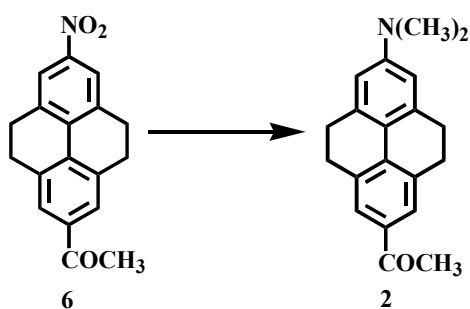
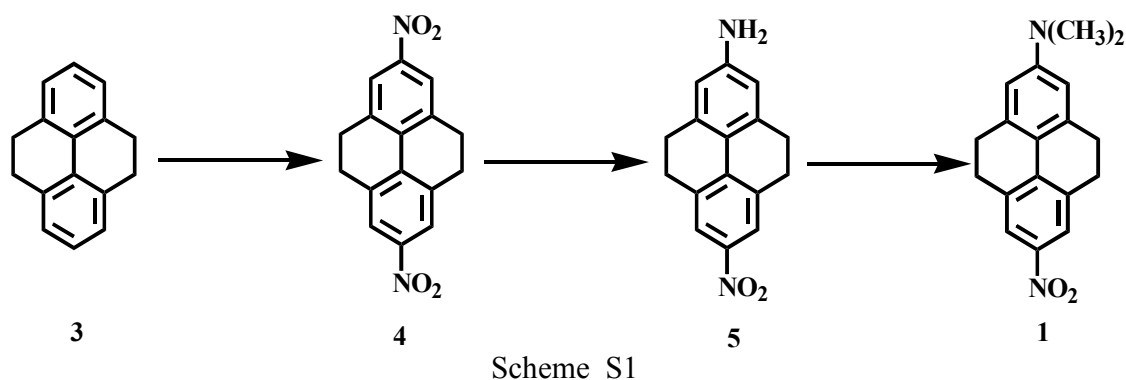


Synthesis and Photophysical Studies of Donor Acceptor Substituted Tetrahydropyrenes

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Supplementary Information

The compounds **1** and **2** were prepared according to Schemes S1 and S2. The synthesis starts from tetrahydropyrene, which is prepared according to a literature procedure.¹



Synthesis of 4: The compound **5** is obtained by the nitration of **4** (2 gm, 9.7 mmol) using concentrated nitric acid (35 mL). The mixture was stirred for 2 h. It was poured into crushed ice, the precipitate was filtered, washed with water, dried and purified by triturating with benzene to give 1.8 g (70%) of **5**, mp 312-313 °C. ¹H NMR (CDCl₃, 300

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MHz): δ 3.04 (s, 8 H, benzylic), 8.02 (s, 4 H, aromatic). IR (KBr): 1600, 1522, 1336, 1103, 912, 741 cm^{-1} .

Synthesis of 5: The compound **5** (250 mg, 0.84 mmol) is partially reduced in a mixture (1:1) of methanol and THF using sodium hydrosulfide, prepared by the reaction between sodium ethoxide and hydrogen sulfide, (0.8 mL, 114 mmol) under reflux for 2h. The solvent was evaporated and the residue was extracted with dichloromethane. Dichloromethane was removed and the residue chromatographed over silica gel using a mixture (3:1) of chloroform and hexane to give 120 mg (53%), of **6** mp 166-167 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 2.8–3.1 (m, 8 H, benzylic), 6.42 (s, 2 H, aromatic), 7.9 (s, 2 H aromatic). ^{13}C NMR (CDCl_3): δ 28.06, 28.15, 112.38, 120.12, 121.20, 134.53, 137.74, 138.28, 144.83, 147.69. IR (KBr): 3430, 3343, 2950, 2831, 1600, 1517, 1315, 1160, 1087, 901, 770 cm^{-1} .

Synthesis of 1: For the synthesis of **1** a solution of **6** (200 mg, 0.75 mmol) in THF was added to a suspension of sodium hydride (90 mg, 3.76 mmol) in THF followed by iodomethane (266 mg, 1.9 mmol). The reaction mixture was refluxed for 6 h and treated with crushed ice. The solvent was removed under reduced pressure and the residue was extracted with dichloromethane. The organic layer was separated, washed with water and the solvent removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture (3:2) of chloroform and hexane to give 160 mg (73%) of **1**, mp 219-220 °C. ^1H NMR (CDCl_3 , 300 MHz): δ 2.85–2.89 (m, 8 H, benzylic), 3.03 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 6.46 (s, 2 H, ArH), 7.9 (s, 2 H, ArH). ^{13}C NMR (CDCl_3): δ 28.29, 28.56, 40.24, 109.55, 118.06, 121.17, 134.2, 137.86, 138.03, 144.5, 151.09. IR (KBr): 2934,

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2831, 1615, 1506, 1434, 1310, 1191, 1082, 881, 725 cm^{-1} . Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$:
C, 73.45; H, 6.16; N, 9.5. Found: C, 73.28; H, 6.22; N, 9.08.

Synthesis of 2: The synthesis of **2** was carried out according to Scheme S2. The compound **6** (100 mg, 0.43 mmol)¹ was hydrogenated in the presence of formaldehyde (40 mg, 1.29 mmol) in ethanol for 12 h using Pd/C (10%) as catalyst. The reaction mixture was filtered, the solvent was removed under reduced pressure and the residue was chromatographed over silica gel using a mixture (1:9) of hexane and chloroform to give **3**, (70 mg, 71%), mp. 174-175 °C. ¹H NMR (CDCl_3 , 300 MHz): δ 2.5 (s, 3 H, COCH_3), 2.89 (s, 8 H, benzylic), 3.0 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 6.46 (s, 2 H ArH), 7.64 (s, 2 H, ArH). ¹³C NMR (CDCl_3): δ 26.3, 28.4, 28.9, 40.4, 109.9, 126.1, 133.6, 134.1, 136.2, 137.6, 150.7, 197.6. IR (KBr): 2925, 2365, 1672, 1590, 1480, 1430, 1340, 1280, 1190, 1150, 1080, 950, 870 cm^{-1} . Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.5; H, 7.03; N, 5.17.

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