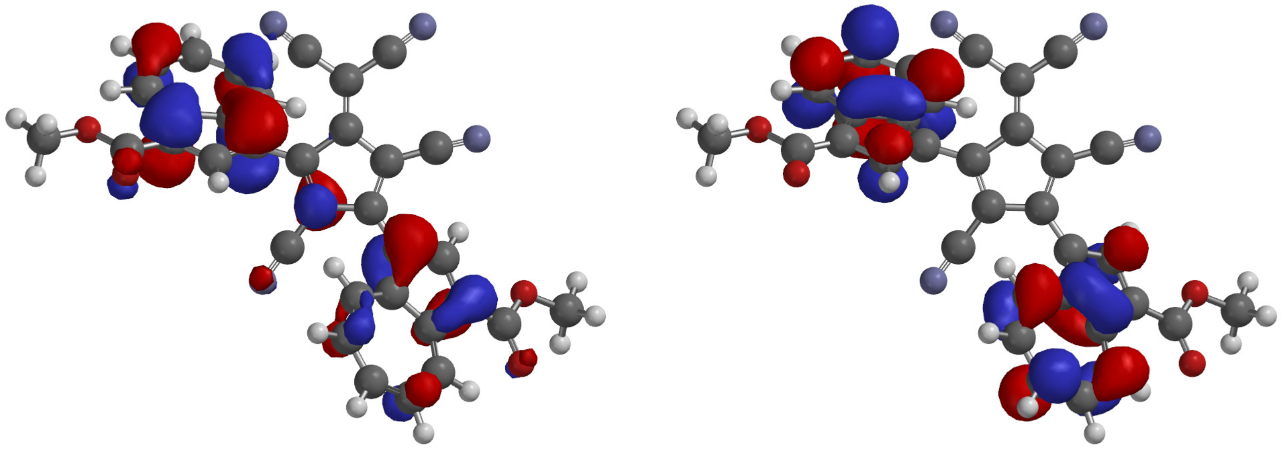


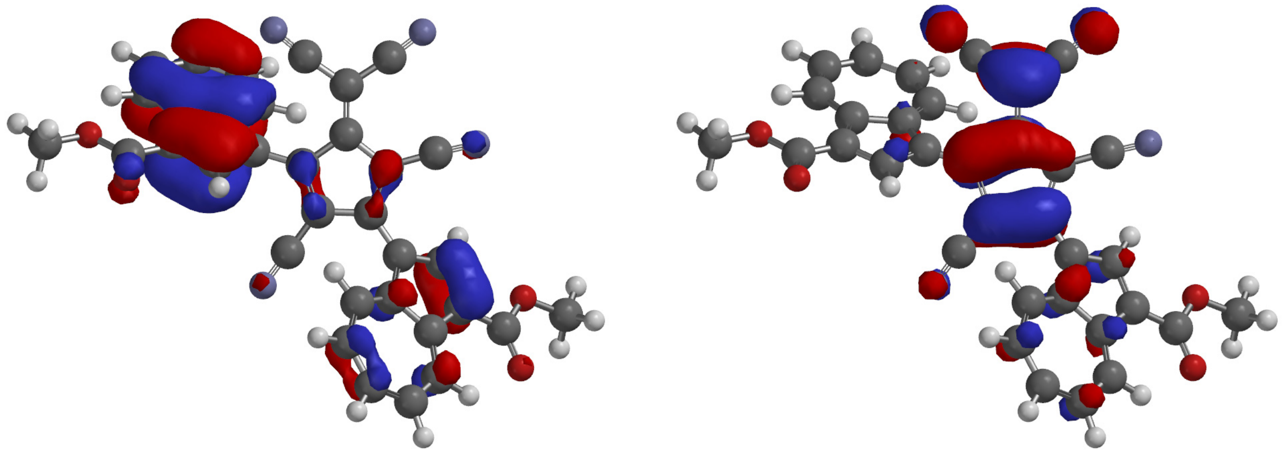
Figure S-12. Differential pulse voltammogram of **9** (1 mM) in benzonitrile containing Et_4NClO_4 (0.1 M) as a supporting electrolyte; scan rate = 10 mVs^{-1}.



HOMO LUMO+2



HOMO−1 LUMO+1



HOMO−2 LUMO

Figure S-13. Frontier Kohn-Sham orbitals of **9”** at the B3LYP/6-31G** level.