Supporting Information

Phosphindole Fused Pyrrolo[3,2-*b*]pyrroles: New Single-Molecule Junction for Charge Transport

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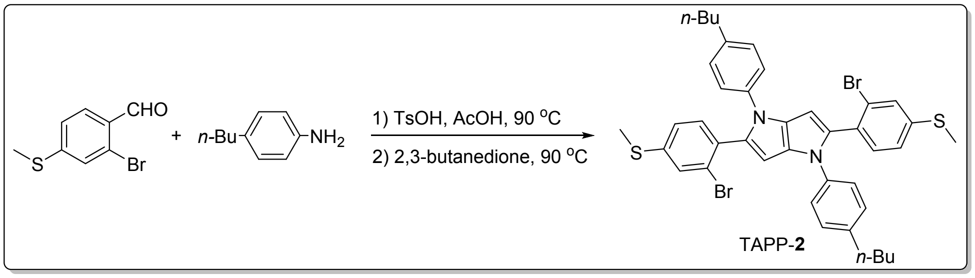
Experimental Procedures

General methods. All air- and moisture-sensitive manipulations were carried out routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DRX-300 Spectrometer. ^{1}H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. ^{31}P NMR downfield chemical shifts were expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. All coupling constants (J values) are reported in Hertz (Hz). HRMS were obtained on an Agilent 1290-6540 Q-Tof spectrometer by electrospray ionization (ESI). Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer. UV-Visible spectra were recorded at room temperature on a VARIAN Cary 5000 spectrophotometer. The emission spectra were recorded on a Hitachi Fluorescence spectrophotometer F-4600 or F-7000. The electrochemical studies were carried out under nitrogen using an RST3000 electrochemical workstation for cyclic voltammetry with the three-electrode configuration: the working electrode was a glassy carbon electrode, the reference electrode was a saturated calomel electrode and the counter-electrode was a platinum wire. All potential were referenced to the ferrocene/ferrocenium (Fe/Fe$^+$) couple. For the measurements, concentrations of 0.5 μM of the electroactive species were used in freshly distilled and degassed dichloromethane and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). Decomposition point determination were performed by using a thermogravimetric analysis (on a NETZSCH STA409 PC/PG TG-DTA) under dry argon flow at a heating rate of 10 °C/min. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer.

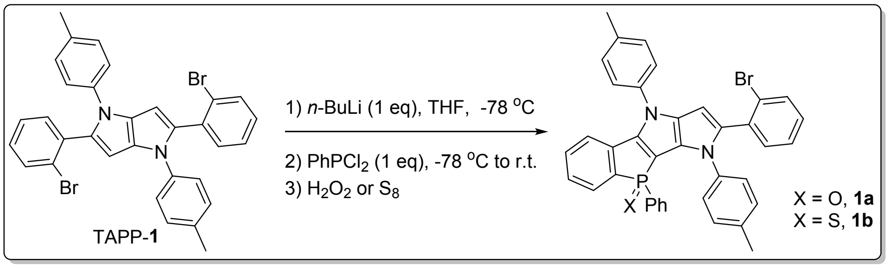
Synthesis of the starting materials. TAPP-**1** was synthesized according to the literature procedure[1].



*2,5-Bis(2-bromo-4-(methylthio)phenyl)-1,4-bis(4-butylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (TAPP-**2**)*. To a solution of 2-bromo-4-(methylthio)benzaldehyde (920 mg, 4 mmol) and 4-butylaniline (0.63 mL, 4 mmol) in glacial acetic acid (4 mL) was added TsOH monohydrate (76 mg, 0.4 mmol, 10 mol %). After stirring at 90 °C for 30 min, 2,3-butanedione (0.175 mL, 2 mmol) was added dropwise. The mixture was heated at 90 °C for 3 h. The mixture was diluted with ethyl acetate and the organic phase was washed with water, brine and dried with anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography (petroleum ether : CH_2Cl_2 = 5:1) on silica gel to give **2** as a yellow solid (390 mg, 25%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 7.2 Hz, 6H, CH_3), 1.29-1.41 (m, 4H, CH_2), 1.54-1.64 (m, 4H, CH_2), 2.47 (s, 6H, SCH_3), 2.58 (t, J = 7.8 Hz, 4H, CH_2), 6.43 (s, 2H, ArH), 7.03-7.14 (m, 12H, ArH), 7.41 (d, J = 1.8 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.98 ($2CH_3$), 15.47 ($2SCH_3$), 22.40 ($2CH_2$), 33.45 ($2CH_2$), 35.11 ($2CH_2$), 96.42 (2CH), 123.97 (4CH), 124.62 (2C), 124.67 (2CH), 128.85 (4CH), 129.69 (2C), 129.72 (2CH), 131.51 (2C), 132.88 (2CH), 132.94 (2C), 137.42 (2C), 139.37 (2C), 139.78 (2C); HRMS(ESI) Calcd. for $C_{40}H_{41}Br_2N_2S_2$ [M+H]$^+$ 771.1072, found 771.1066.

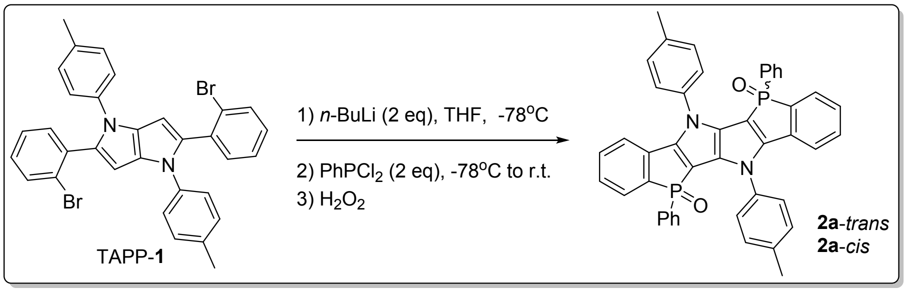
Synthesis of phosphindol-pyrrolo[3,2-*b*]pyrroles and bisphosphindol- pyrrolo[3,2-*b*]pyrroles.



To a solution of TAPP-**1** (600 mg, 1 mmol) in anhydrous tetrahydrofuran (THF) (30 mL) was added n-BuLi (0.63 mL, 1 mmol, 1.6 M in n-hexane) dropwise under nitrogen at -78 °C. After stirring at -78 °C for 30 min, $PhPCl_2$ (136 μL, 1 mmol) was added. The mixture was kept at -78 °C for 10 min and then warmed to room temperature. After stirring 2 h at rt, H_2O_2 (0.5 mL, 30 % aq) or S_8 (32 mg, 1 mmol) was added. Once the reaction was finished (monitored by TLC or ^{31}P NMR spectroscopy), the mixture was diluted with AcOEt, and the organic phase was washed with water, brine and dried with anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel and recrystallization.

*2-(2-Bromophenyl)-9-phenyl-1,4-di-p-tolyl-1,4-dihydrophosphindolo[3,2-b]pyrrolo[2,3-d]pyrrole 9-oxide (**1a**)*: purified by column chromatography (CH_2Cl_2 : AcOEt = 5:1) and recrystallization (from CH_2Cl_2/*n*-hexane/MeOH) to give a yellow solid (360 mg, 57 %). ^{31}P NMR (121 MHz, $CDCl_3$): δ = 19.2; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 6.20 (s, 1H, ArH), 6.80 (dd, J_1 = 7.5 Hz, J_2 = 3.3 Hz, 1H, ArH), 6.91-7.17 (m, 9H, ArH), 7.22-7.26 (m, 2H, ArH), 7.35-7.38 (m, 3H, ArH), 7.44-7.51 (m, 4H, ArH), 7.58 (dd, J_1 = 13.2 Hz, J_2 = 7.5 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.99 (CH_3), 21.32 (CH_3), 95.86 (CH), 100.80 (d, J_{CP} = 128.9 Hz, C), 119.13 (d, J_{CP} = 8.8 Hz, CH), 124.20 (C), 124.63 (2CH), 126.25 (2CH), 126.82 (d, J_{CP} = 12.1 Hz, CH), 126.90 (CH), 127.81 (d, J_{CP} = 4.5 Hz, C), 128.13(d, J_{CP} = 13.0 Hz, 2CH), 128.92 (CH), 129.65 (2CH), 129.99 (d, J_{CP} = 9.1 Hz, CH), 130.31 (2CH), 131.36 (d, J_{CP} = 11.2 Hz, 2CH), 131.49 (CH), 131.77 (d, J_{CP} = 110.5 Hz, C), 131.95 (CH), 132.98 (d, J_{CP} = 4.4 Hz, 2CH), 134.32 (C), 134.77 (C), 135.55 (C), 135.69 (C), 135.87 (d, J_{CP} = 8.6 Hz, C), 136.32 (C), 136.67 (d, J_{CP} = 13.7 Hz, C), 137.73 (d, J_{CP} = 107.6 Hz, C), 138.52 (C), 143.69 (d, J_{CP} = 34.1 Hz, C); HRMS(ESI) Calcd. for $C_{38}H_{29}BrN_2OP$ $[M+H]^+$ 639.1195, found 639.1205.

2-(2-bromophenyl)-9-phenyl-1,4-di-p-tolyl-1,4-dihydrophosphindolo[3,2-b]pyrrolo[2,3-d]pyrrole 9-sulfide (***1b***): purified by column chromatography (petroleum ether : CH_2Cl_2 = 1:1) and recrystallization (from CH_2Cl_2/*n*-hexane/MeOH) to give a yellow solid (440 mg, 68 %). ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.9; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 6.24 (d, *J* = 0.8 Hz, 1H, ArH), 6.86-6.94 (m, 3H, ArH), 7.01-7.22 (m, 9H, ArH), 7.31-7.39 (m, 3H, ArH), 7.48-7.56 (m, 4H, ArH), 7.63 (dd, J_1 = 15.0 Hz, J_2 = 6.0 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.06 (CH_3), 21.34 (CH_3), 95.87 (CH), 102.03 (d, J_{CP} = 110.8 Hz, C), 119.37 (d, J_{CP} = 8.3 Hz, CH), 124.17 (C), 125.49 (2CH), 126.18 (d, J_{CP} = 14.3 Hz, C), 126.27 (2CH), 126.87 (CH), 126.95 (d, J_{CP} = 12.0 Hz, CH), 127.42 (d, J_{CP} = 5.0 Hz, C), 128.10 (d, J_{CP} = 13.2 Hz, 2CH), 128.90 (CH), 129.53 (2CH), 129.78 (d, J_{CP} = 10.6 Hz, CH), 130.32 (2CH), 131.11 (d, J_{CP} = 12.2 Hz, 2CH), 131.29 (d, J_{CP} = 3.0 Hz, CH), 131.46 (d, J_{CP} = 1.7 Hz, CH), 131.71 (d, J_{CP} = 86.5 Hz, C), 133.01 (2CH), 134.23 (C), 135.16 (C), 135.67 (C), 135.80 (C), 136.10 (d, J_{CP} = 8.8 Hz, C), 136.11 (C), 138.51 (C), 140.63 (d, J_{CP} = 91.3 Hz, C), 142.23 (d, J_{CP} = 30.8 Hz, C); HRMS(ESI) Calcd. for $C_{38}H_{29}BrN_2PS$ $[M+H]^+$ 655.0967, found 655.0972

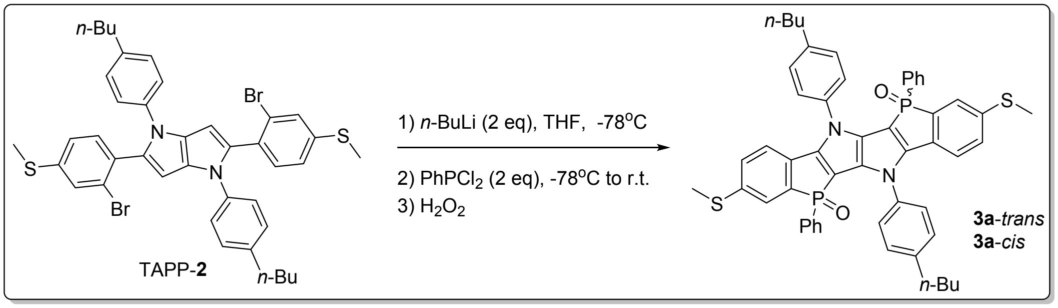


*6,12-Diphenyl-5,11-di-p-tolyl-5,11-dihydrophosphindolo[3,2-b]phosphindolo[2',3':4,5]pyrrolo[2,3-d]pyrrole 6,12-dioxide (**2a**-trans/cis)*. To a solution of TAPP-**1** (600 mg, 1 mmol) in anhydrous THF (30 mL) was added *n*-BuLi (1.25 mL, 2 mmol, 1.6 M in *n*-hexane) dropwise under nitrogen at -78 °C. After stirring at -78 °C for 30 min, $PhPCl_2$ (272 µL, 2 mmol) was added. The mixture was kept at -78 °C for 10 min and then warmed to room temperature. After stirring 2 h at rt, H_2O_2 (0.5 mL, 30 % aq) was added. The reaction was monitored by ^{31}P NMR spectroscopy after 30 min. The mixture was diluted with ethyl acetate, and the organic phase was washed with water, brine and dried with anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography (CH_2Cl_2 : AcOEt = 5:1 for **2a**-*trans* and AcOEt for **2a**-*cis*) and recrystallization (both from CH_2Cl_2/*n*-hexane/MeOH) to give **2a**-*trans* as a yellow solid (265 mg, 37 %) and **2a**-*cis* as a yellow solid (293 mg, 43 %).

2a-*trans*: ^{31}P NMR (121 MHz, $CDCl_3$): δ = 18.2; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 6H, CH_3), 6.78 (dd, J_1 = 7.2 Hz, J_2 = 3.0 Hz, 4H, ArH), 7.05-7.16 (m, 6H, ArH), 7.25-7.31 (m, 5H, ArH), 7.41-7.48 (m, 9H, ArH), 7.68 (br, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.23 ($2CH_3$), 101.43 (d, J_{CP} = 127.1 Hz, 2C), 119.39 (d, J_{CP} = 9.0 Hz, 2CH), 125.97 (4CH), 127.26 (d, J_{CP} = 12.1 Hz, 2CH), 128.22 (d, J_{CP} = 13.2 Hz, 4CH), 130.00 (d, J_{CP} = 9.4 Hz, 2CH), 130.38 (br, 4CH), 130.89 (d, J_{CP} = 111.1 Hz, 2C), 131.08 (d, J_{CP} = 11.3 Hz, 4CH), 131.71 (d, J_{CP} = 2.4 Hz, 2CH), 132.05 (2CH), 133.49-133.65 (m, 2C), 134.83 (2C), 136.08 (d, J_{CP} = 13.9 Hz, 2C), 137.33 (d, J_{CP} = 107.8 Hz, 2C), 138.71 (2C), 144.61 (d, J_{CP} = 33.0 Hz, 2C); HRMS(ESI) Calcd. for $C_{44}H_{33}N_2O_2P_2$ $[M+H]^+$ 683.2012, found 683.2021. Anal. Calcd. for $C_{44}H_{32}N_2O_2P_2$: C, 77.41; H, 4.72; N, 4.10, found: C, 77.06; H, 4.76; N, 3.88.

2a-*cis*: ^{31}P NMR (121 MHz, $CDCl_3$): δ = 18.2; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48 (s, 6H, CH_3), 6.79 (dd, J_1 = 7.2 Hz, J_2 = 3.0 Hz, 4H, ArH), 7.07-7.18 (m, 6H, ArH), 7.23-7.29 (m, 5H, ArH), 7.37-7.51 (m, 9H, ArH), 7.71 (br, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.31 ($2CH_3$), 101.85 (d, J_{CP} = 127.6 Hz, 2C), 119.50 (d, J_{CP} = 9.1 Hz, 2CH), 126.17 (br, 4CH), 127.26 (d, J_{CP} = 11.9 Hz, 2CH), 128.18 (d, J_{CP} = 13.1 Hz, 4CH), 130.16 (d, J_{CP} = 9.4 Hz, 2CH), 131.08 (d, J_{CP} = 11.3 Hz, 4CH), 131.43 (d, J_{CP} = 111.0 Hz, 2C), 131.62 (d, J_{CP} = 2.5 Hz, 2CH), 132.16 (2CH), 133.18-133.36 (m, 2C), 134.88 (2C), 136.37 (d, J_{CP} = 14.0 Hz, 2C), 136.96 (d, J_{CP} =

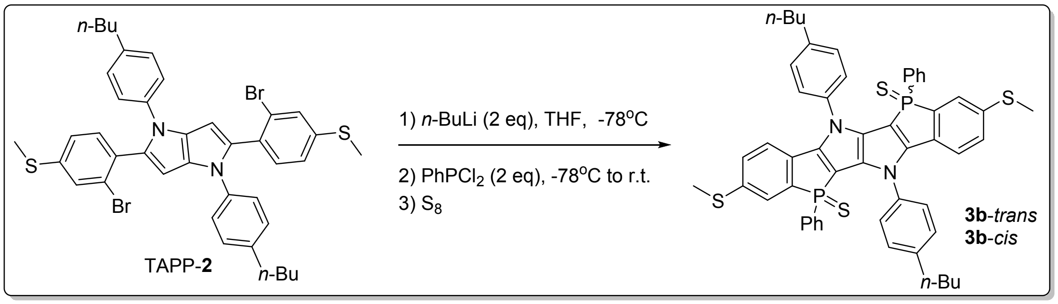
107.9 Hz, 2C), 138.83 (2C), 144.14 (d, J_{CP} = 33.6 Hz, 2C), one CH broad peak missing; HRMS(ESI) Calcd. for $C_{44}H_{33}N_2O_2P_2$ [M+H]$^+$ 683.2012, found 683.2014. Anal. Calcd. for $C_{44}H_{32}N_2O_2P_2$: C, 77.41; H, 4.72; N, 4.10, found: C, 77.13; H, 4.74; N, 3.96.



*5,11-Bis(4-butylphenyl)-2,8-bis(methylthio)-6,12-diphenyl-5,11-dihydrophosphindolo[3,2-b]phosphindolo[2',3':4,5]pyrrolo[2,3-d]pyrrole 6,12-dioxide (**3a**-trans/cis)*: To a solution of TAPP-**2** (385 mg, 0.5 mmol) in anhydrous THF (15 mL) was added n-BuLi (0.63 mL, 1 mmol, 1.6 M in n-hexane) dropwise under nitrogen at -78 °C. After stirring at -78 °C for 30 min, $PhPCl_2$ (136 µL, 1 mmol) was added. The mixture was kept at -78 °C for 10 min and then warmed to room temperature. After stirring 2 h at rt, H_2O_2 (0.12 mL, 1 mmol, 30 % aq) was added. The reaction was monitored by ^{31}P NMR spectroscopy after 30 min. The mixture was diluted with ethyl acetate, and the organic phase was washed with water, brine and dried with anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography (CH_2Cl_2 : AcOEt = 5:1 for **3a**-*trans* and AcOEt for **3a**-*cis*) and recrystallization (both from CH_2Cl_2/n-hexane/MeOH) to give **3a**-*trans* as a yellow solid (93 mg, 22 %) and **3a**-*cis* as a yellow solid (113 mg, 26 %).

3a-*trans*: ^{31}P NMR (121 MHz, $CDCl_3$): δ = 18.3; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, J = 7.2 Hz, 6H, CH_3), 1.35-1.47 (m, 4H, CH_2), 1.60-1.70 (m, 4H, CH_2), 2.37 (s, 6H, SCH_3), 2.67 (t, J = 7.8 Hz, 4H, CH_2), 6.69 (dd, J_1 = 8.1 Hz, J_2 = 3.6 Hz, 2H, ArH), 6.98 (d, J = 8.1 Hz, 6H, ArH), 7.27-7.43 (m, 14H, ArH), 7.69 (br, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.05 ($2CH_3$), 15.70 ($2SCH_3$), 22.38 ($2CH_2$), 33.54 ($2CH_2$), 35.30 ($2CH_2$), 100.70 (d, J_{CP} = 128.3 Hz, 2C), 119.51 (d, J_{CP} = 9.5 Hz, 2CH), 125.82 (4CH), 127.78 (d, J_{CP} = 10.3 Hz, 2CH), 128.29 (d, J_{CP} = 13.3 Hz, 4CH), 129.45 (2CH), 130.72 (d, J_{CP} = 111.4 Hz, 2C), 131.05 (d, J_{CP} = 11.5 Hz, 4CH), 131.77 (2CH), 132.70 (d, J_{CP} = 13.7 Hz, 2C), 133.22-133.39 (m, 2C), 134.84 (2C), 138.22 (d, J_{CP} = 12.8 Hz, 2C), 138.41 (d, J_{CP} = 105.9 Hz, 2C), 143.65 (2C), 144.41 (d, J_{CP} = 32.6 Hz, 2C), one CH broad peak missing; HRMS(ESI) Calcd. for $C_{52}H_{49}N_2O_2P_2S_2$ [M+H]$^+$ 859.2705, found 859.2700. Anal. Calcd. for $C_{52}H_{48}N_2O_2P_2S_2$: C, 72.71; H, 5.63; N, 3.26, found: C, 72.60; H, 5.86; N, 2.92.

3a-*cis*: ^{31}P NMR (121 MHz, $CDCl_3$): δ = 18.4; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, J = 7.2 Hz, 6H, CH_3), 1.39-1.51 (m, 4H, CH_2), 1.65-1.75 (m, 4H, CH_2), 2.38 (s, 6H, SCH_3), 2.72 (t, J = 7.5 Hz, 4H, CH_2), 6.70 (dd, J_1 = 8.1 Hz, J_2 = 3.6 Hz, 2H, ArH), 7.01 (d, J = 8.1 Hz, 6H, ArH), 7.23-7.44 (m, 14H, ArH), 7.69 (br, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.05 ($2CH_3$), 15.73 ($2SCH_3$), 22.43 ($2CH_2$), 33.62 ($2CH_2$), 35.35 ($2CH_2$), 101.16 (d, J_{CP} = 128.6 Hz, 2C), 119.67 (d, J_{CP} = 9.4 Hz, 2CH), 125.94 (br, 4CH), 127.89 (d, J_{CP} = 10.0 Hz, 2CH), 128.25 (d, J_{CP} = 13.3 Hz, 4CH), 129.59 (2CH), 131.04 (d, J_{CP} = 11.4 Hz, 4CH), 131.18 (d, J_{CP} = 111.4 Hz, 2C), 131.73 (2CH), 132.98 (d, J_{CP} = 13.8 Hz, 2C), 132.93-133.10 (m, 2C), 134.88 (2C), 138.04 (d, J_{CP} = 106.1 Hz, 2C), 138.30 (d, J_{CP} = 12.9 Hz, 2C), 143.81 (2C), 143.92 (d, J_{CP} = 33.0 Hz, 2C), one CH broad peak missing; HRMS(ESI) Calcd. for $C_{52}H_{49}N_2O_2P_2S_2$ [M+H]$^+$ 859.2705, found 859.2704. Anal. Calcd. for $C_{52}H_{48}N_2O_2P_2S_2$: C, 72.71; H, 5.63; N, 3.26, found: C, 72.80; H, 5.92; N, 2.94.



*5,11-Bis(4-butylphenyl)-2,8-bis(methylthio)-6,12-diphenyl-5,11-dihydrophosphindolo[3,2-b]phosphindolo[2',3':4,5]pyrrolo[2,3-d]pyrrole 6,12-disulfide (**3b**-trans/cis)*: To a solution of TAPP-**2** (385 mg, 0.5 mmol) in anhydrous THF (15 mL) was added *n*-BuLi (0.63 mL, 1 mmol, 1.6 M in *n*-hexane) dropwise under nitrogen at -78 °C. After stirring at -78 °C for 30 min, $PhPCl_2$ (136 µL, 1 mmol) was added. The mixture was kept at -78 °C for 10 min and then warmed to room temperature. After stirring 2 h at rt, S_8 powder (32 mg, 1 mmol) was added. The reaction was monitored by ^{31}P NMR spectroscopy after 2 h. The mixture was diluted with ethyl acetate, and the organic phase was washed with water, brine and dried with anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography (petroleum ether : CH_2Cl_2 = 3:1 for **3b**-*trans* and petroleum ether : CH_2Cl_2 = 1:1 for **3b**-*cis*) and recrystallization (both from CH_2Cl_2/*n*-hexane) to give **3b**-*trans* as a yellow solid (120 mg, 30 %) and **3b**-*cis* as a yellow solid (98 mg, 24 %).

3b-*trans*: ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.1; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (t, *J* = 7.2 Hz, 6H, CH_3), 1.38-1.50 (m, 4H, CH_2), 1.63-1.73 (m, 4H, CH_2), 2.38 (s, 6H, SCH_3), 2.72 (t, *J* = 7.5 Hz, 4H, CH_2), 6.71 (dd, J_1 = 8.1 Hz, J_2 = 3.6 Hz, 2H, ArH), 6.84-7.06 (m, 6H, ArH), 7.24-7.44 (m, 10H, ArH), 7.51 (dd, J_1 = 15.0 Hz, J_2 = 7.2 Hz, 4H, ArH), 7.84 (br, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.10 ($2CH_3$), 15.70 ($2SCH_3$), 22.31 ($2CH_2$), 33.64 ($2CH_2$), 35.34 ($2CH_2$), 102.31 (d, J_{CP} = 110.8 Hz, 2C), 119.72 (d, J_{CP} = 9.1 Hz, 2CH), 126.04 (4CH), 127.28 (d, J_{CP} = 12.0 Hz, 2CH), 128.26 (d, J_{CP} = 13.7 Hz, 4CH), 129.06 (2CH), 130.60 (d, J_{CP} = 86.9 Hz, 2C), 130.97 (d, J_{CP} = 12.7 Hz, 4CH), 131.66 (2CH), 131.90 (d, J_{CP} = 11.5 Hz, 2C), 132.81-132.99 (m, 2C), 134.73 (2C), 138.43 (d, J_{CP} = 13.7 Hz, 2C), 141.50 (d, J_{CP} = 89.1 Hz, 2C), 142.95 (d, J_{CP} = 29.3 Hz, 2C), 143.82 (2C), one CH broad peak missing; HRMS(ESI) Calcd. for $C_{52}H_{49}N_2P_2S_4$ $[M+H]^+$ 891.2248, found 891.2252. Anal. Calcd. for $C_{52}H_{48}N_2P_2S_4$: C, 70.09; H, 5.43; N, 3.14, found: C, 70.10; H, 5.55; N, 2.76.

3b-*cis*: ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.4; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.2 Hz, 6H, CH_3), 1.40-1.53 (m, 4H, CH_2), 1.67-1.77 (m, 4H, CH_2), 2.38 (s, 6H, SCH_3), 2.75 (t, *J* = 7.5 Hz, 4H, CH_2), 6.71 (dd, J_1 = 8.1 Hz, J_2 = 3.6 Hz, 2H, ArH), 6.89-7.06 (m, 6H, ArH), 7.21-7.27 (m, 4H, ArH), 7.32-7.51 (m, 10H, ArH), 7.86 (br, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.07 ($2CH_3$), 15.77 ($2SCH_3$), 22.34 ($2CH_2$), 33.69 ($2CH_2$), 35.38 ($2CH_2$), 102.78 (d, J_{CP} = 110.2 Hz, 2C), 119.78 (d, J_{CP} = 9.1 Hz, 2CH), 127.54 (d, J_{CP} = 11.7 Hz, 2CH), 128.19 (d, J_{CP} = 13.6 Hz, 4CH), 129.21 (2CH), 130.89 (d, J_{CP} = 12.5 Hz, 4CH), 131.46 (d, J_{CP} = 87.0 Hz, 2C), 131.49 (2CH), 132.20 (d, J_{CP} = 11.5 Hz, 2C), 132.68-132.86 (m, 2C), 134.80 (2C), 138.40 (d, J_{CP} = 13.7 Hz, 2C), 141.17 (d, J_{CP} = 89.3 Hz, 2C), 142.60 (d, J_{CP} = 29.4 Hz, 2C), 143.96 (2C), two CH broad peaks missing; HRMS(ESI) Calcd. for $C_{52}H_{49}N_2P_2S_4$ $[M+H]^+$ 891.2248, found 891.2251. Anal. Calcd. for $C_{52}H_{48}N_2P_2S_4$: C, 70.09; H, 5.43; N, 3.14, found: C, 69.93; H, 5.71; N, 2.85.

Single-molecule conductance measurements. The single-molecule junctions were fabricated using scanning tunneling microscope break junction (STM-BJ) technique. We carried out the STM-BJ experiments as following procedures. Oxidized Si substrate covered by 200 nm evaporated Au with 20 nm Cr as adhesion layer was chosen as the bottom electrode. A gold wire with a diameter of 0.25 mm (99.99%, Jiaming, Beijing) was flame-annealed and fixed on the STM-BJ setup as the top electrode. The electrodes were immersed in the solution with a concentration of 0.1 mM, in mixed solvent of 1:4 (*v/v*) tetrahydrofuran (THF, Aldrich, p.a.) and 1,3,5-trimethylbenzene (TMB, Aldrich, p.a.). The Au/molecule/Au junctions were formed and broken by the approaching and leaving of the top electrode. Recorded conductance values were analyzed by a lab-developed program (WA-BJ code) to construct the conductance histogram, 2D conductance-distance histogram and the relative distance distribution.[2]

Results and Discussion

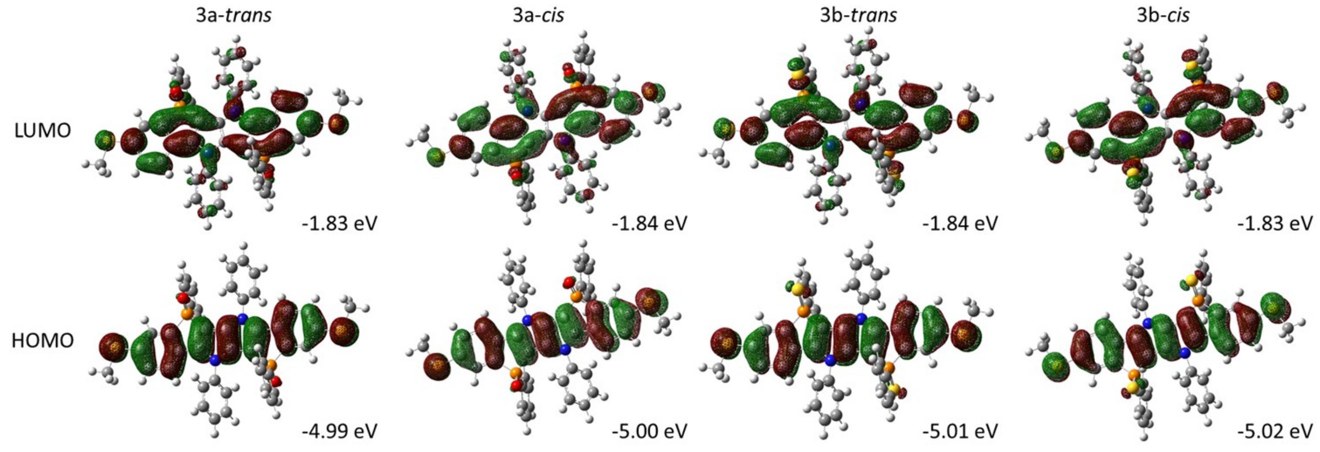


Figure S1. Calculated molecular orbits (MOs) of **3a-***trans*/*cis* and **3b-***trans*/*cis*[3].

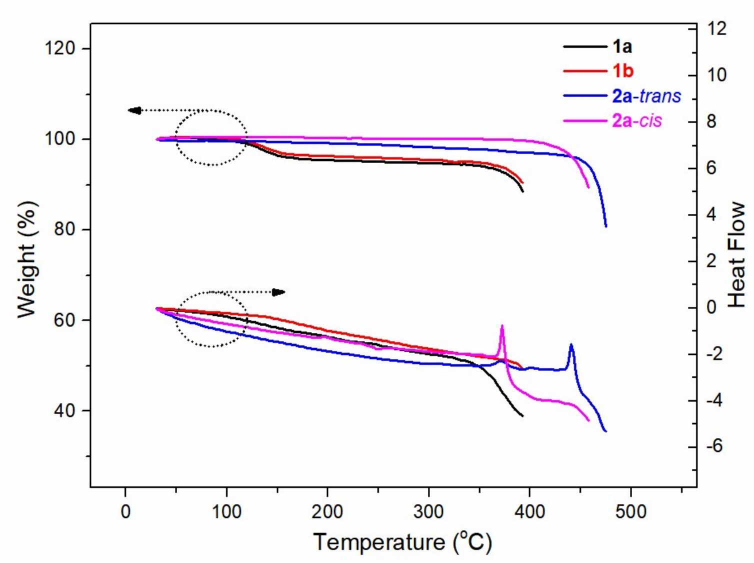


Figure S2. TGA (left Y axis) and DSC (right Y axis) of **1a**, **1b** and **2a**-*trans*/*cis* under argon at a heating rate of 10 °C/min.

Table S1. Melting point and decomposition temperature of **1a**, **1b**, **2a**-*trans* and **2a**-*cis*.

Compd	T_m[°C][a]	T_d[°C][b]
1a	–[c]	341
1b	–[c]	362
2a-*trans*	441	477
2a-*cis*	372	446

[a] Melting point were performed by DSC. [b] Decomposition temperature were defined as 5% of weight loss under argon, 10 °C/min. [c] Not observed.

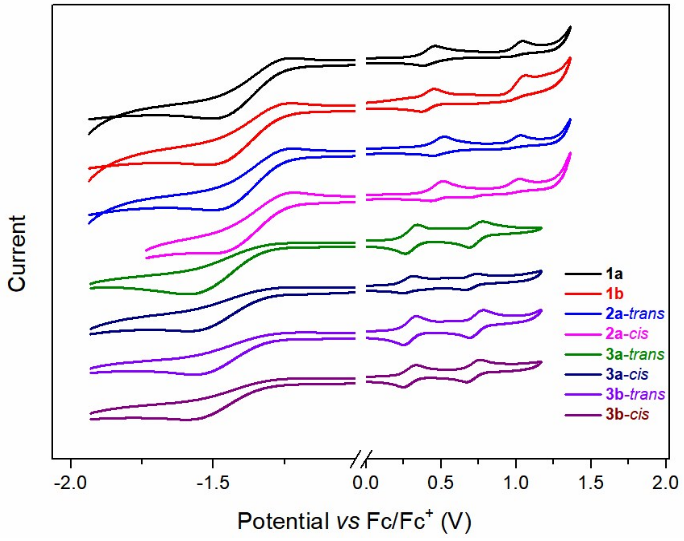


Figure S3. Cyclic voltammograms of **1a**, **1b**, **2a**-*trans*/*cis*, **3a**-*trans*/*cis* and **3b**-*trans*/*cis* (*vs* Fc/Fc⁺, 0.5 μM in CH_2Cl_2, scan rate: 100 mV/s).

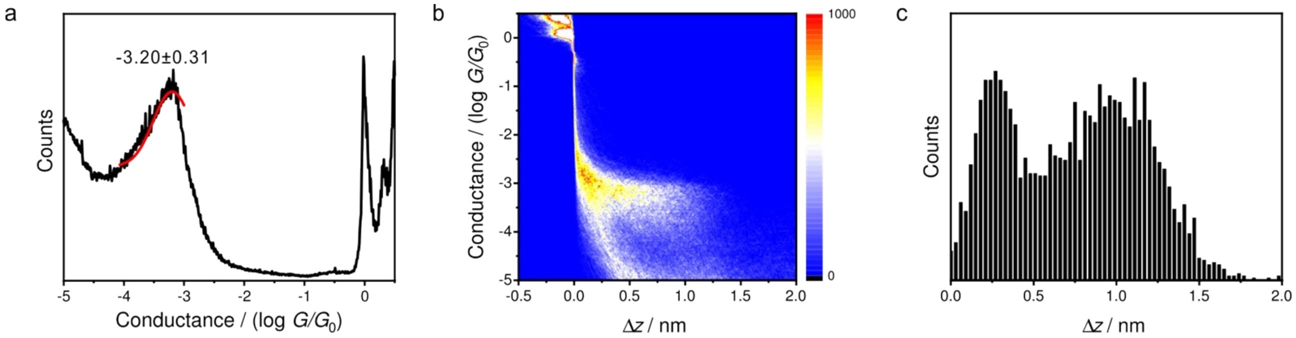


Figure S4. (a) Conductance histogram, (b) 2D conductance-distance histogram and (c) the relative distance distribution of **3a**-*trans* junctions.

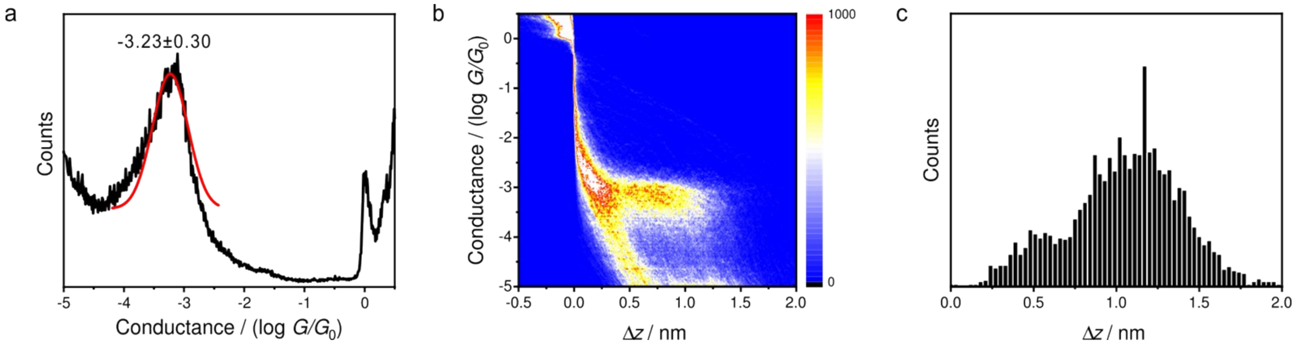


Figure S5. (a) Conductance histogram, (b) 2D conductance-distance histogram and (c) the relative distance distribution of **3a**-*cis* junctions.

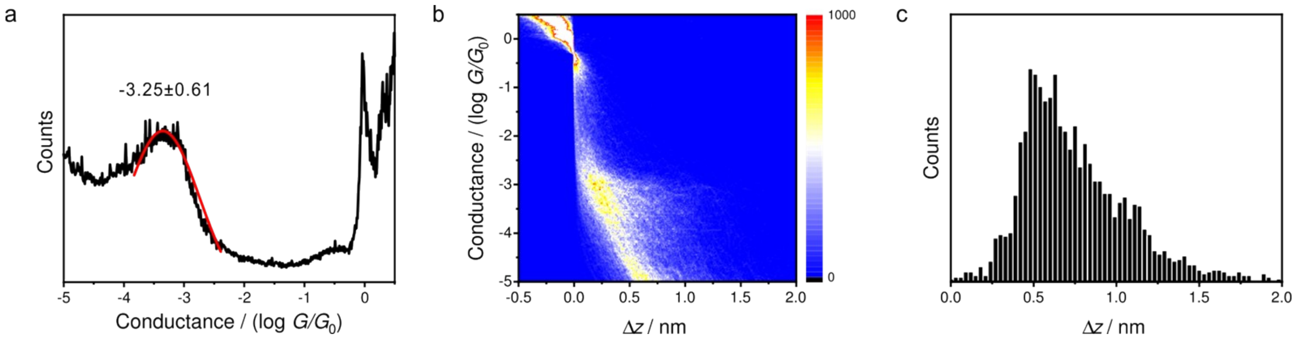


Figure S6. (a) Conductance histogram, (b) 2D conductance-distance histogram and (c) the relative distance distribution of **3b**-*trans* junctions.

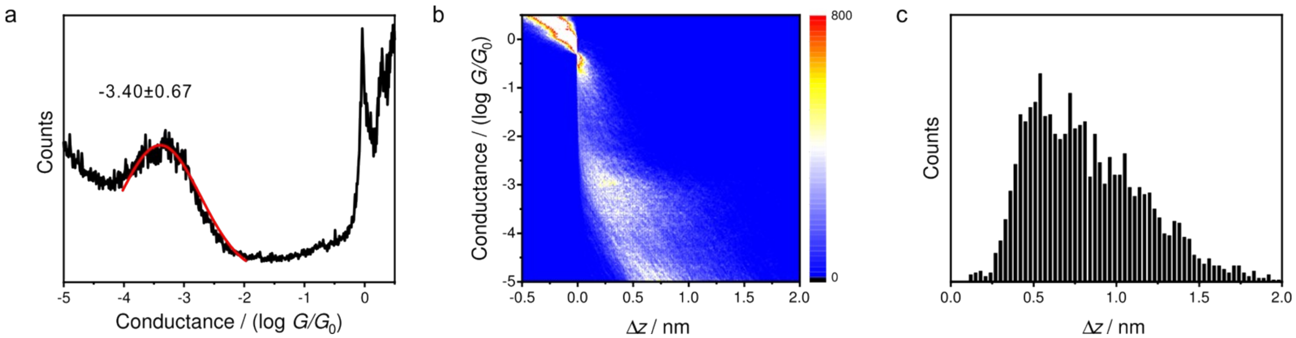


Figure S7. (a) Conductance histogram, (b) 2D conductance-distance histogram and (c) the relative distance distribution of **3b**-*cis* junctions.

Calculated conductance of 3a-*trans/cis* and 3b-*trans/cis*. The structures of molecules in vacuum are optimized to a force threshold of 0.01eV/Å. The structures of the optimized molecules are shown in Figure S8. Then the optimized molecule is placed between two gold electrodes as depicted in Figure S9. The edge sulfur atoms near the gold electrodes are located at the top site of the [111] surface of the gold electrodes. The distance between the edge sulfur atoms and the nearest gold atoms are set to be 3.9 Å to fit the average conductance in the experiment. The charge transport through the device is modeled as a coherent tunneling. The transmission can be calculated from the Landauer-Büttiker formalism $T(E) = Tr[\Gamma_L G(E) \Gamma_R G^+(E)]$, where $G(E)$ and $G^+(E)$ are retarded and advanced Green's function of the scattering region. $\Gamma_{L/R}$ denotes the coupling matrix between the scattering region and the left/right electrode. The generalized gradient approximation with the Perdew-Burke-Ernzerhof parametrization is adopted for the exchange correlation functional and double zeta polarized basis sets are used for all the atoms. The k-mesh of 1×1×100 are used in the transport calculation. All the calculation are performed by the Atomistic Tookit[4,5] version 2017.2. The conductance is calculated as $G = \frac{2e}{h} T(E_{fermi})$, where $\frac{2e}{h}$ is the quantum conductance and E_{fermi} is the Fermi energy of the gold electrode. The calculated conductance is listed in Table S2.

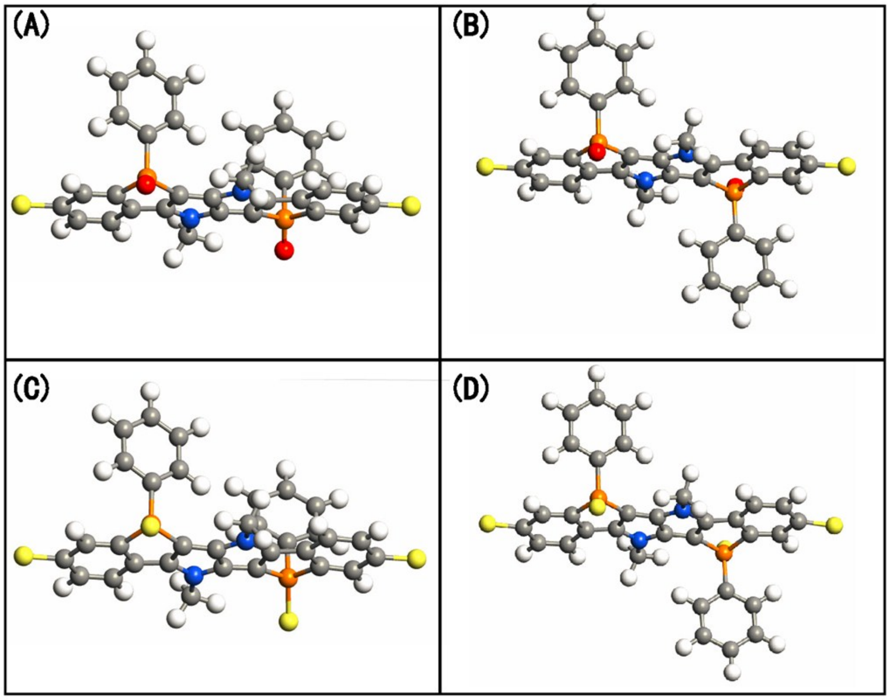


Figure S8. The optimized structures of the molecule: (A) **3a**-*cis*, (B) **3a**-*trans*, (C) **3b**-*cis*, (D) **3b**-*trans*.

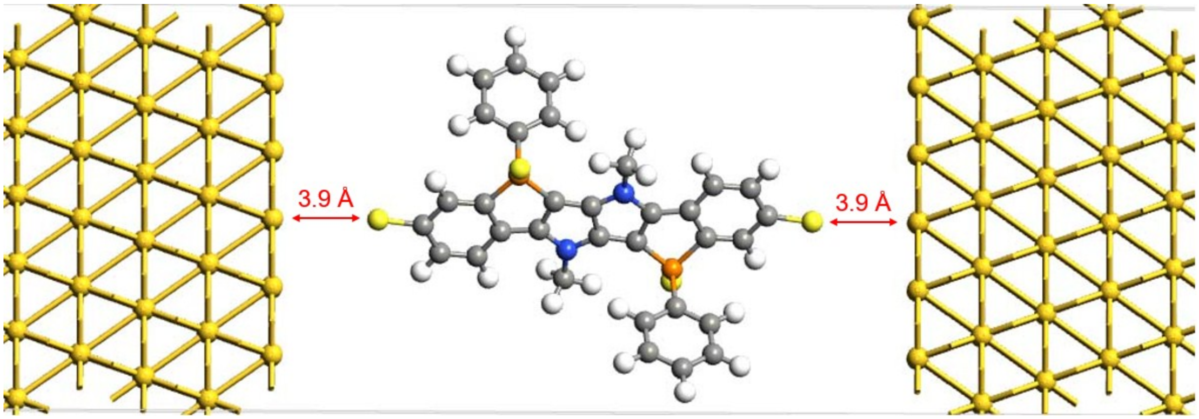


Figure S9. Structures of the gold-molecule-gold simulation models. To reduce the computational cost, the long butyl chains in the molecules were omitted. The initial Au-S distance is 3.9 Å and the adsorption configuration is "top" site of Au (111) surface.

Table S2. The calculated transmission and its logarithm at the Fermi level of the gold electrode.

Compd	T_{cal}	$\log(T)_{cal}$	$\log(T)_{exp}$
3a-*trans*	0.00179	-2.75	-3.20
3a-*cis*	0.00149	-2.83	-3.23
3b-*trans*	0.00166	-2.78	-3.25
3b-*cis*	0.00122	-2.91	-3.40

X-ray Crystallographic Studies of Compound 2a-*trans* and 2a-*cis*

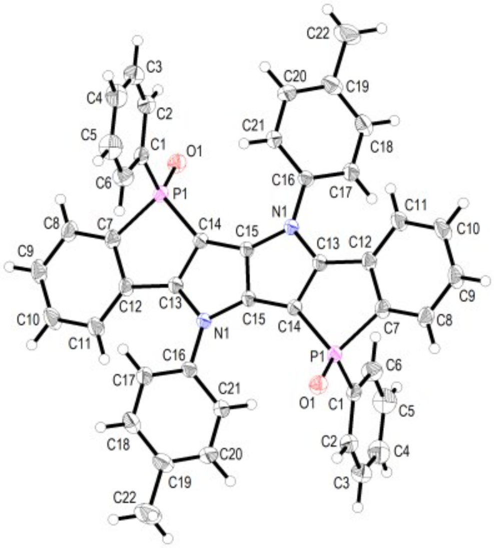


Figure S10. X-ray crystal structure of **2a**-*trans*. CCDC reference number: 1553255.

Table S3. Crystal data and structure refinement for **2a**-trans.

Identification code	1553255
Empirical formula	$C_{44}H_{32}N_2O_2P_2$
Formula weight	682.65
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.4342(6)
b/Å	9.2098(7)
c/Å	12.2670(9)
α/°	68.985(7)
β/°	88.068(6)
γ/°	74.661(7)
Volume/Å^3	855.82(12)

Z	1
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	1.483
F(000)	356.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.738 to 134.148
Index ranges	$-10 \le h \le 9$, $-9 \le k \le 10$, $-9 \le l \le 14$
Reflections collected	6012
Independent reflections	3046 [R_{int} = 0.0317, R_{sigma} = 0.0456]
Data/restraints/parameters	3046/0/227
Goodness-of-fit on F^2	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0458, wR_2 = 0.1135
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.1246
Largest diff. peak/hole / e Å^{-3}	0.36/-0.30

Table S4. Bond Lengths for **2a**-*trans*.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.386(3)	C13	N1	1.381(3)
C1	C6	1.387(3)	C14	C15	1.406(3)
C1	P1	1.803(2)	C14	P1	1.787(2)
C2	C3	1.386(4)	C15	C15^1	1.384(4)
C3	C4	1.367(4)	C15	N1^1	1.390(3)
C4	C5	1.382(4)	C16	C17	1.387(3)
C5	C6	1.381(4)	C16	C21	1.378(3)
C7	C8	1.373(3)	C16	N1	1.435(3)
C7	C12	1.408(3)	C17	C18	1.383(3)
C7	P1	1.818(2)	C18	C19	1.381(4)
C8	C9	1.390(4)	C19	C20	1.384(4)
C9	C10	1.375(4)	C19	C22	1.517(4)
C10	C11	1.398(3)	C20	C21	1.380(3)
C11	C12	1.388(3)	N1	C15^1	1.390(3)
C12	C13	1.473(3)	O1	P1	1.4761(16)
C13	C14	1.389(3)			

Table S5. Bond Angles for **2a**-*trans*.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	119.5(2)	C15	C14	P1	144.74(17)
C2	C1	P1	119.16(19)	C15^{1}	C15	C14	108.9(2)
C6	C1	P1	121.35(19)	C15^{1}	C15	N1^{1}	108.4(2)
C1	C2	C3	120.0(3)	N1^{1}	C15	C14	142.7(2)
C4	C3	C2	120.1(3)	C17	C16	N1	120.4(2)
C3	C4	C5	120.5(3)	C21	C16	C17	120.0(2)
C6	C5	C4	119.7(3)	C21	C16	N1	119.5(2)
C5	C6	C1	120.2(3)	C18	C17	C16	119.5(2)
C8	C7	C12	121.4(2)	C19	C18	C17	121.2(2)
C8	C7	P1	126.40(19)	C18	C19	C20	118.2(2)
C12	C7	P1	111.93(16)	C18	C19	C22	120.3(3)
C7	C8	C9	118.8(2)	C20	C19	C22	121.5(3)
C10	C9	C8	120.4(2)	C21	C20	C19	121.5(2)
C9	C10	C11	121.4(2)	C16	C21	C20	119.6(2)
C12	C11	C10	118.4(2)	C13	N1	C15^{1}	106.65(17)
C7	C12	C13	109.9(2)	C13	N1	C16	128.56(17)
C11	C12	C7	119.5(2)	C15^{1}	N1	C16	124.07(17)
C11	C12	C13	130.4(2)	C1	P1	C7	108.67(10)
C14	C13	C12	116.71(19)	C14	P1	C1	106.68(10)
N1	C13	C12	132.6(2)	C14	P1	C7	91.44(10)
N1	C13	C14	110.67(18)	O1	P1	C1	111.71(10)
C13	C14	C15	105.35(19)	O1	P1	C7	116.13(10)
C13	C14	P1	109.57(15)	O1	P1	C14	120.18(10)

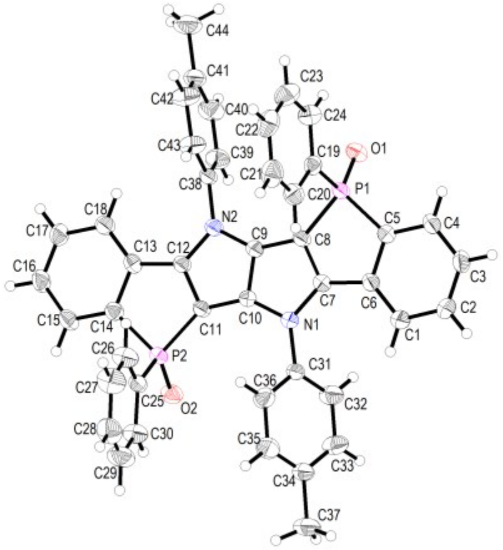


Figure S11. X-ray crystal structure of **2a**-*cis*. CCDC reference number: 1578987.

Table S6. Crystal data and structure refinement for **2a**-*cis*.

Identification code	1578987
Empirical formula	$C_{45}H_{34}Cl_2N_2O_2P_2$
Formula weight	767.58
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.2229(5)
b/Å	10.3244(7)
c/Å	19.8604(11)
α/°	91.554(5)
β/°	104.445(4)
γ/°	108.309(5)
Volume/Å^3	1914.41(19)
Z	2
ρ_{calc}g/cm^3	1.332
μ/mm^{-1}	2.639
F(000)	796.0
Crystal size/mm^3	0.2 × 0.16 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.082 to 134.152

Index ranges	-8 ≤ h ≤ 12, -12 ≤ k ≤ 12, -23 ≤ l ≤ 23
Reflections collected	13658
Independent reflections	6833 [R_{int} = 0.0344, R_{sigma} = 0.0520]
Data/restraints/parameters	6833/0/480
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1767
Final R indexes [all data]	R_1 = 0.0870, wR_2 = 0.2006
Largest diff. peak/hole / e Å^{-3}	0.43/-0.74

Table S7. Bond Lengths for **2a**-*cis*.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.401(5)	C21	C22	1.382(7)
C1	C6	1.378(5)	C22	C23	1.367(7)
C2	C3	1.370(5)	C23	C24	1.379(5)
C3	C4	1.376(5)	C25	C26	1.366(5)
C4	C5	1.381(4)	C25	C30	1.383(5)
C5	C6	1.405(4)	C25	P2	1.815(3)
C5	P1	1.822(3)	C26	C27	1.382(6)
C6	C7	1.475(4)	C27	C28	1.373(7)
C7	C8	1.391(4)	C28	C29	1.338(7)
C7	N1	1.378(4)	C29	C30	1.384(6)
C8	C9	1.406(4)	C31	C32	1.378(5)
C8	P1	1.786(3)	C31	C36	1.354(5)
C9	C10	1.390(4)	C31	N1	1.434(4)
C9	N2	1.384(4)	C32	C33	1.375(5)
C10	C11	1.408(4)	C33	C34	1.383(6)
C10	N1	1.393(4)	C34	C35	1.356(6)
C11	C12	1.391(4)	C34	C37	1.514(5)
C11	P2	1.787(3)	C35	C36	1.385(6)
C12	C13	1.463(4)	C38	C39	1.369(5)
C12	N2	1.366(4)	C38	C43	1.367(5)
C13	C14	1.419(4)	C38	N2	1.443(4)
C13	C18	1.380(5)	C39	C40	1.377(5)
C14	C15	1.380(4)	C40	C41	1.376(6)

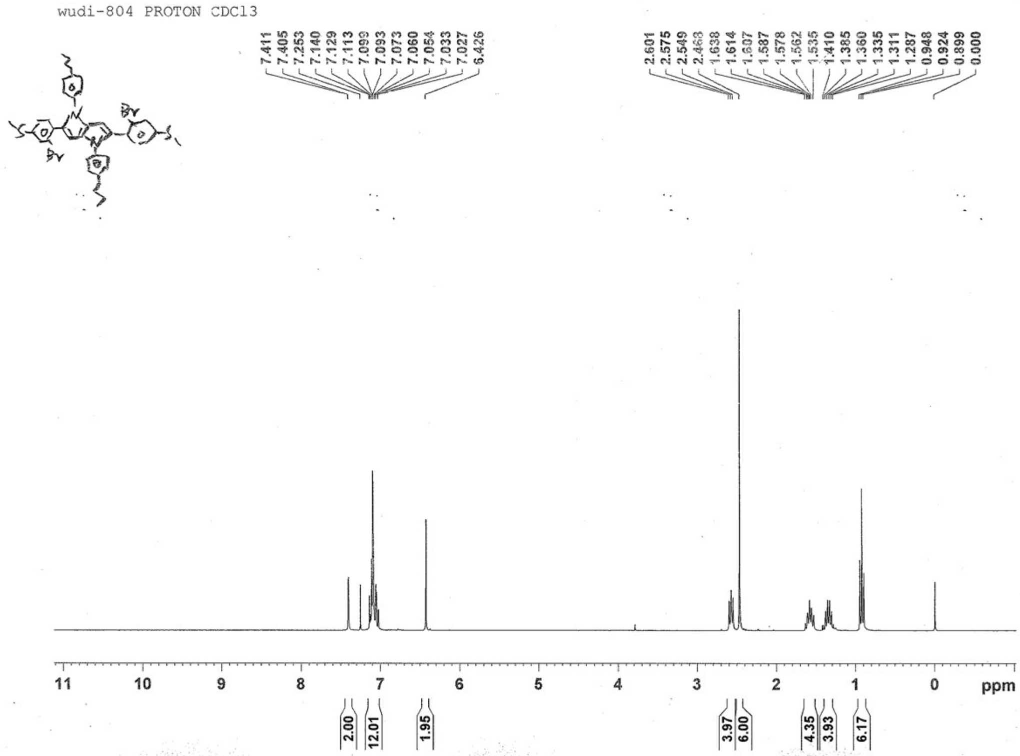
C14	P2	1.821(3)	C41	C42	1.372(6)
C15	C16	1.393(5)	C41	C44	1.513(5)
C16	C17	1.373(5)	C42	C43	1.380(5)
C17	C18	1.384(5)	O1	P1	1.483(2)
C19	C20	1.383(5)	O2	P2	1.486(2)
C19	C24	1.387(5)	C45	Cl1	1.687(7)
C19	P1	1.808(3)	C45	Cl2	1.730(7)
C20	C21	1.373(6)			

Table S8. Bond Angles for **2a**-*cis*.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C6	C1	C2	118.8(3)	C26	C25	P2	123.2(3)
C3	C2	C1	121.2(3)	C30	C25	P2	117.9(3)
C2	C3	C4	120.3(3)	C25	C26	C27	120.2(4)
C3	C4	C5	119.4(3)	C28	C27	C26	120.1(4)
C4	C5	C6	120.8(3)	C29	C28	C27	120.1(4)
C4	C5	P1	127.2(3)	C28	C29	C30	120.5(4)
C6	C5	P1	112.0(2)	C25	C30	C29	120.1(4)
C1	C6	C5	119.5(3)	C32	C31	N1	120.2(3)
C1	C6	C7	130.6(3)	C36	C31	C32	119.6(3)
C5	C6	C7	110.0(3)	C36	C31	N1	120.1(3)
C8	C7	C6	116.7(3)	C33	C32	C31	119.8(4)
N1	C7	C6	132.8(3)	C32	C33	C34	120.9(4)
N1	C7	C8	110.4(3)	C33	C34	C37	121.0(4)
C7	C8	C9	105.8(3)	C35	C34	C33	118.3(4)
C7	C8	P1	109.8(2)	C35	C34	C37	120.7(4)
C9	C8	P1	143.5(2)	C34	C35	C36	121.3(4)
C10	C9	C8	108.5(3)	C31	C36	C35	120.1(4)
N2	C9	C8	143.0(3)	C39	C38	N2	119.9(3)
N2	C9	C10	108.4(3)	C43	C38	C39	119.6(3)
C9	C10	C11	108.5(3)	C43	C38	N2	120.5(3)
C9	C10	N1	108.3(3)	C38	C39	C40	119.5(4)
N1	C10	C11	143.2(3)	C41	C40	C39	122.1(4)
C10	C11	P2	145.3(2)	C40	C41	C44	120.9(4)

C12	C11	C10	105.1(2)	C42	C41	C40	117.3(4)
C12	C11	P2	109.7(2)	C42	C41	C44	121.8(4)
C11	C12	C13	117.3(3)	C41	C42	C43	121.4(4)
N2	C12	C11	111.1(3)	C38	C43	C42	120.2(4)
N2	C12	C13	131.6(3)	C7	N1	C10	107.0(2)
C14	C13	C12	109.9(3)	C7	N1	C31	130.1(3)
C18	C13	C12	130.4(3)	C10	N1	C31	122.8(2)
C18	C13	C14	119.7(3)	C9	N2	C38	125.5(2)
C13	C14	P2	111.7(2)	C12	N2	C9	106.9(2)
C15	C14	C13	120.4(3)	C12	N2	C38	127.5(2)
C15	C14	P2	127.8(3)	C8	P1	C5	91.39(14)
C14	C15	C16	118.9(3)	C8	P1	C19	106.13(14)
C17	C16	C15	120.5(3)	C19	P1	C5	107.03(15)
C16	C17	C18	121.4(3)	O1	P1	C5	117.64(14)
C13	C18	C17	119.1(3)	O1	P1	C8	120.07(14)
C20	C19	C24	119.1(3)	O1	P1	C19	112.19(15)
C20	C19	P1	122.1(3)	C11	P2	C14	91.49(14)
C24	C19	P1	118.8(3)	C11	P2	C25	109.41(14)
C21	C20	C19	120.3(4)	C25	P2	C14	109.82(15)
C20	C21	C22	120.1(4)	O2	P2	C11	119.53(14)
C23	C22	C21	120.1(4)	O2	P2	C14	115.32(15)
C22	C23	C24	120.1(4)	O2	P2	C25	109.93(15)
C23	C24	C19	120.3(4)	Cl1	C45	Cl2	113.7(3)
C26	C25	C30	118.9(3)				

NMR spectrum



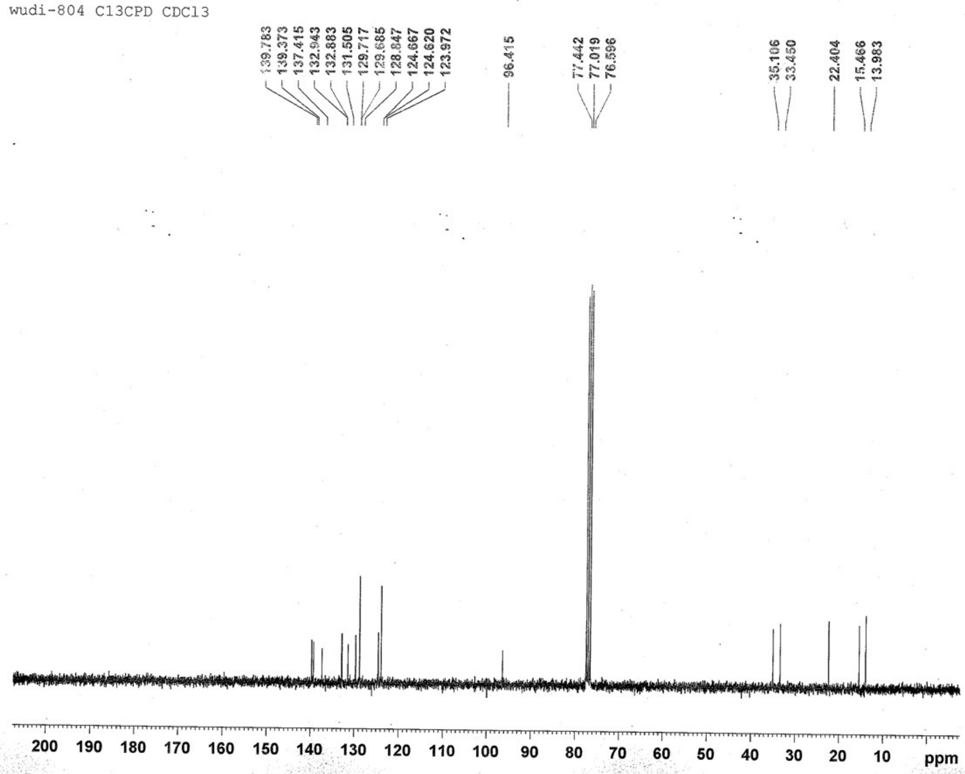
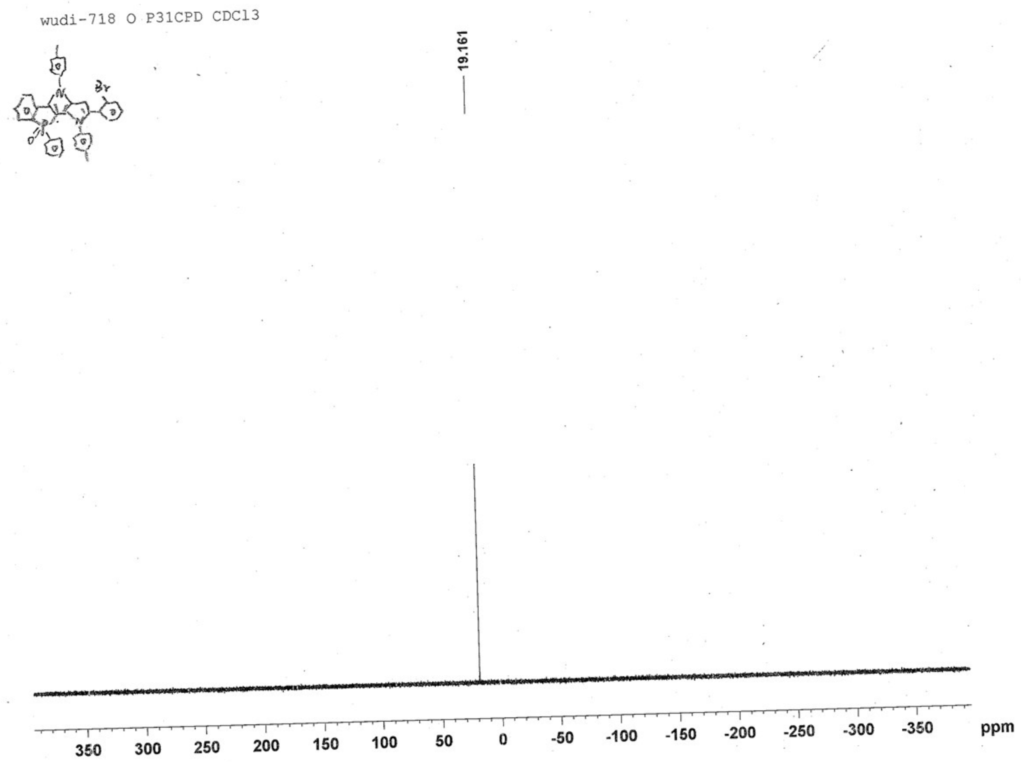
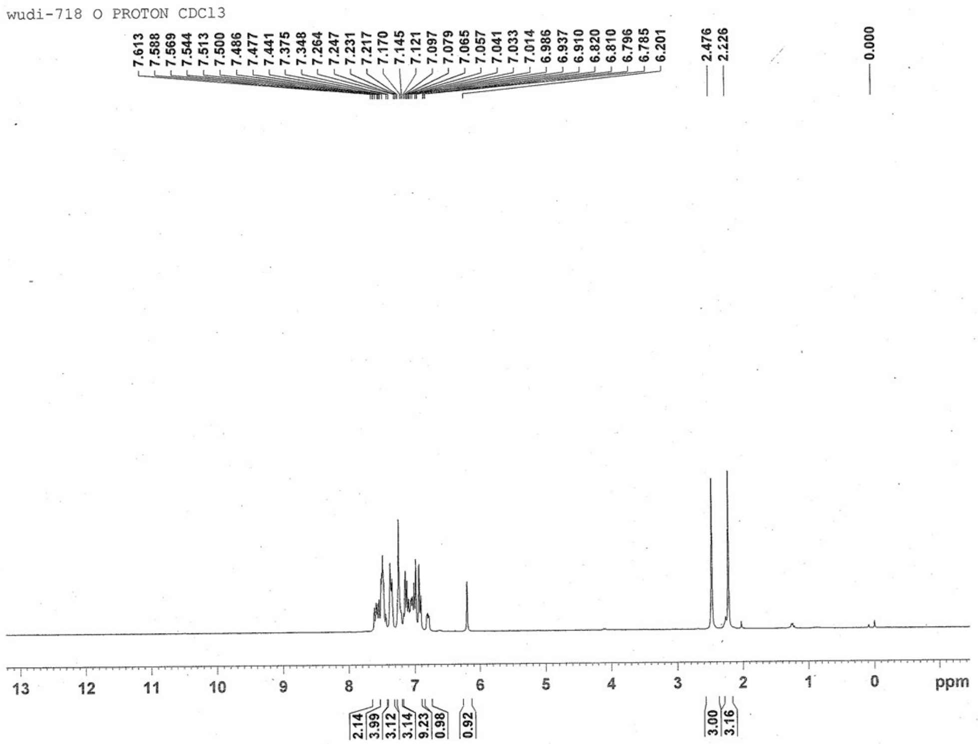


Figure S12. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of TAPP-**2** at 293 K.





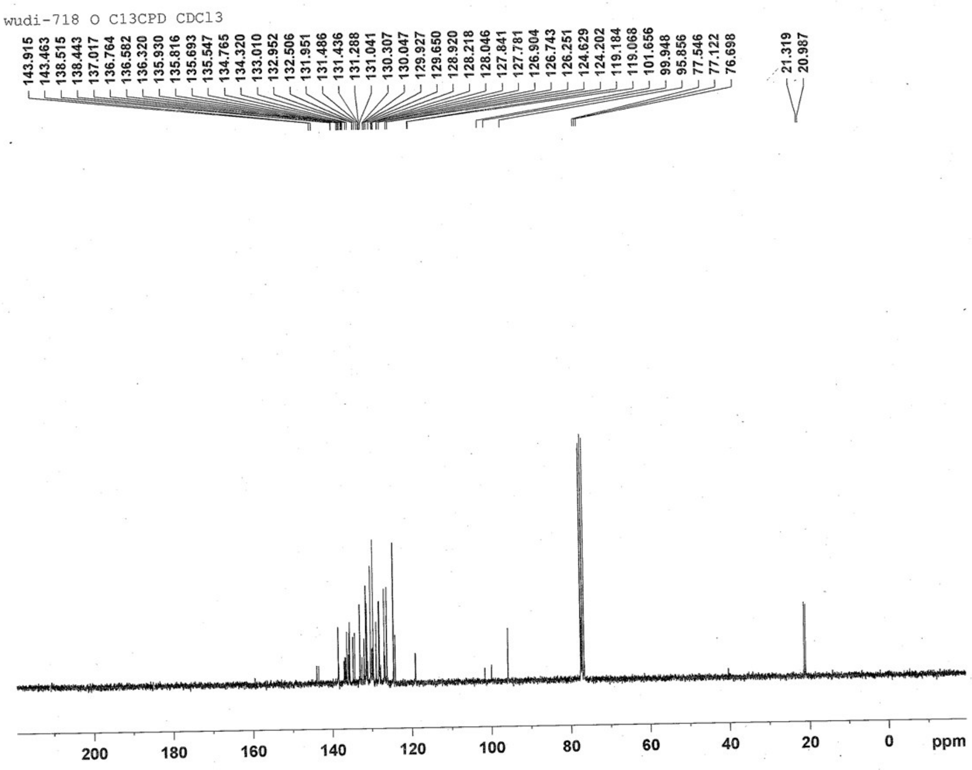
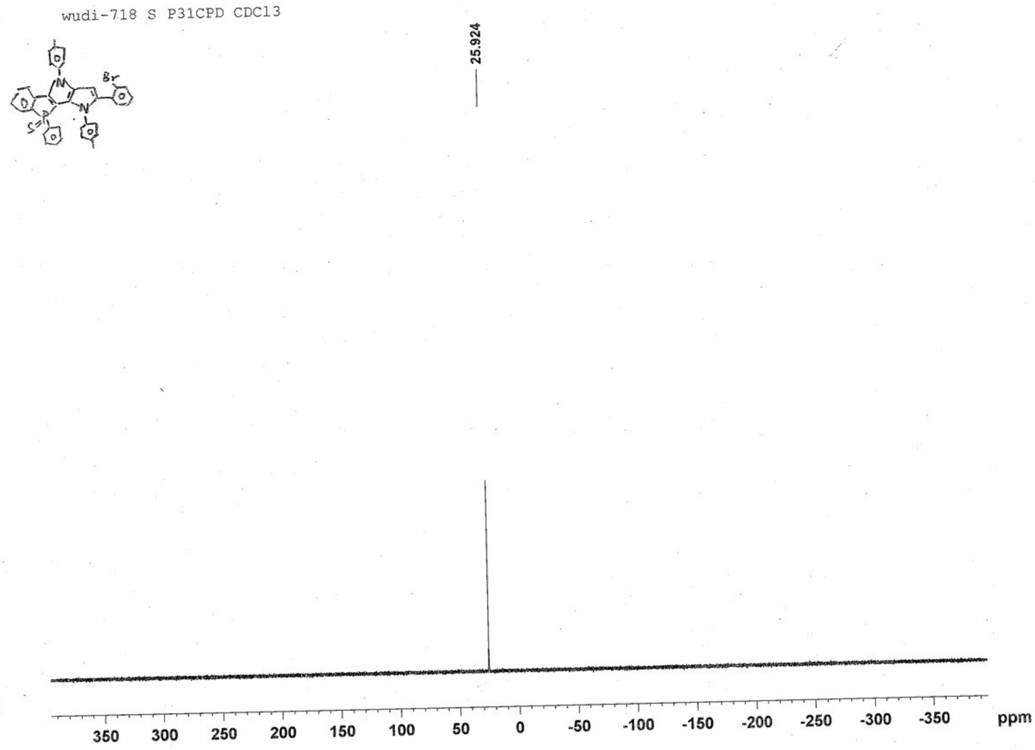


Figure S13. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of **1a** at 293 K.



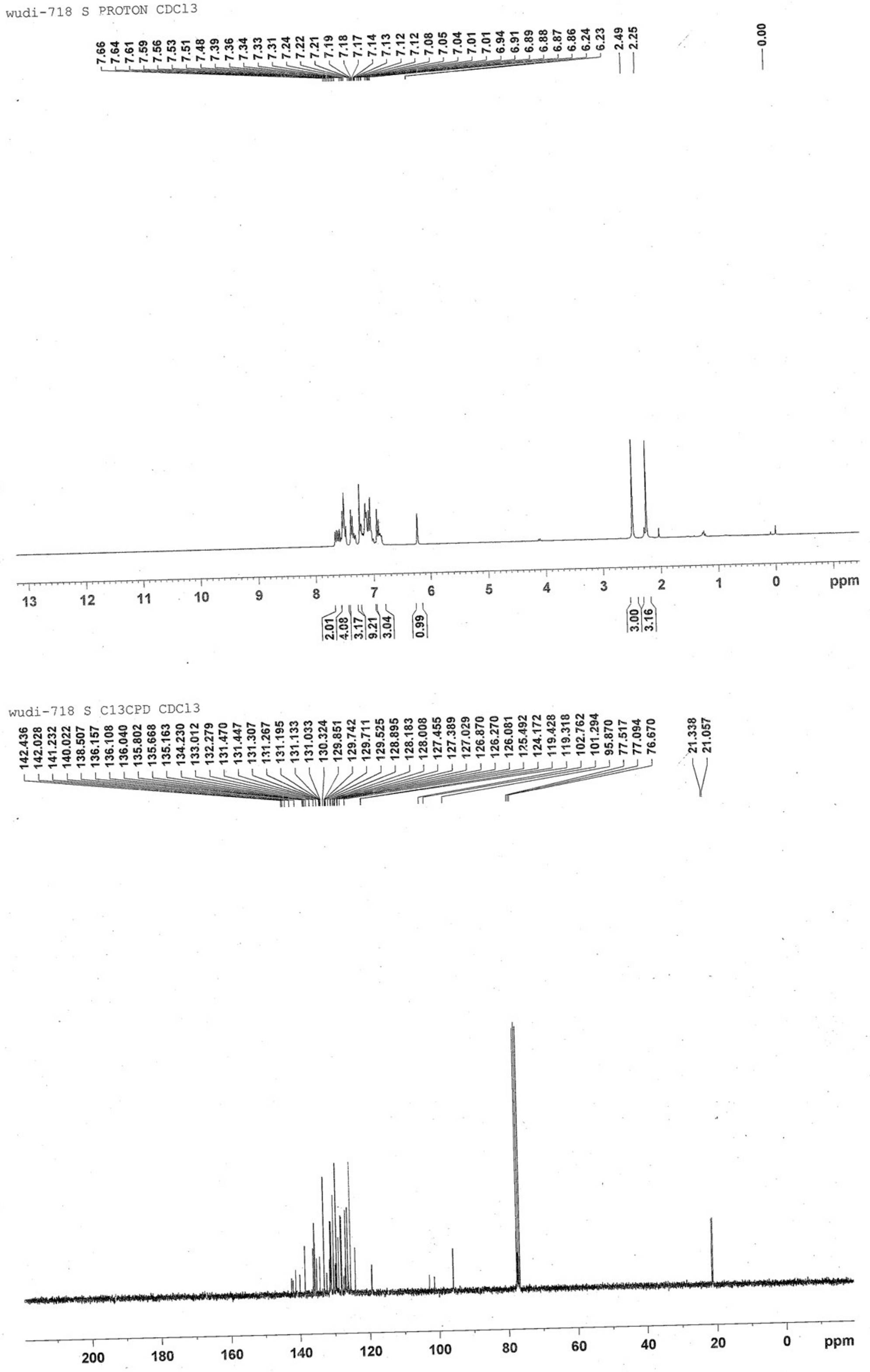
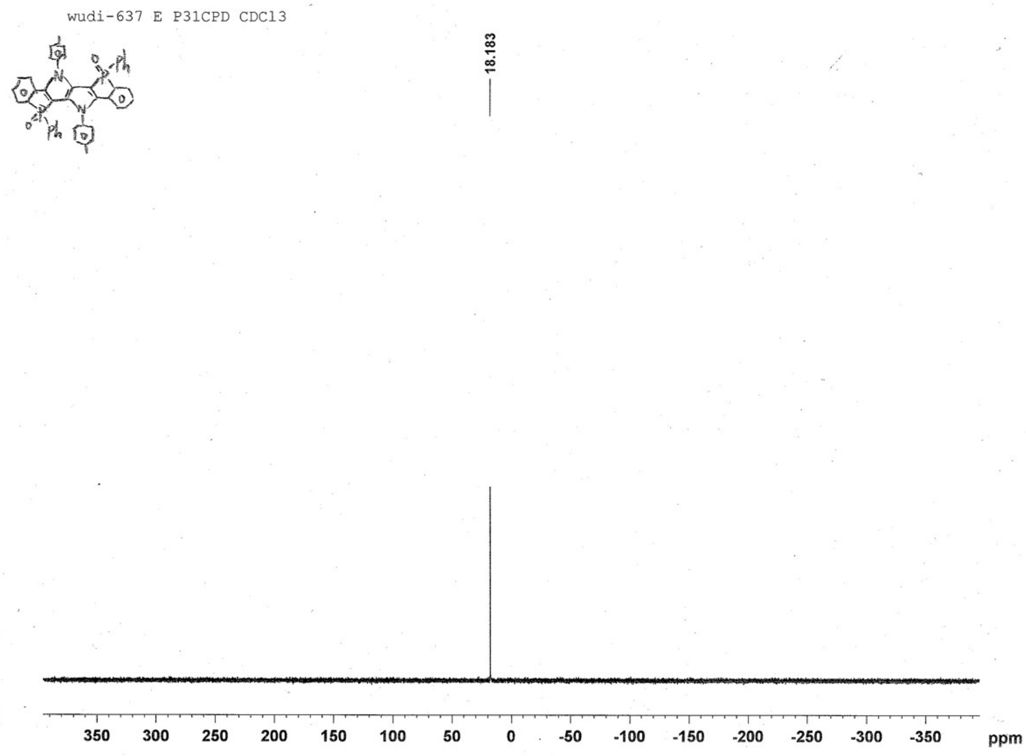
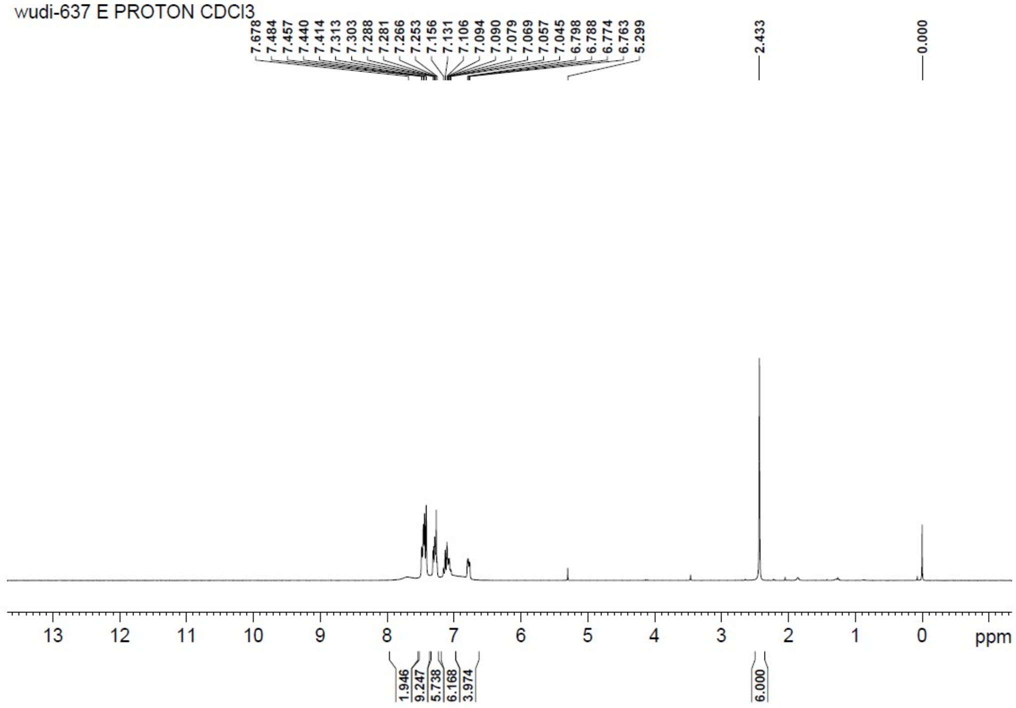


Figure S14. ^{1}H NMR (300 MHz, CDCl$_3$) and ^{13}C NMR (75 MHz, CDCl$_3$) of **1b** at 293 K.


wudi-637 E P31CPD CDCl3
18.183
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm


wudi-637 E PROTON CDCl3
7.678
7.484
7.457
7.440
7.414
7.313
7.303
7.288
7.281
7.266
7.253
7.156
7.131
7.106
7.094
7.090
7.079
7.069
7.057
7.045
6.798
6.788
6.774
6.763
5.299
2.433
0.000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.946
9.247
5.738
6.168
3.974
6.000

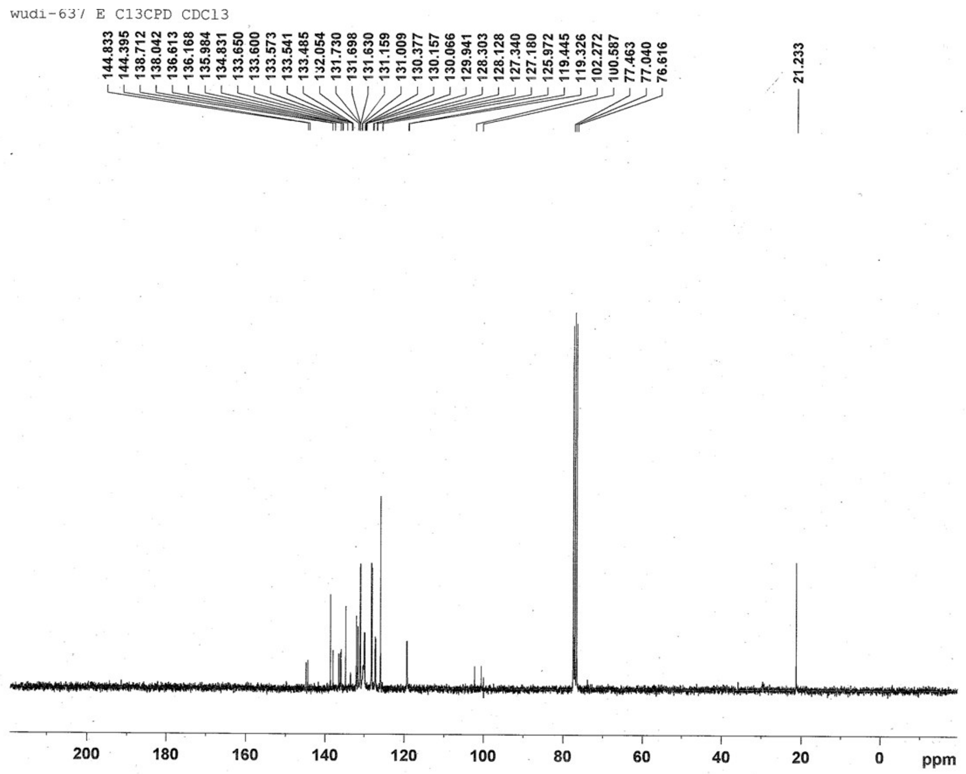
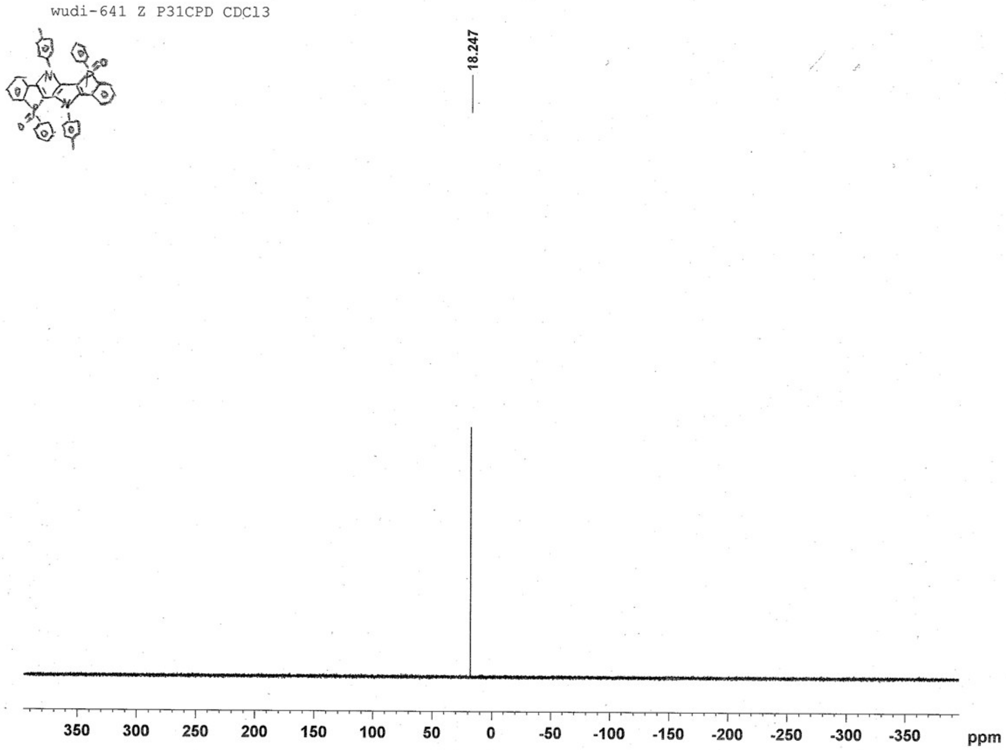


Figure S15. ^{1}H NMR (300 MHz, CDCl$_3$) and ^{13}C NMR (75 MHz, CDCl$_3$) of **2a**-*trans* at 293 K.



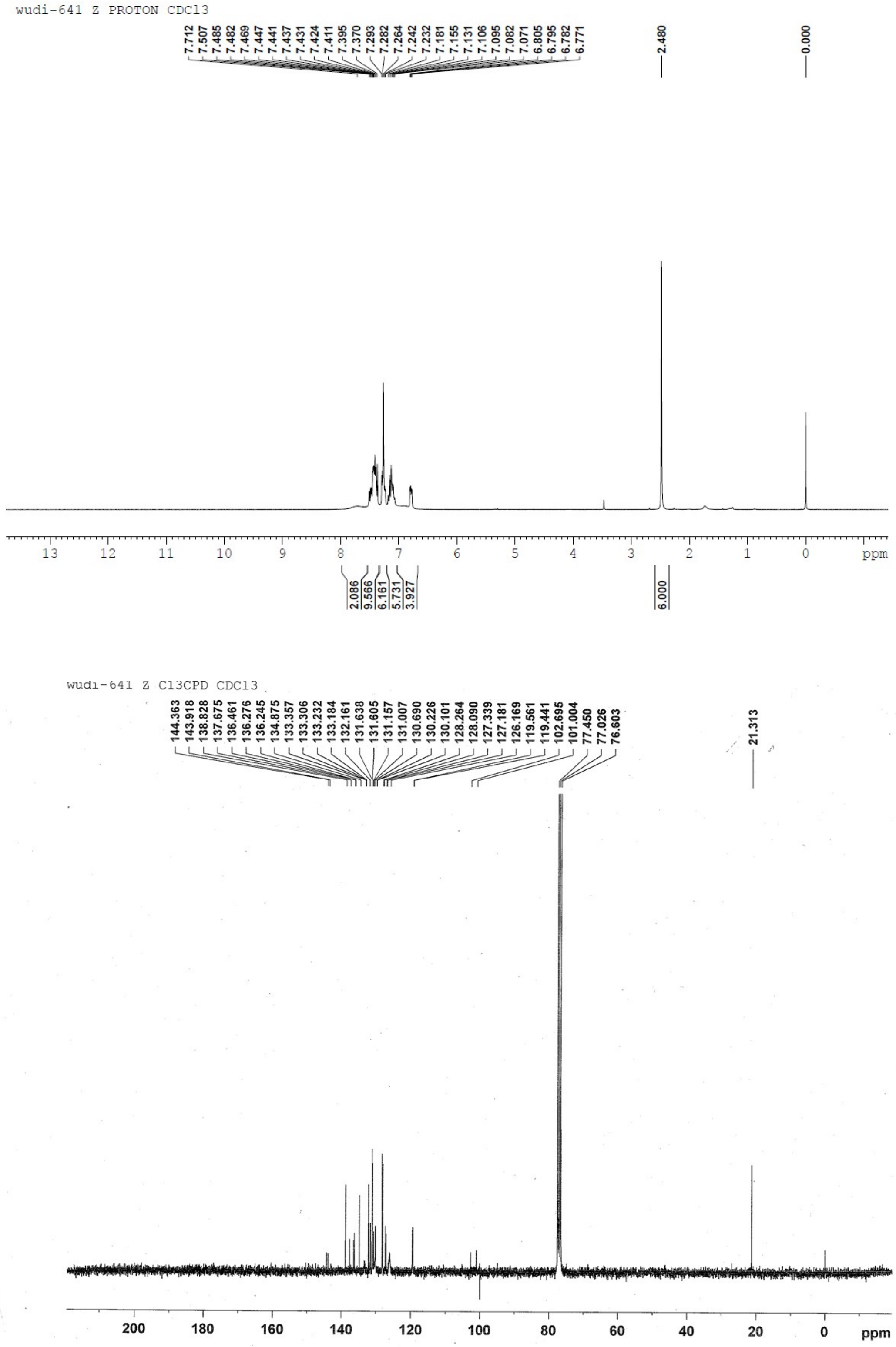
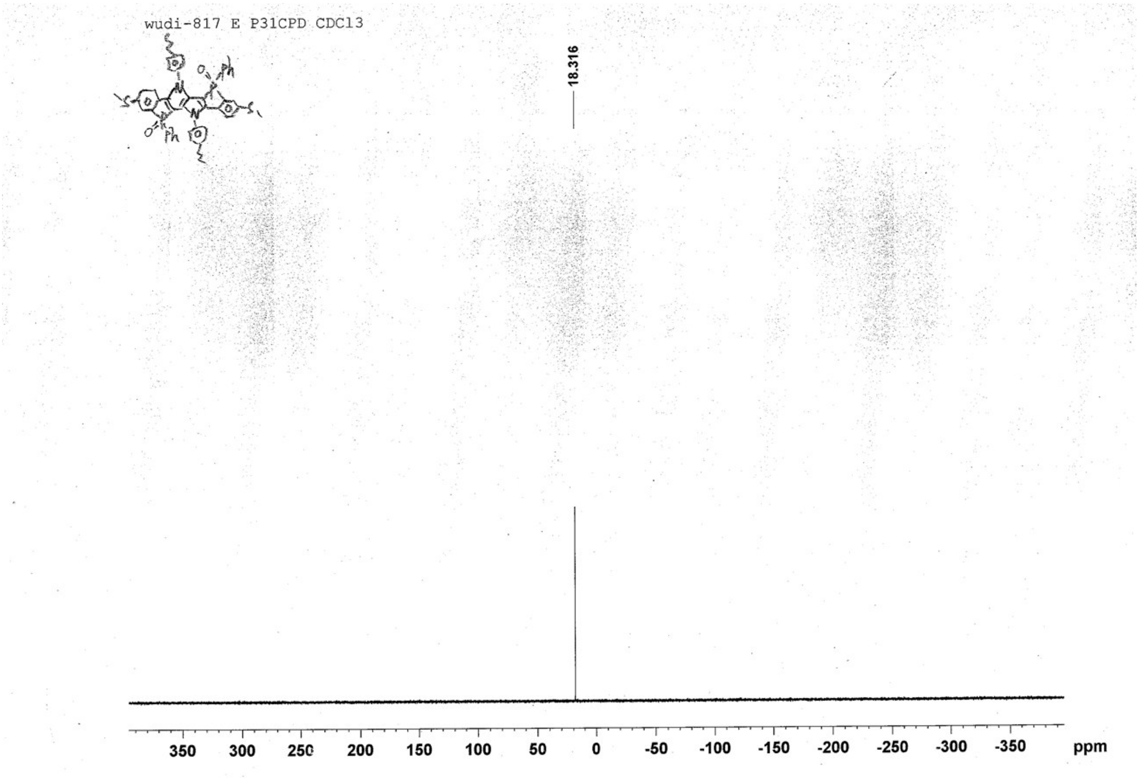
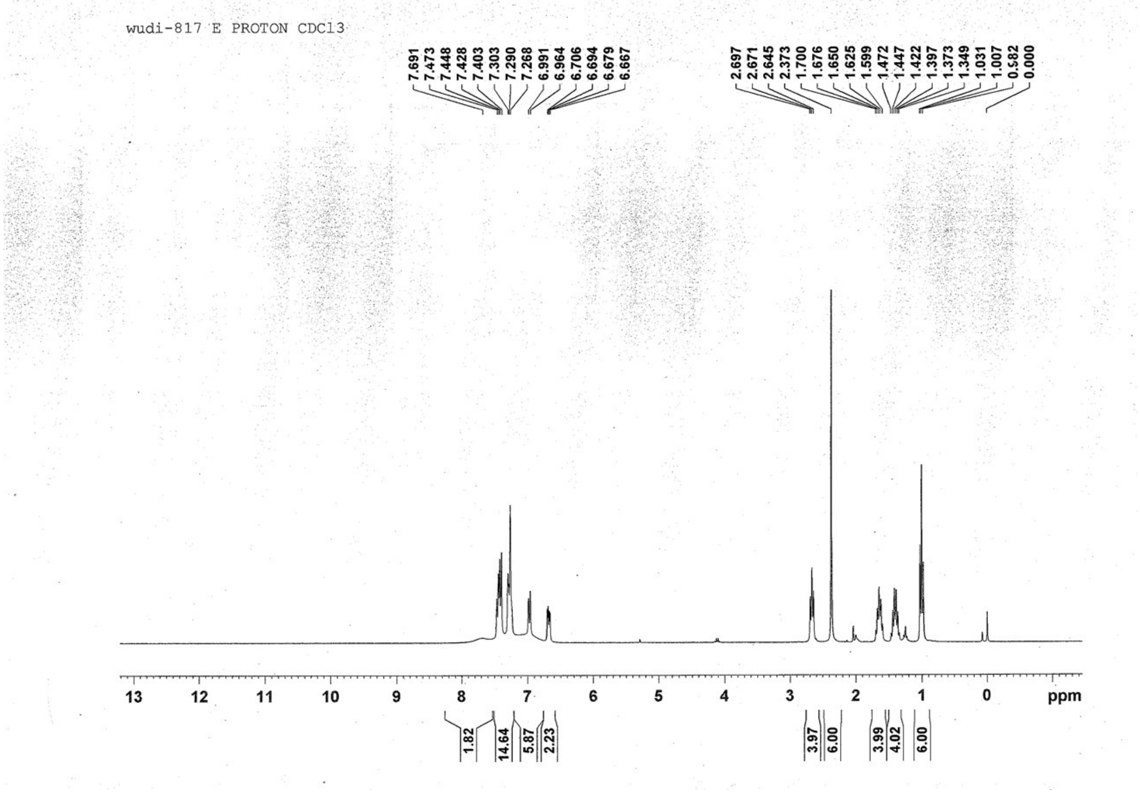


Figure S16. ${}^{1}H$ NMR (300 MHz, $CDCl_3$) and ${}^{13}C$ NMR (75 MHz, $CDCl_3$) of **2a**-*cis* at 293 K.


wudi-817 E P31CPD CDCl3
18.316
350 300 250 200 150 100 50 0 -50 -100 -150 -200 -250 -300 -350 ppm
Ph
Ph


wudi-817 E PROTON CDCl3
7.691
7.473
7.448
7.428
7.403
7.303
7.290
7.268
6.991
6.964
6.706
6.694
6.679
6.667
2.697
2.671
2.645
2.373
1.700
1.676
1.650
1.625
1.599
1.472
1.447
1.422
1.397
1.373
1.349
1.031
1.007
0.982
0.000
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.82
14.64
5.87
2.23
3.97
6.00
3.99
4.02
6.00

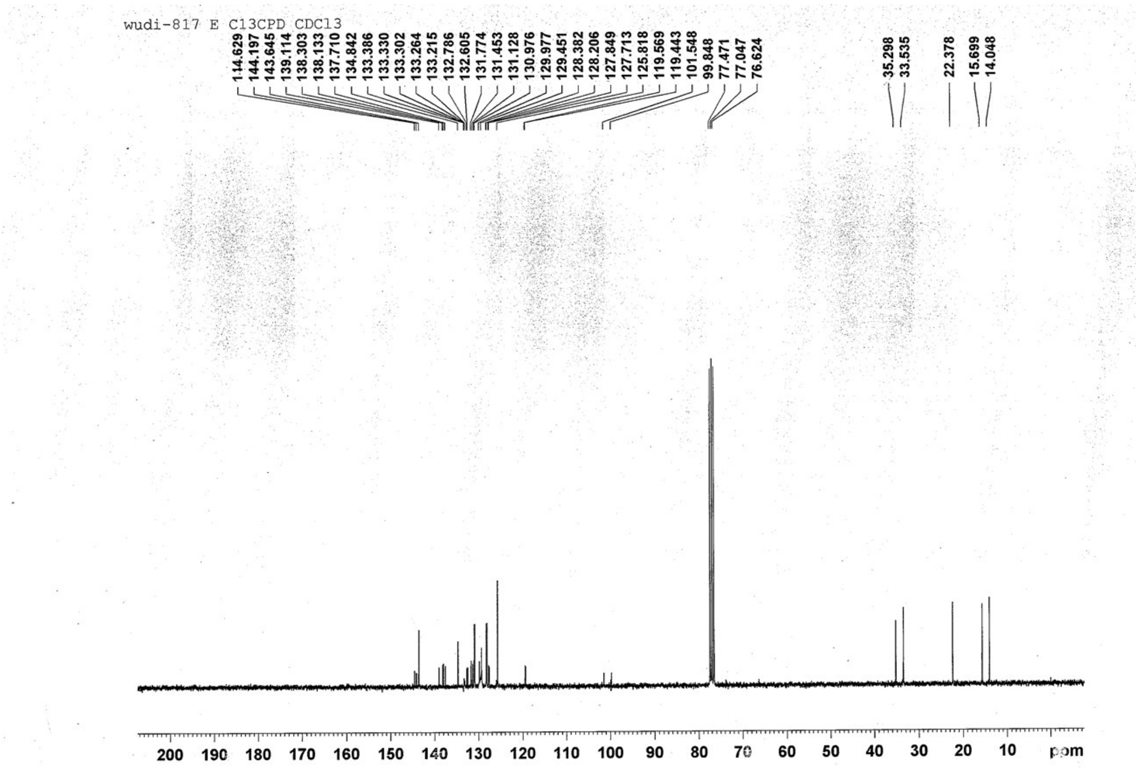
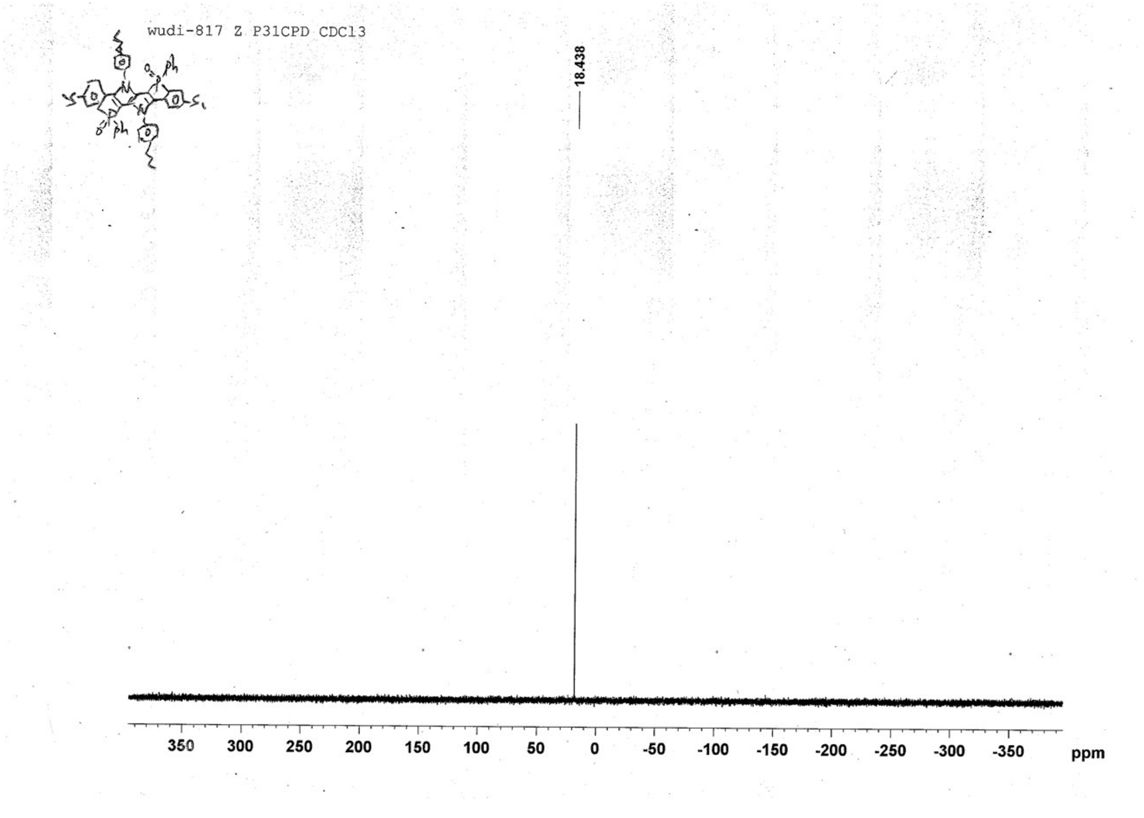


Figure S17. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of **3a**-*trans* at 293 K.



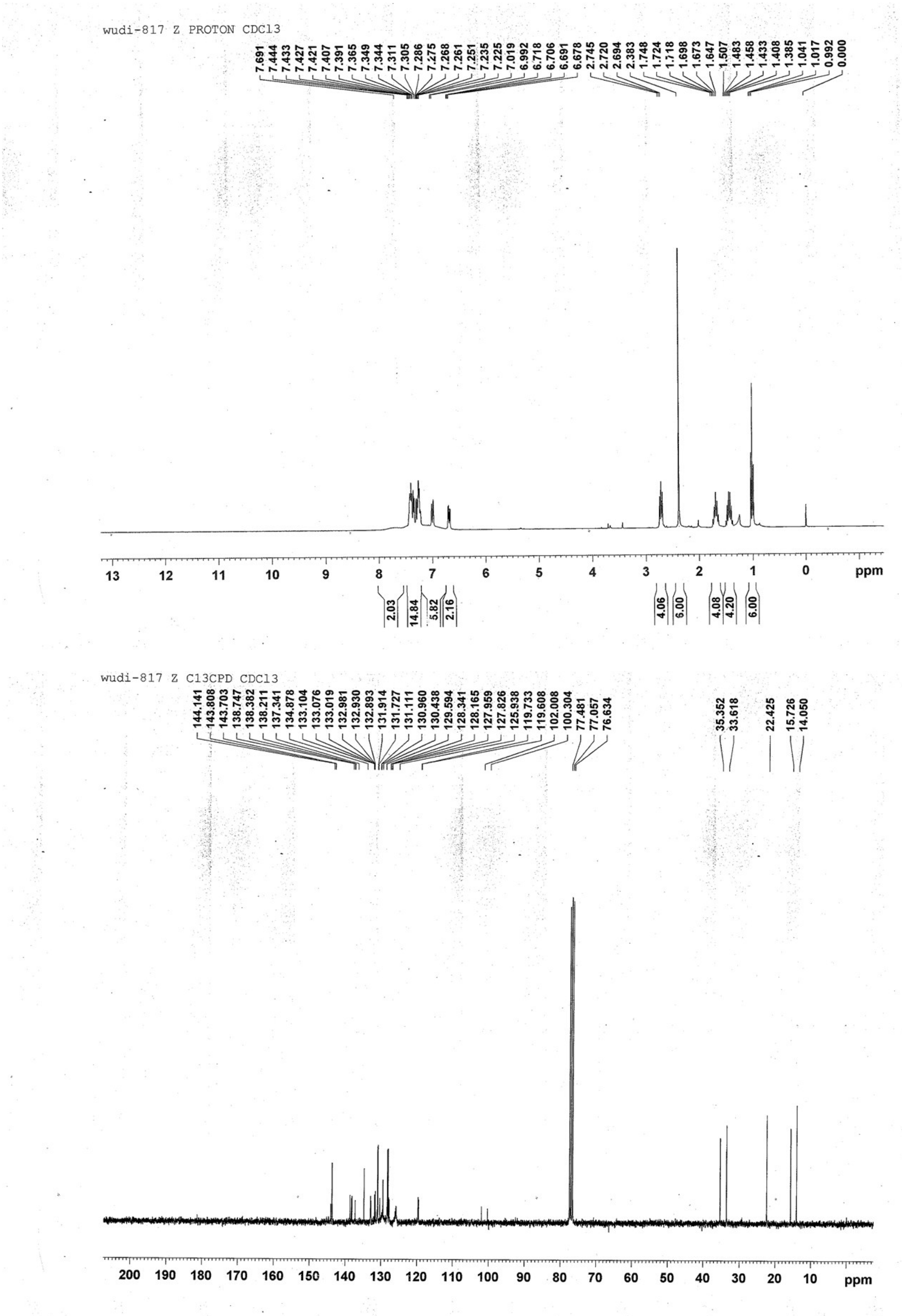
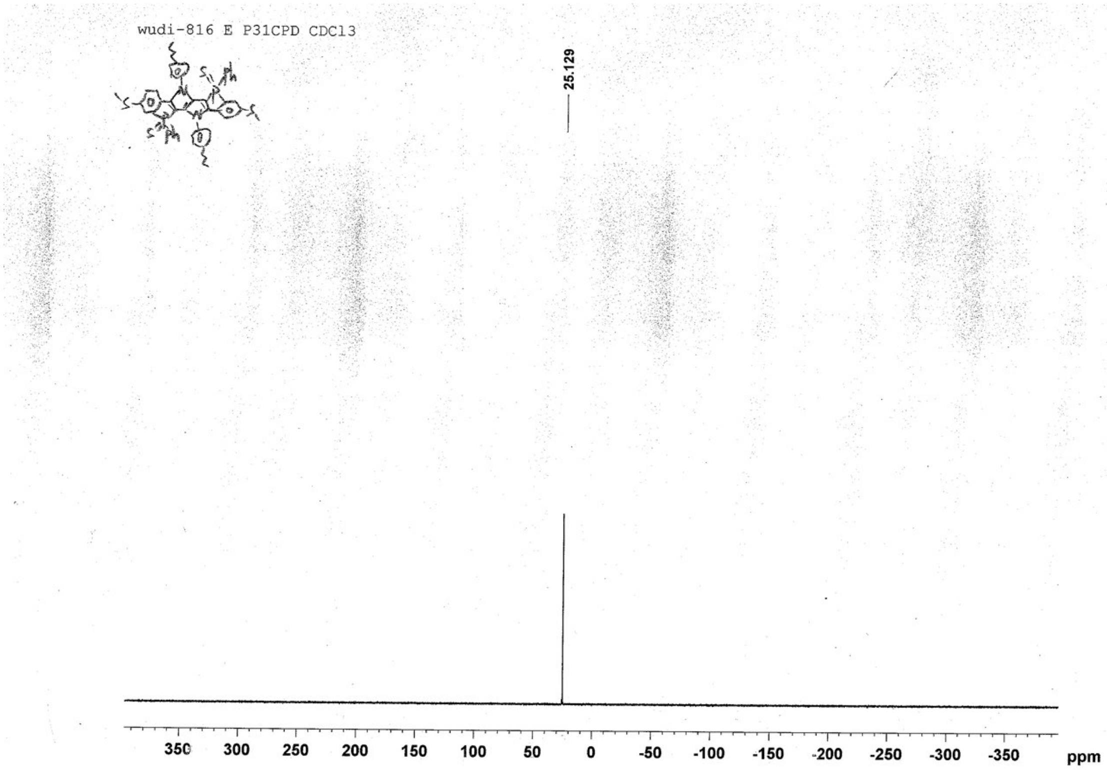
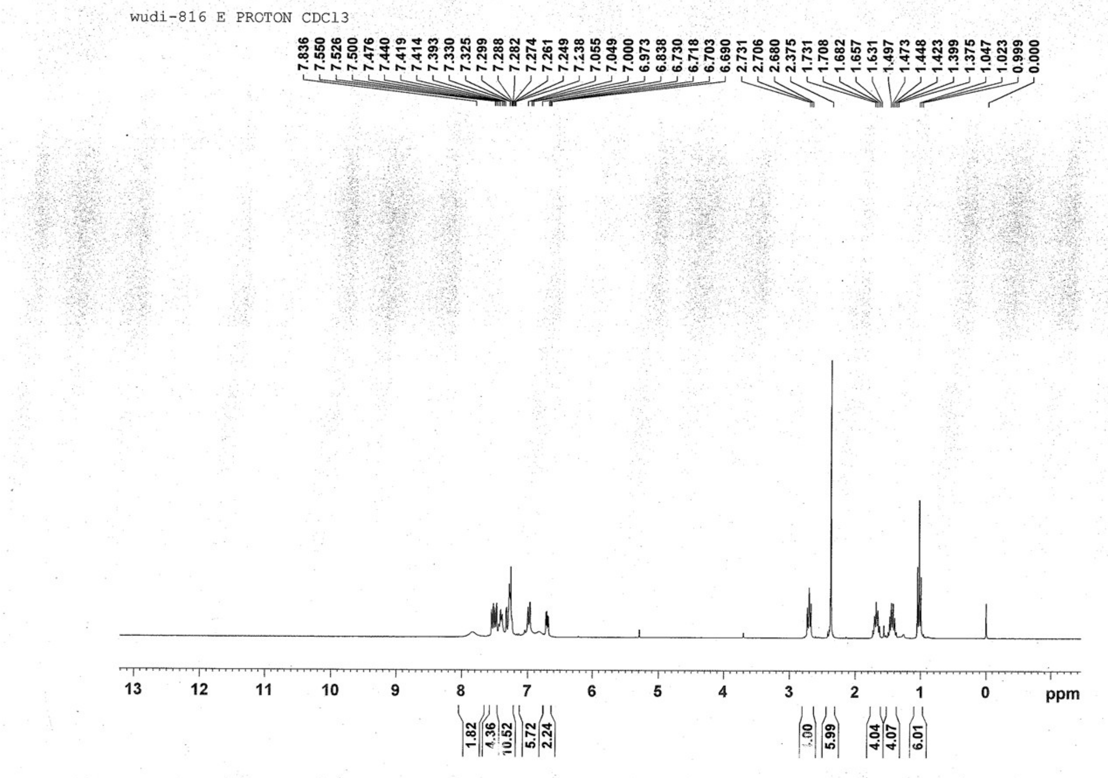


Figure S18. ^{1}H NMR (300 MHz, CDCl$_3$) and ^{13}C NMR (75 MHz, CDCl$_3$) of **3a**-*cis* at 293 K.


wudi-816 E P31CPD CDCl3
25.129
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
ppm


wudi-816 E PROTON CDCl3
7.836
7.550
7.526
7.500
7.476
7.440
7.419
7.414
7.393
7.330
7.325
7.299
7.288
7.282
7.274
7.261
7.249
7.238
7.055
7.049
7.000
6.973
6.838
6.730
6.718
6.703
6.690
2.731
2.706
2.680
2.375
1.731
1.708
1.682
1.657
1.631
1.497
1.473
1.448
1.423
1.399
1.375
1.047
1.023
0.999
0.000
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.82
4.36
10.52
5.72
2.24
4.00
5.99
4.04
4.07
6.01

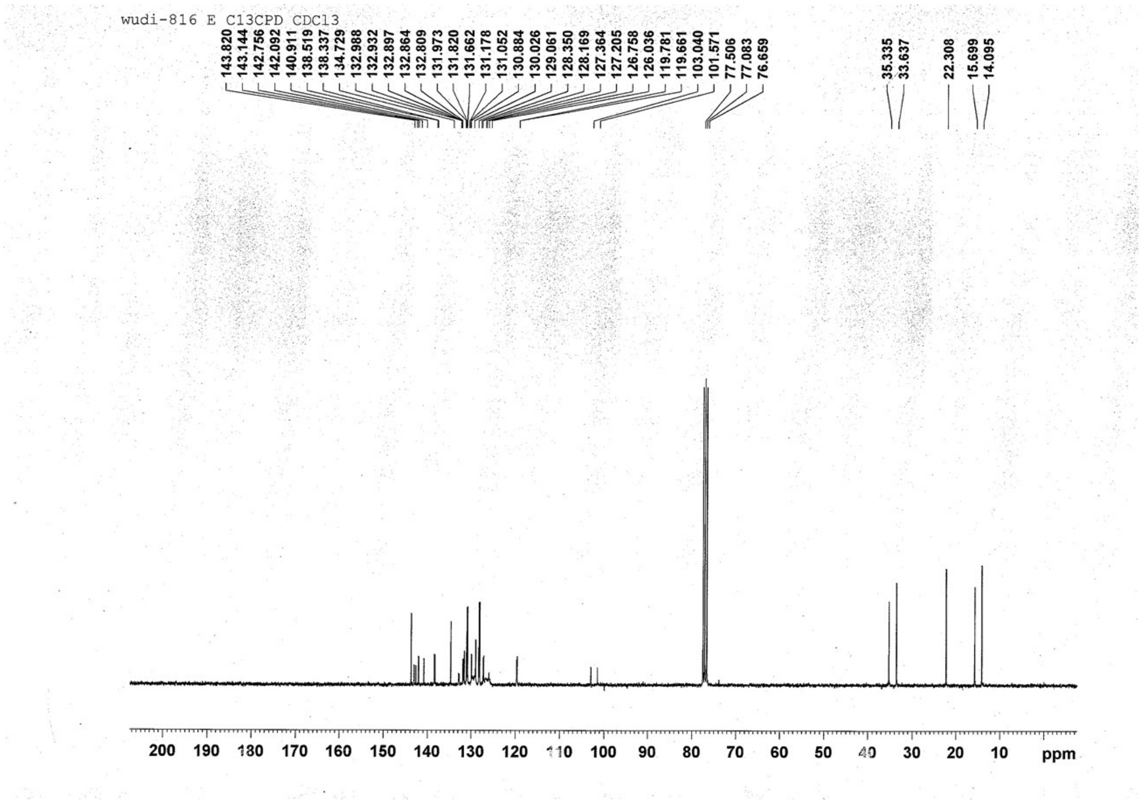
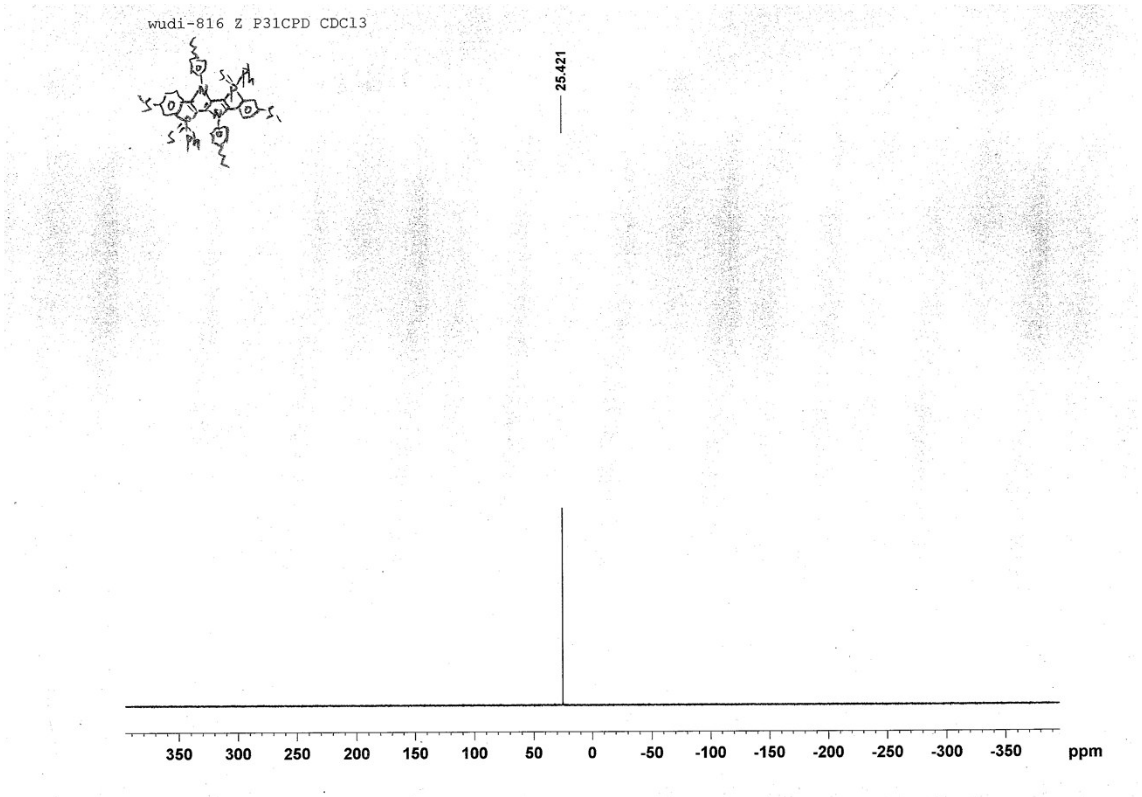


Figure S19. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) of **3b**-*trans* at 293 K.



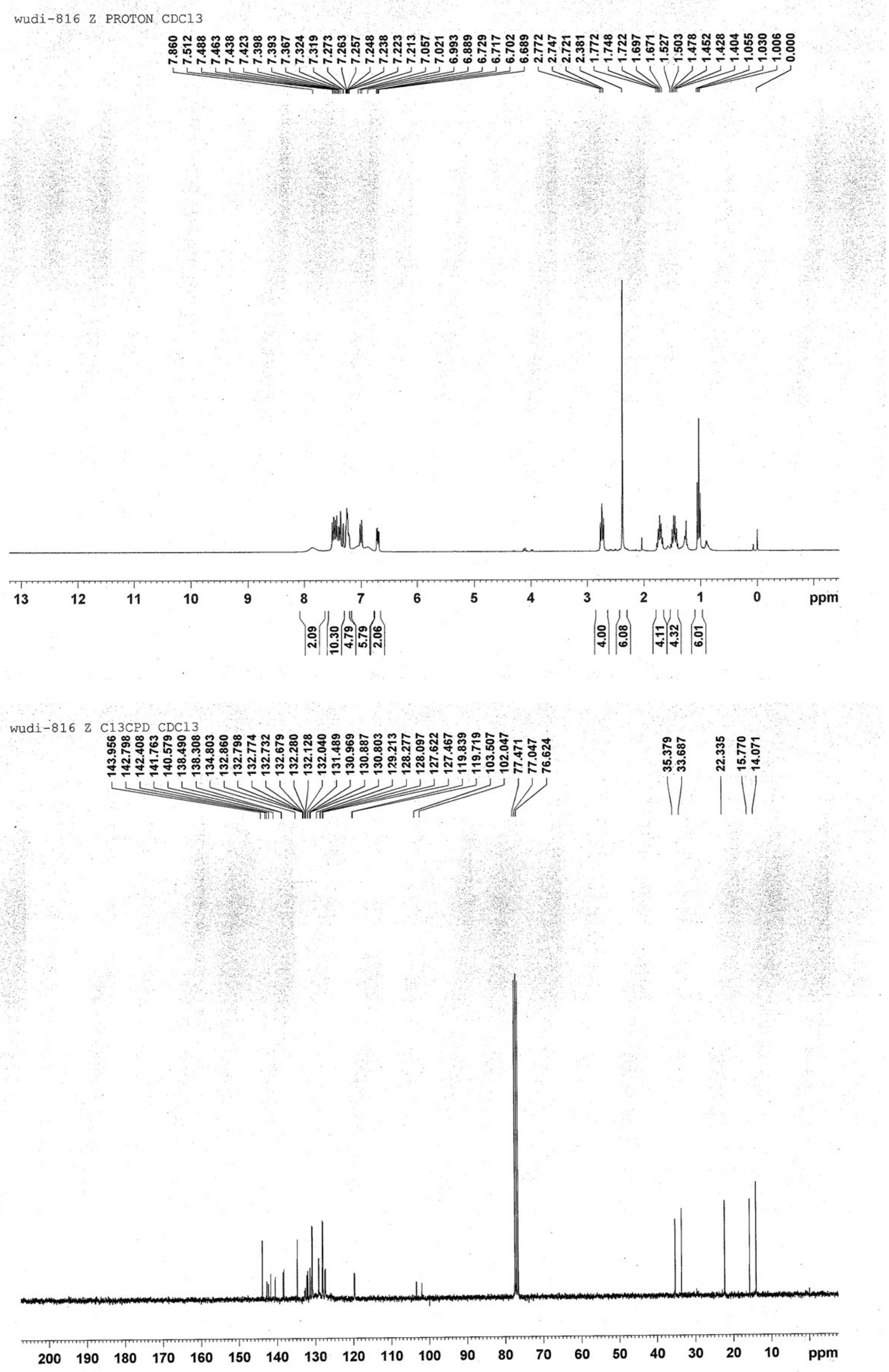


Figure S20. ^{1}H NMR (300 MHz, CDCl$_3$) and ^{13}C NMR (75 MHz, CDCl$_3$) of **3b**-*cis* at 293 K.

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