Supporting Information

Synthesis and Optical Properties of Redox-Active Triphenylamine-Based Derivatives with Methoxy Protecting Groups

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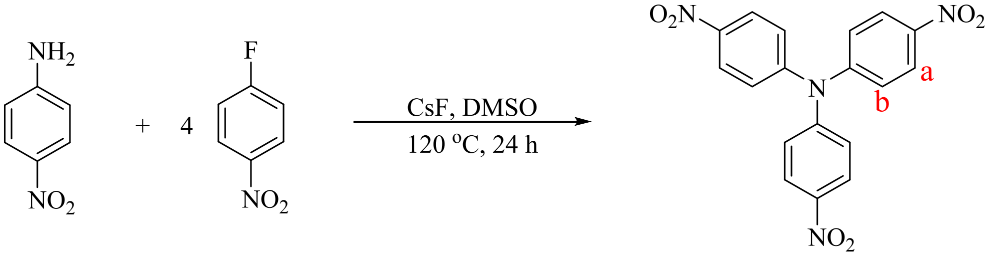
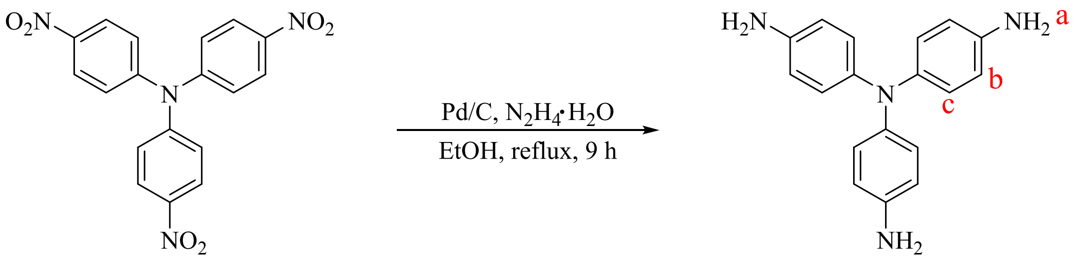
Experimental Section

Tris(4-nitrophenyl)amine (TPA-3NO_2)



Cesium fluoride (CsF, 15.2 g, 0.1 mol) was added into a 150 mL three-necked round-bottom flask and dry by the pumped vacuum system under 100 ℃ for 2 hours. After cooling to the room temperature, 4-nitroaniline (6.74 g, 0.044 mol), *p*-fluoronitrobenzene (14.63 g, 11.0 mL, 0.10 mol) and DMSO 120 mL were added into the reactor, stirring at 120 ℃ and tracked by TLC. After the disappearance of 4-nitroaniline, the mixture was cooled to the room temperature and poured into methanol to obtain 16.23 g of yellow crystal (97% yield), mp: 388 ℃. FT-IR (KBr, cm^{-1}): v = 3107, 3074, 1581, 1508, 1339, 1314, 1271, 1111, 849. ^1H NMR (400 MHz, DMSO-d_6, δ): 8.27-8.24 (d, 6 H, H_a), 7.37-7.35 (d, 6 H, H_b).

4,4',4''-Triaminotriphenylamine (TPA-3NH_2)



TPA-3NO$_2$ (8.00 g, 21.0 mmol), palladium 10% on activated carbon (Pd/C, 1.2 g) and 250 mL of ethanol was added into a 500 mL three-necked round-bottom flask and heated to reflux. 8.3 mL of hydrazine monohydrate was then added into the reactor dropwisely. Until the bubble change from orange into colorless, the reactor was then filtered to remove the Pd/C and the filtrate was cooled to the room temperature. Pale yellow crystal could be obtained to give 5.24 g (86% yield), mp: 242-243 °C. FT-IR (KBr, cm^{-1}): v = 3406, 3336, 3208, 3031, 2922, 2849, 1622, 1502, 1261, 829. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 6.61-6.59 (d, 6 H, H$_c$), 6.45-6.43 (d, 6 H, H$_b$), 4.69 (s, 6 H, H$_a$).

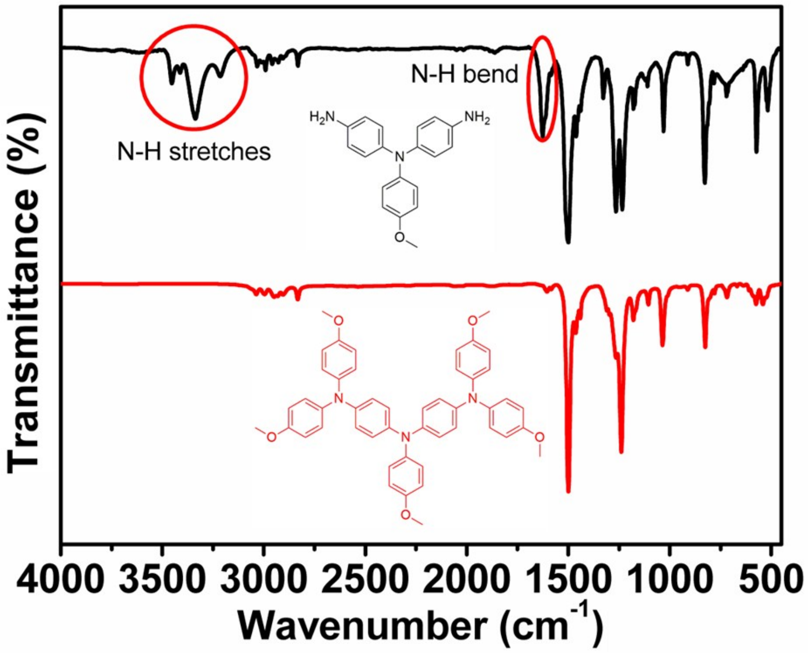


Figure S1. IR spectra of **TPA-2NH$_2$** and **BDATPA**.

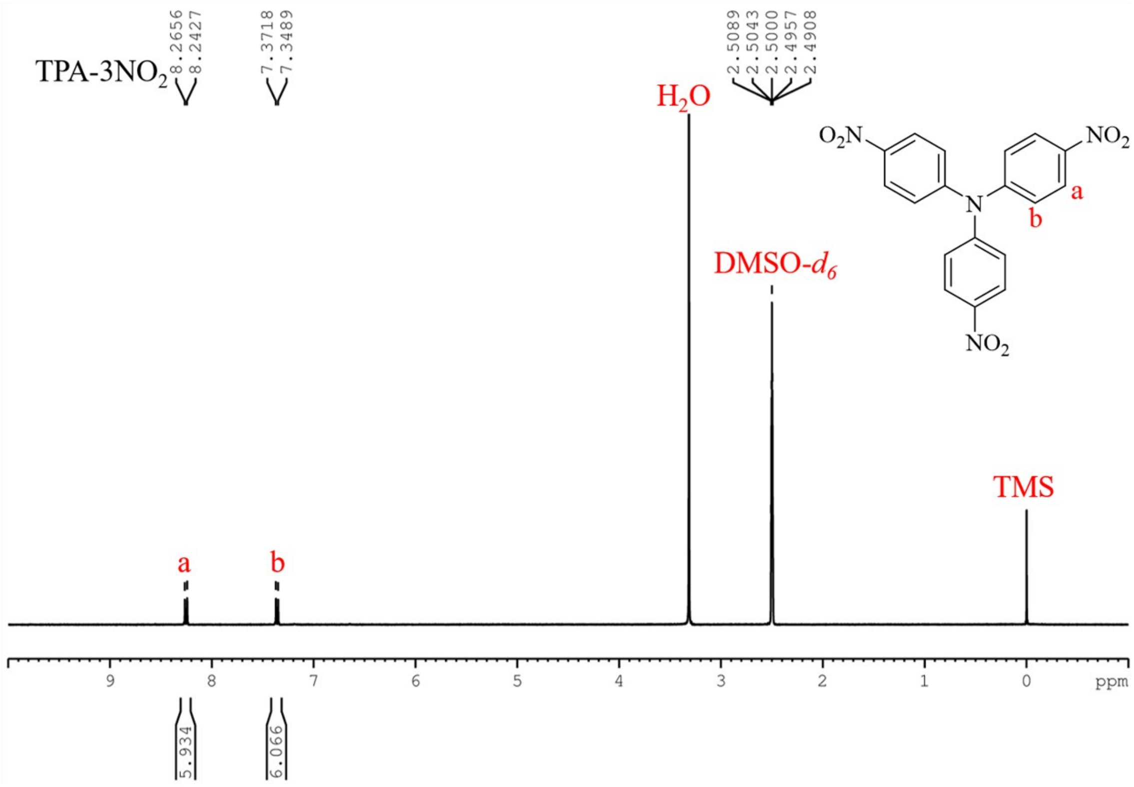


Figure S2. ^{1}H NMR spectrum of **TPA-3NO$_2$** in DMSO-*d$_6$*.

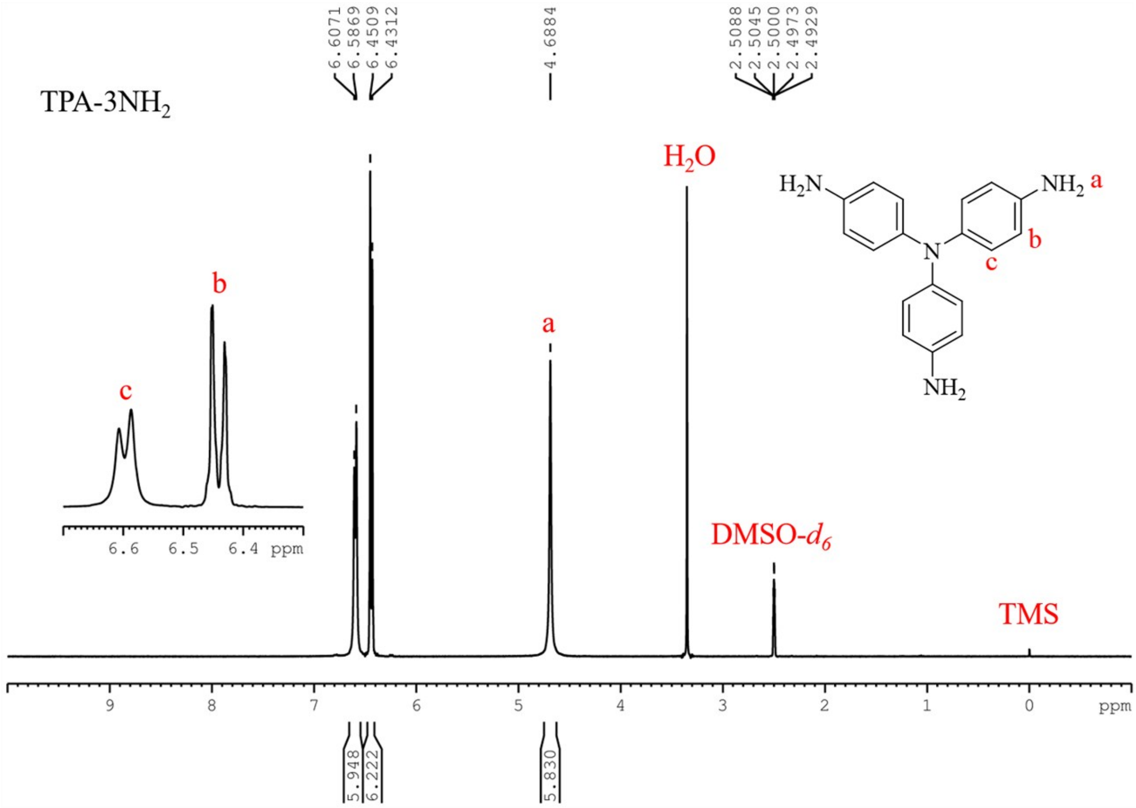


Figure S3. ^{1}H NMR spectrum of **TPA-3NH$_2$** in DMSO-*d$_6$*.

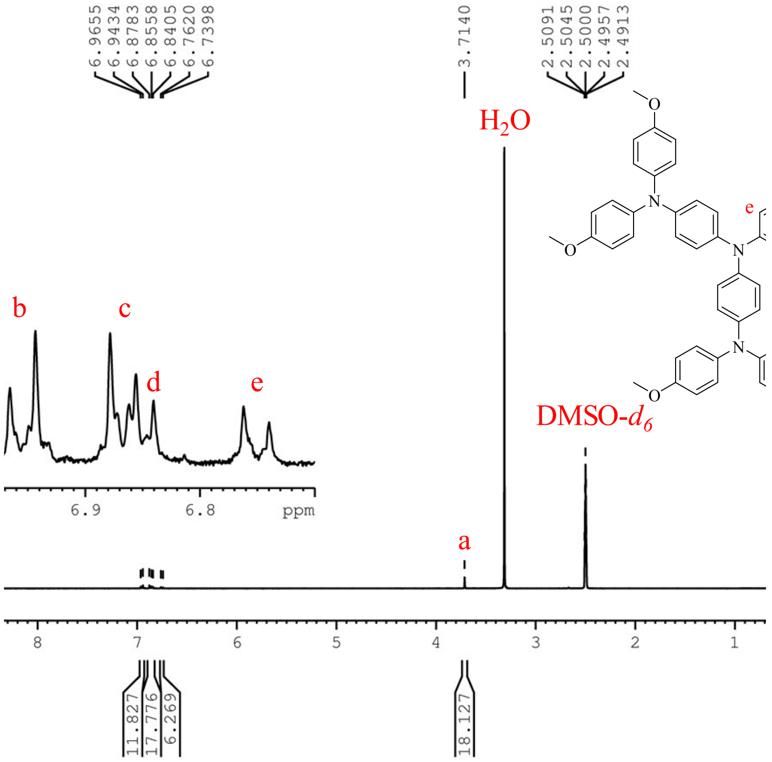


Figure S4. ^{1}H NMR spectrum of **TPAPA** in DMSO-d_6.

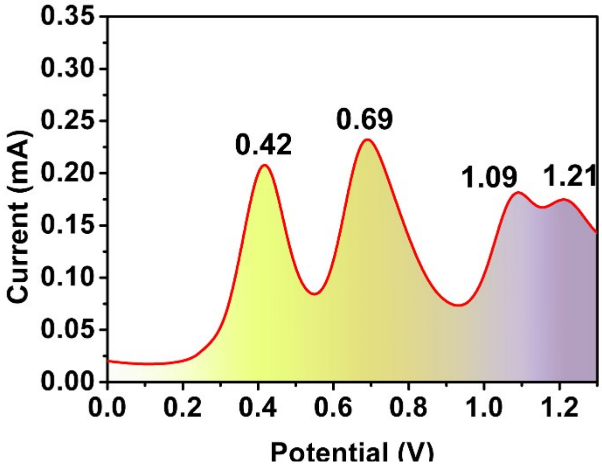


Figure S5. Differential pulse voltammetry diagram of **TPAPA** at the scan rate of 2mV/s, pulse amplitude of 50 mV, pulse width of 25 ms, and pulse period of 0.2 s.

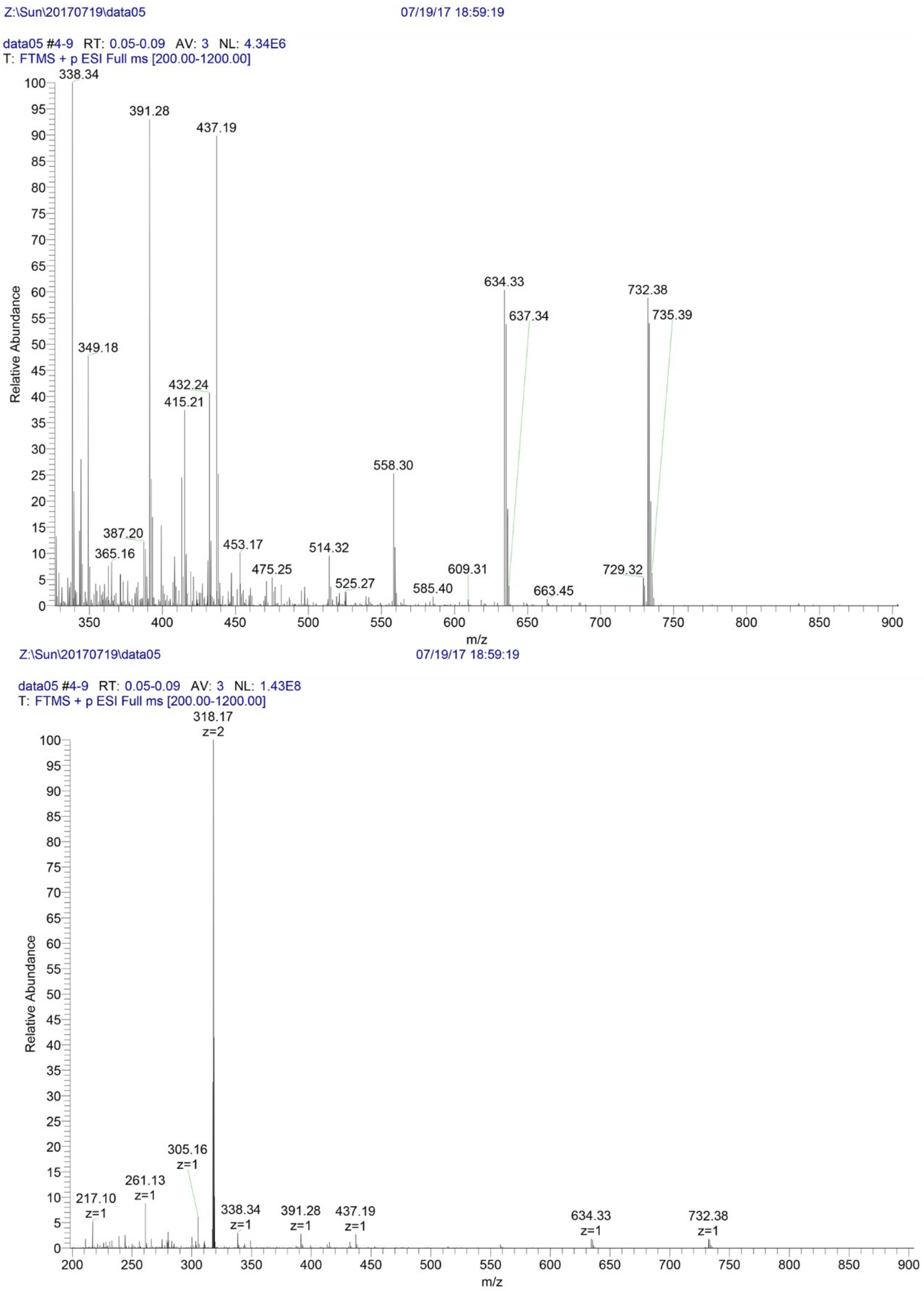


Figure S6. Mass spectra of **BDATPA**.