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Four-stage amphoteric redox property and biradicaloid character of tetra-*tert*-butyldicyclopenta[*b*;*d*]thieno[1,2,3-*cd*; 5,6,7-*c'd'*]diphenalene

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Material and methods. All experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under an argon atmosphere in well-dried glassware. Solvents were dried and distilled according to the standard procedures. Column chromatography was performed with silica gel [Wako gel C-200 (Wako)] or basic alumina [200 mesh (Wako)]. Infrared spectra were recorded on a Perkin Elmer FT 1640 IR spectrometer. Electronic spectra were measured by a Shimadzu UV-3100PC spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on JEOL EX-270, JEOL GSX-400, JEOL GSX-500, and Varian UNITY plus 600 spectrometers. Positive EI, FAB, and FD mass spectra were taken by using JEOL JMS SX-102 and Shimadzu QP-5000 mass spectrometers. ESR spectra were obtained with a JEOL JES-FE2XG spectrometer. Cyclic voltammetric measurements were made with a Yanagimoto P1100 spectrometer. Cyclic voltammogram of the compound was recorded with glassy carbon working electrode and Pt counter electrode in CH_2Cl_2 containing 0.1 M $(n\text{-Bu})_4NClO_4$ as the supporting electrolyte. The experiments employed a SCE reference electrode. Electrochemical experiments were done under a argon atmosphere at room temperature.

2,5,8,11-tetra-*tert*-butyl-3,9-/-3,10-/-4,9-dimethyldiacenaphtho[1,2-*b*;1',2'-*d*]thiophene (3). A suspension of compound **2** (7.00 g, 25.1 mmol) and sulfur (3.22 g, 12.6 mmol) in 112 mL of DMF was refluxed for 2 hr After cooling, water of 100 mL was added to the reaction mixture. The resulting yellow precipitate was collected by filtration, washed with water, and dried. The crude product was purified by column chromatography on silica gel [benzene/hexane (1:10, v/v)] followed by recrystallization to give **3** (6.64 g, 90%) as reddish orange needles: mp >300 ˚C. TLC R_f 0.42 [benzene/hexane (1:10, v/v)]. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.21 (s), 8.18 (s), 8.13 (s), 8.11 (d, J = 1.3 Hz), 7.99(d, J = 1.3 Hz), 7.98 (s), 7.934 (d, J = 1.3 Hz), 7.925 (s), 7.81 (s), 7.80 (s), 7.77 (d, J = 1.3 Hz), 7.76 (d, J = 1.3 Hz), 3.02 (s), 3.00 (s), 1.68 (s), 1.66 (s), 1.60 (s), 1.58 (s), 1.56 (s), 1.50 (s). FAB MS (NBA) *m/z* 584 (M^+). Anal. Calcd for $C_{42}H_{48}S$: C, 86.25; H, 8.27. Found: C, 86.28; H, 8.43.

2,5,8,11-tetra-*tert*-butyl-3,9-/-3,10-/-4,9-bis(bromomethyl)diacenaphtho[1,2-*b*;1',2'-*d*]thiophene (4). A mixture of compound **3** (2.00 g, 3.42 mmol), *N*-bromosuccinimide (1.21 g, 6.82 mmol), and benzoylperoxide (0.17 g, 0.70 mmol) in 200 mL of benzene were refluxed for 10 min. The reaction mixture was cooled and concentrated *in vacuo*. The resulting orange powder was washed with ethanol repeatedly to give crude **4** (2.79 g). This material was used for a further reaction with no purification.

2,5,8,11-tetra-*tert*-butyl-3,9-/-3,10-/-4,9-bis [2,2-bis(ethoxycarbonyl) ethyl]

diacenaphtho[1,2-*b*;1’,2’-*d*]thiophene (5). Diethyl malonate (6.5 mL, 42.6 mmol) was added to a sodium ethoxide solution freshly prepared from 100 mL of anhydrous ethanol and sodium (420 mg, 18.3 mmol). To the clear solution was added **4** (2.79 g) dissolved in benzene (100 mL). After stirring for 21 h, the reaction mixture was washed with water. The organic layer was separated and the aqueous layer was extracted repeatedly with benzene. The combined organic layers were dried over $MgSO_4$ and filtered. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (benzene) to give **5** (2.05 g, 67%, 2 steps) as red oil: TLC R_f 0.48 (benzene). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.75-8.23 (m,6H), 3.95-4.28 (m,14H), 1.49-1.67 (m,36H), 1.05 (q,12H). FAB MS (NBA) *m/z* 900 (M$^+$).

2,5,8,11-tetra-*tert*-butyl-3,9-/-3,10-/-4,9-bis(2-carboxyethyl)diacenaphtho[1,2-*b*;1’,2’-*d*]thiophene (6). A suspension of **5** (3.5 g, 3.91 mmol) in ethanol (140 mL) and 10% aqueous potassium hydroxide solution (100 mL) was refluxed for 3 h. The reaction mixture was cooled and concentrated *in vacuo*. A suspension of the obtained yellow solid in 3N hydrochloric acid (130 mL) was heated with refluxing for 5 h. The resulting red precipitate was collected and washed with water to give crude **6** (2.43 g, 89%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.78-8.21(m,6H), 3.86 (m,4H), 2.89-2.96 (m,4H), 1.52-1.71 (m,36H). FAB MS (NBA) *m/z* 700 (M$^+$). IR (KBr) 3443, 1709 cm^{-1}.

4,8,12,15-tetra-*tert*-butyl-1,2,3,9,10,11-hexahydro-1,9-/-1,11-/-3,9-dioxo-dicyclopenta[*b*;*d*]thieno[1,2,3-*cd*:5,6,7-*c'd'*]diphenalene (7). A mixture of compound **6** (167 mg, 0.25 mmol) and oxalyl chloride (3 mL) was heated with refluxing for 2 h. The reaction mixture was cooled and concentrated *in vacuo*. The resulting orange solid dissolved in dichloromethane (5 mL) was cooled to -78 ˚C. Anhydrous $AlCl_3$ (233 mg, 1.75 mmol) was added to the solution and the reaction mixture was allowed to warm to –30 ˚C over 2 h, and stirred at –30 ˚C for 2 h. 3N hydrochloric acid was added to the mixture and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. After column chromatography on silica gel (benzene), pure **7** (125 mg, 75%) was obtained as a reddish brown powder: mp >300 ˚C. TLC R_f 0.58 (benzene). ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.36 (s) , 8.35 (s), 8.24 (s), 8.23 (s), 8.01 (s); 7.99 (s), 7.90 (s), 7.88 (s), 3.82 (t-like, *J* = 6.93, 6.27 Hz), 3.15 (t-like, *J* = 6.93, 6.27 Hz), 1.70 (s), 1.69 (s), 1.663 (s), 1.658 (s), 1.63 (s), 1.60 (s), 1.57 (s). FAB MS (NBA) *m/z* 664 (M$^+$). IR (KBr) 2963, 2912, 1697 cm^{-1}. Anal. Calcd for $C_{46}H_4O_2S$: C, 83.09; H, 7.28. Found: C, 82.89; H, 7.22.

4,8,12,15-tetra-*tert*-butyl-1,2,3,9,10,11-hexahydro-1,9-/-1,11-/-3,9-hydoxy-dicyclopenta[*b*;*d*]thieno[1,2,3-*cd*:5,6,7-*c'd'*]diphenalene (8). A mixture of **7** (868 mg, 1.31 mmol) and lithium aluminum hydride (74 mg, 1.95 mmol) in THF (200 mL) was stirred for 4 h at room temperature. After addition of dichloromethane, the mixture was washed with brine. The organic layer was separated and the aqueous layer was extracted repeatedly with dichloromethane. The combined organic layers were dried over Na_2SO_4 and filtered. After column chromatography on silica gel (dichloromethane), pure diols (156 mg, 86 %) was obtained as an orange powder. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.23 (s), 8.22 (s), 7.86 (s), 7.85 (s), 5.82 (m), 5.30 (s), 3.63 (t), 3.58 (t), 3.48 (t), 3.42 (t), 2.58–2.14 (m), 1.73 (s), 1.68 (s), 1.67 (s), 1.66 (s), 1.62 (s), 1.59 (s) . FAB MS (NBA) *m/z* 668 (M^+). IR (KBr) 3425, 2954 cm^{-1}

4,8,12,15-tetra-*tert*-butyl-1,9-/-1,11-/-3,9-hydro-dicyclopenta[*b*;*d*]thieno[1,2,3-*cd*:5,6,7-*c'd'*]diphenalene (9). Diols **8** (756 mg, 1.13 mmol) in benzene (160 mL) was heated with refluxing. Catalytic amount of *p*-toluene sulfonic acid monohydrate was added to the solution and the reaction mixture was stirred for 5 min. The mixture was cooled on ice-bath. The crude product was purified by column chromatography on silica gel [benzene/hexane (1:4, v/v)] to give **9** (710 mg, 99%) as an air-sensitive dark red powder. TLC R_f 0.48 [benzene/hexane (1:10, v/v)]. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.35 (s, 2H), 7.99, 7.95 (s, s, 2H), 7.62 (d *J* = 10.23 Hz, 2H), 6.49 (dd, *J* = 10.23, 2.97 Hz, 2H), 4.11 (m, 4H), 1.72, 1.71, 1.65, 1.64 (s, s, s, s, 36 H). FD MS *m/z* 632 (M^+)

4,8,12,15-tetra-*tert*-butyldicyclopenta[*b*;*d*]thieno[1,2,3-*cd*:5,6,7-*c'd'*]diphenalene (1). A mixture of **9** (139 mg, 0.219 mmol) and *p*-chloranil (26.1 mg, 0.241 mmol) in benzene (32 mL) was refluxed for 5 min. The mixture was cooled on ice-bath. The crude product was purified by column chromatography on silica gel [benzene/hexane (1:4, v/v)] to give **1** (121 mg, 87%) as a dark brown powder. Further purification was done by recrystallization from hexane–1,2,3-trichloropropane solution in a sealed degassed tube to give black prisms: mp >300 °C. TLC R_f 0.55 [benzene/hexane (1:10, v/v)]. FD MS *m/z* 630 (M^+). Anal. Calcd for $(C_{46}H_{46}S)(\text{hexane})_{0.8}(\text{trichloropropane})_{0.1}$: C, 85.89; H, 8.14. Found: C, 85.75; H, 8.33.

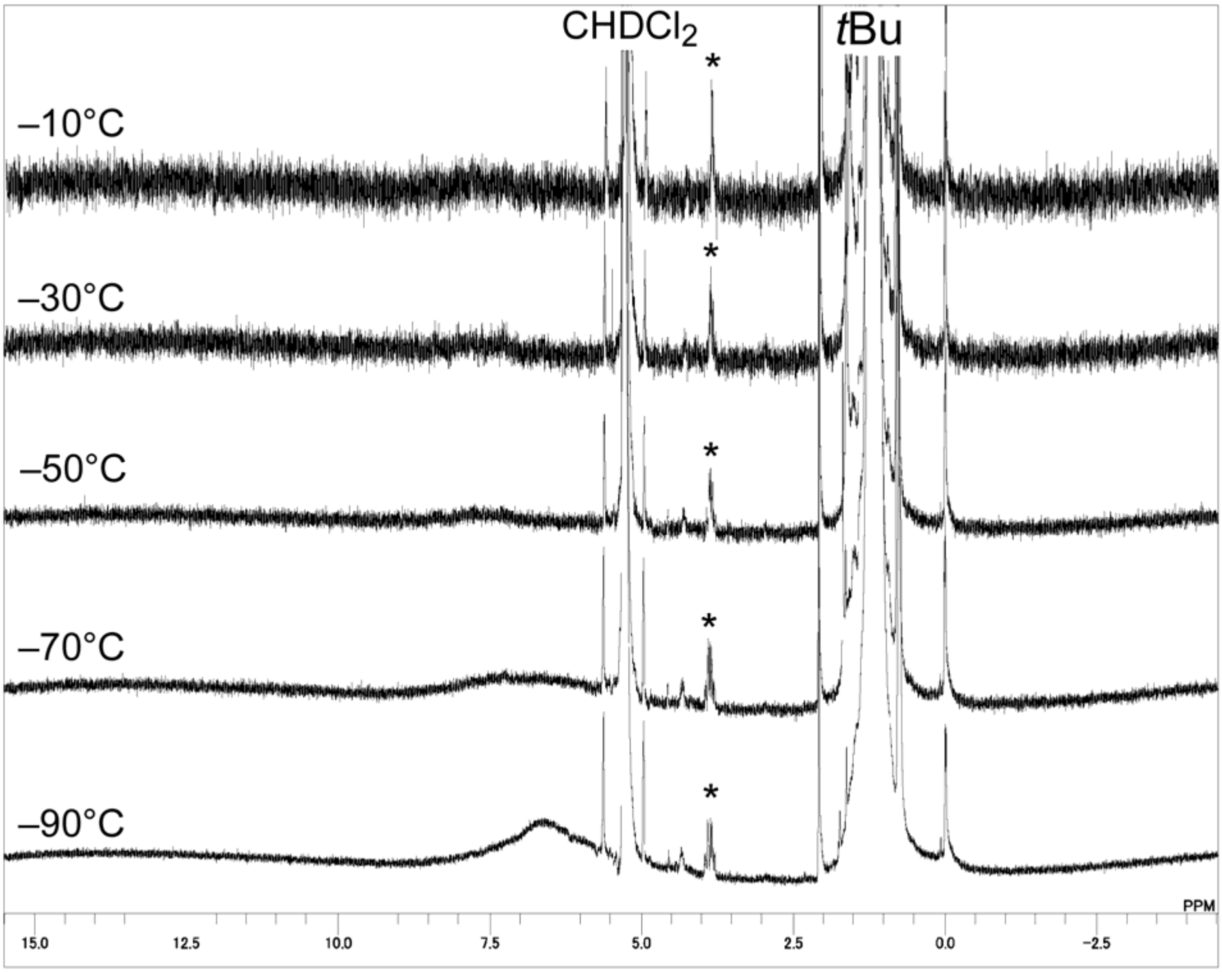

Figure S1. Variable temperature ^{1}H-NMR spectra of **1** in CD_2Cl_2. A small asterisk indicates the peaks of 1,2,3-trichloropropane.

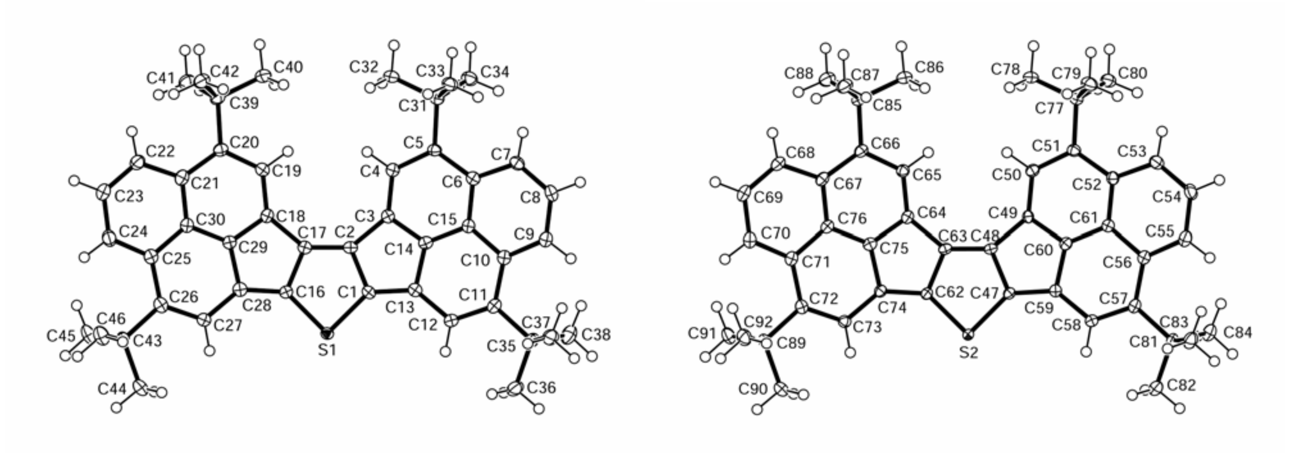

Figure S2.Ortep drawing of monomeric components in dimer A (left) and B (right) of **1**. Displacement ellipsoids are drawn at the 50% probability level.

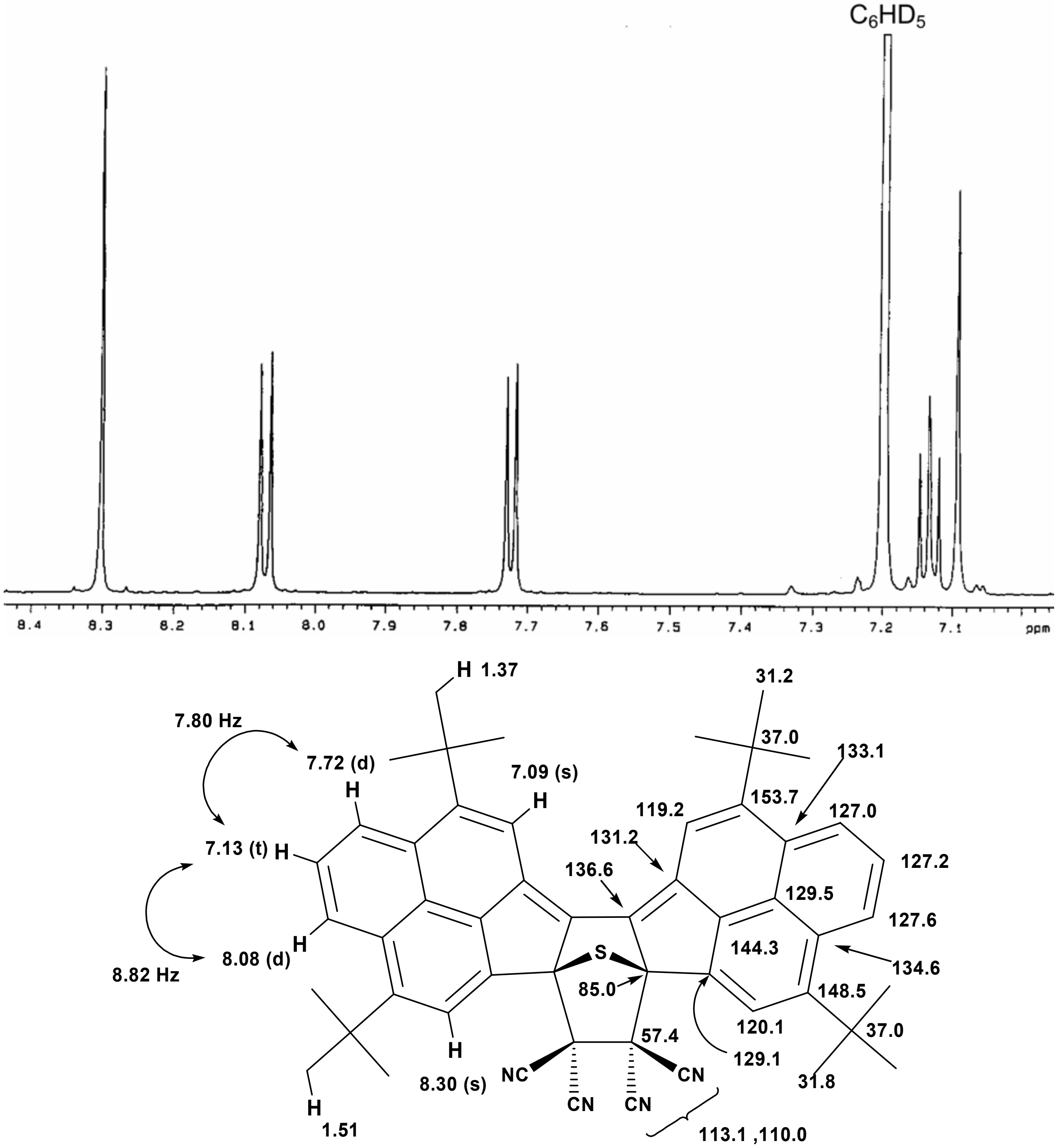

Figure S3. ^{1}H-NMR spectrum (upper) and the assignment of the ^{1}H and ^{13}C NMR signals (lower) of the TCNE adduct of **1**.

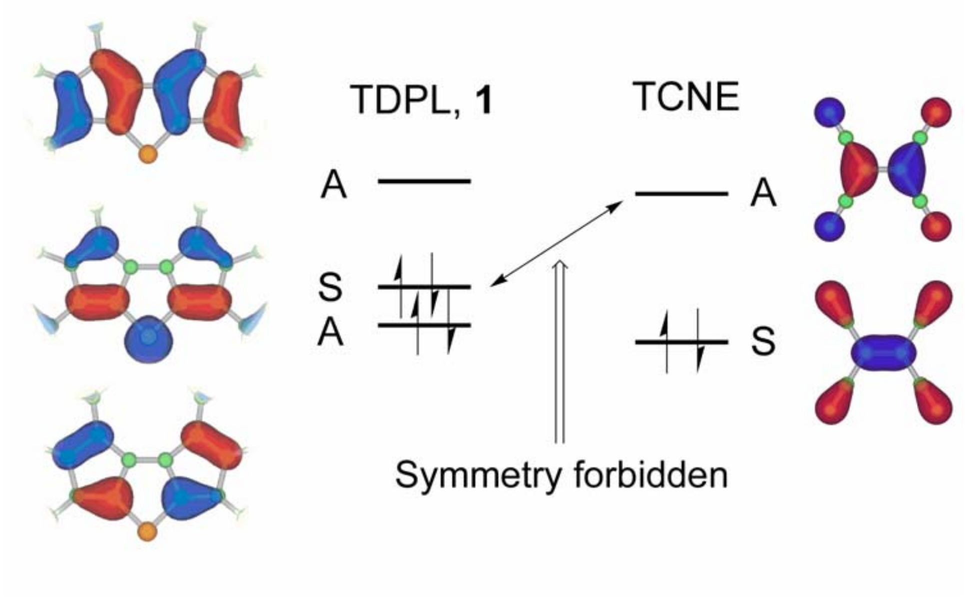

Figure S4. Schematic drawing of the molecular orbital interaction for the [10 + 2] cycloaddition reaction of **1** with TCNE.

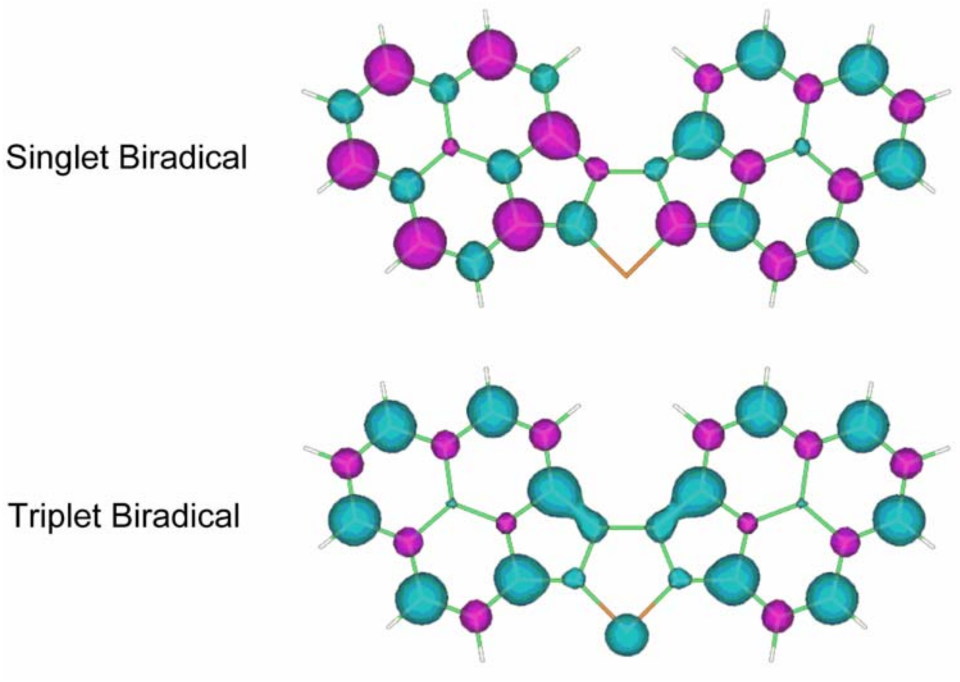

Figure S5. Spin densities of TDPL calculated by UB3LYP/6-31G**.

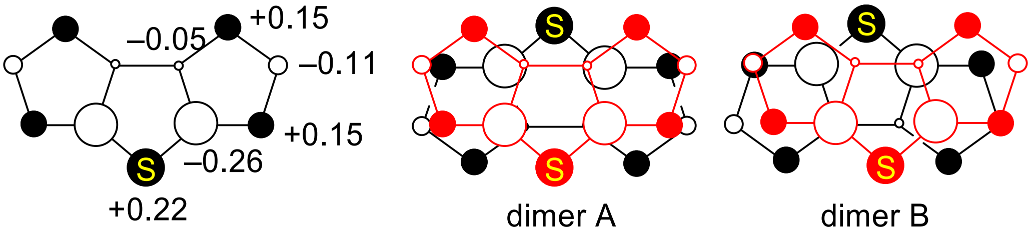

Figure S6. Mulliken charges on the dicyclopenta[*b*;*d*]thiophene moieties of **1** calculated by B3LYP/6-31G**.