Deciphering the excited state intramolecular charge-coupled double proton transfer in an asymmetric quinoline-benzimidazole system

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Materials

Chemicals and solvents were purchased from Aldrich, Spectrochem, Matrix and used without any purification. The organic solvents including DMSO, DMF, CH_3CN, and THF were of HPLC grade. The progress of reactions was monitored by TLC analysis, performed on glass-coated silica gel GF254.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on the JEOL 400 MHz FT-NMR machine using $CDCl_3$-d_1 as solvent using tetramethylsilane (TMS) as an internal standard.

Chemical shifts are reported in ppm with TMS as an internal reference. Coupling constant is expressed in Hz with different multiplicity (s = singlet, d = doublet, t = triplet, m = multiplets). Bruker Micro Toff/ QII (Germany) has been used to determine the HRMS. UV-visible studies were performed on Shimadzu-2600 instrument using a slit width of 1.0 nm and matched quartz cells with 1.0 cm path length. The fluorescence spectra were recorded with Varian Cary Eclipse spectrophotometer. Lifetime fluorescence decay measurements were performed on Horiba spectrophotometer.

Synthesis of HQB

Compound **1** was synthesized by the reaction of 7-hydroxyquinoline (0.5 g, 3.5 mmol) with a solution of NaOH (3 g in 5 mL water) and chloroform (8 mL). The reaction mixture was stirred at 90 ^{o}C for 24 h. On completion of the reaction, the reaction mixture was cooled to room temperature. Solid was separated out and filtered the solid. The crude mixture was washed with water. The filtrate was neutralized with 0.5N HCl solution and extracted with chloroform to give 0.17 g yellow-colored compound **1**.

Further, compound **1** (0.17 g, 1 mmol) was mixed with *o*-phenylenediamine (**2**) (0.1 g, 1 mmol) in 10 mL of nitrobenzene. The reaction mixture was stirred and heated at 110 ^{o}C. On successful consumption of reactant materials, diethyl ether was added to get the crude solid. The solid was filtered and purified by column chromatography using $CHCl_3$ as an eluting solvent to get the pure compound **HQB**. The compound **HQB** was further characterized by NMR and mass spectrometric techniques. ^{1}H NMR ($CDCl_3$; 400 MHz; δ = ppm): 15.45 (s, broad, O*H*), 13.61 (s, broad, N*H*), 8.96 (d, *J* = 3.2 Hz, 1H, ArH), 8.10 (m, 1H, ArH), 7.79 (m, 2H, ArH), 7.43 (m, 1H, ArH), 7.35 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$; 100 MHz; δ = ppm): 163.6, 152.7, 149.3, 147.4, 139.4, 136.9, 131.8, 130.8, 123.4, 122.4, 121.4, 118.4, 117.7, 111.4; ESI-MS: m/e = 262.10. (M^{+}+1); calculated mass = 261.28; Absorption peaks = 360 nm, 315 nm and 305 nm.

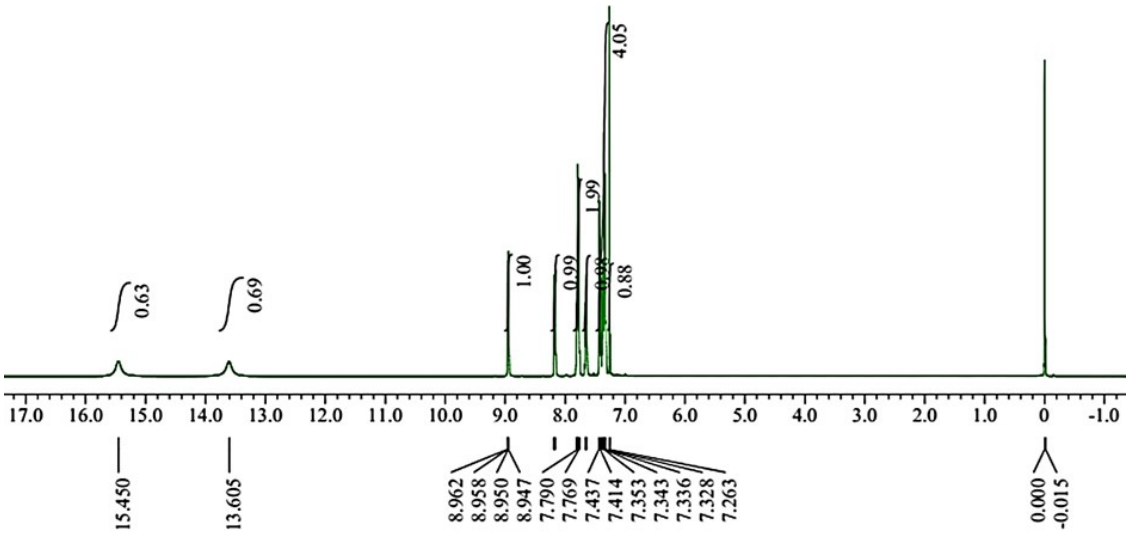

Figure S1. ^{1}H NMR spectra of **HQB**

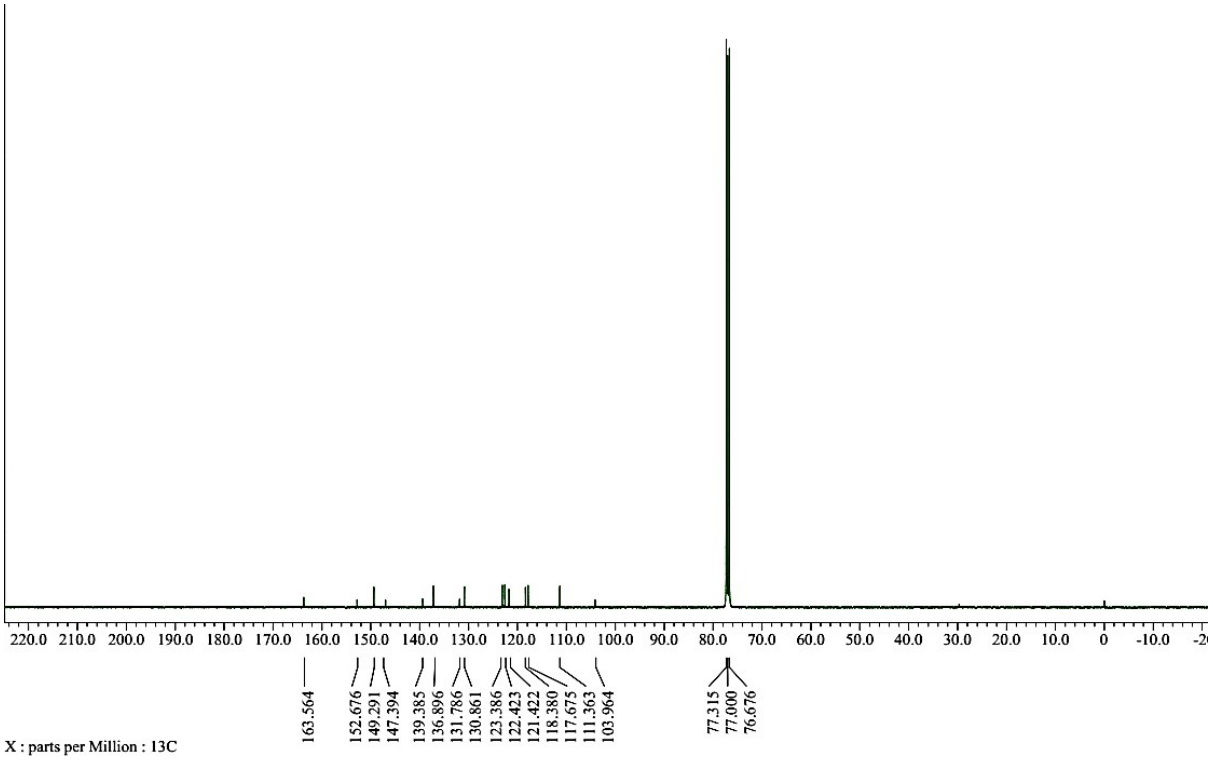

Figure S2. ^{13}C NMR of **HQB**

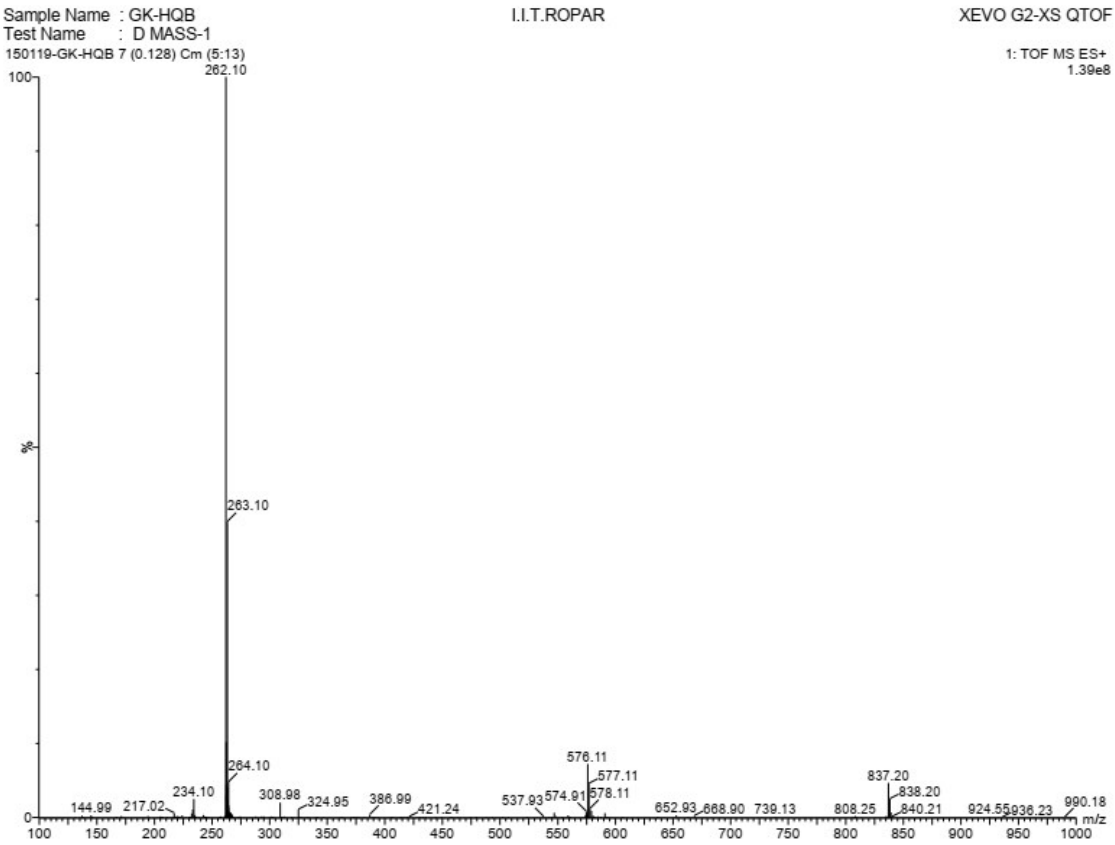

Figure S3. ESI-MS of **HQB**

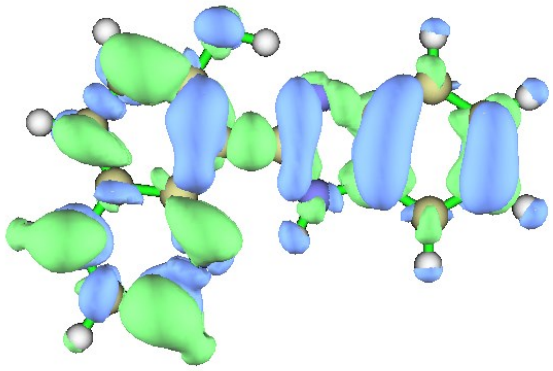

Figure S4. Density difference map of S_0 and S_1 states for **HQB**

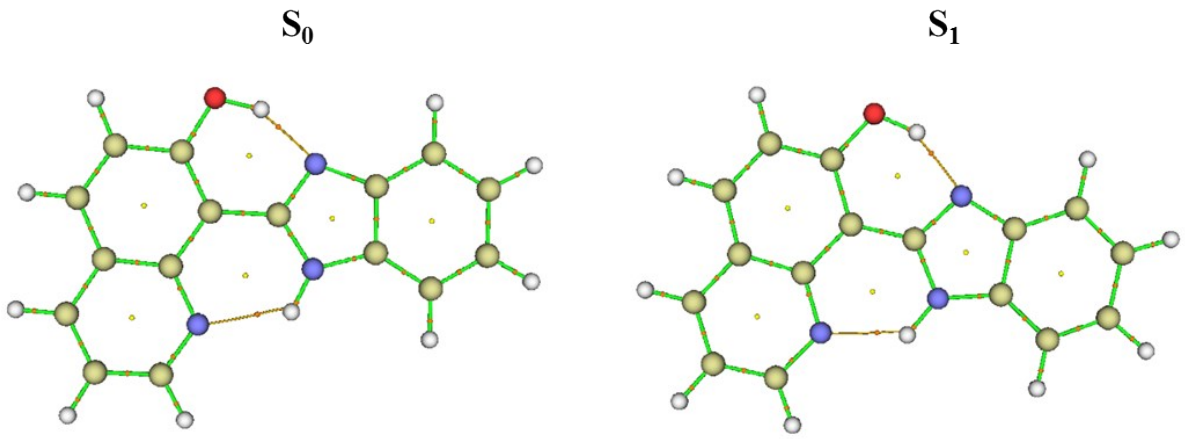

Figure S5. Molecular graph of **HQB** at S_0 and S_1 states

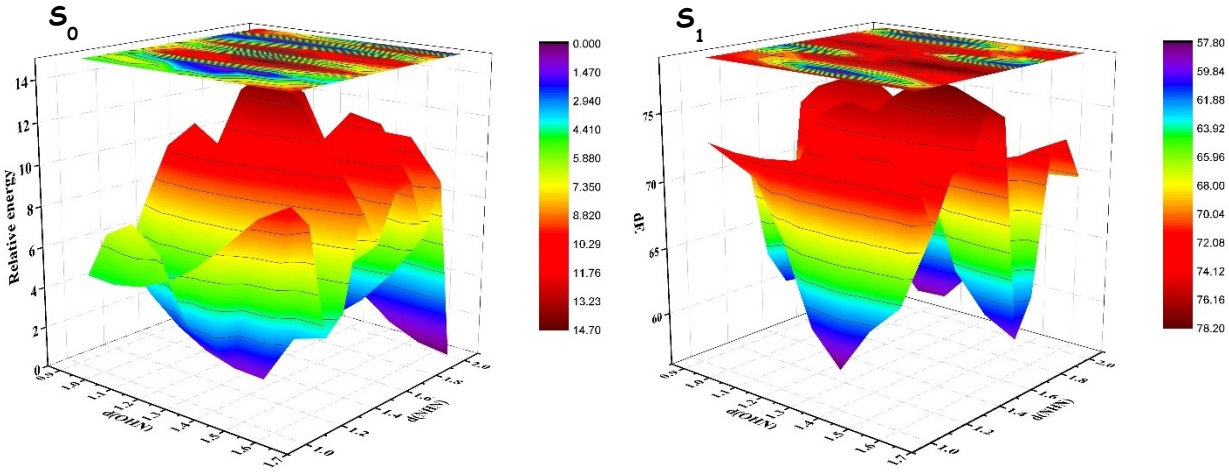

Figure S6. PES of proton transfer in S_0 and S_1 states

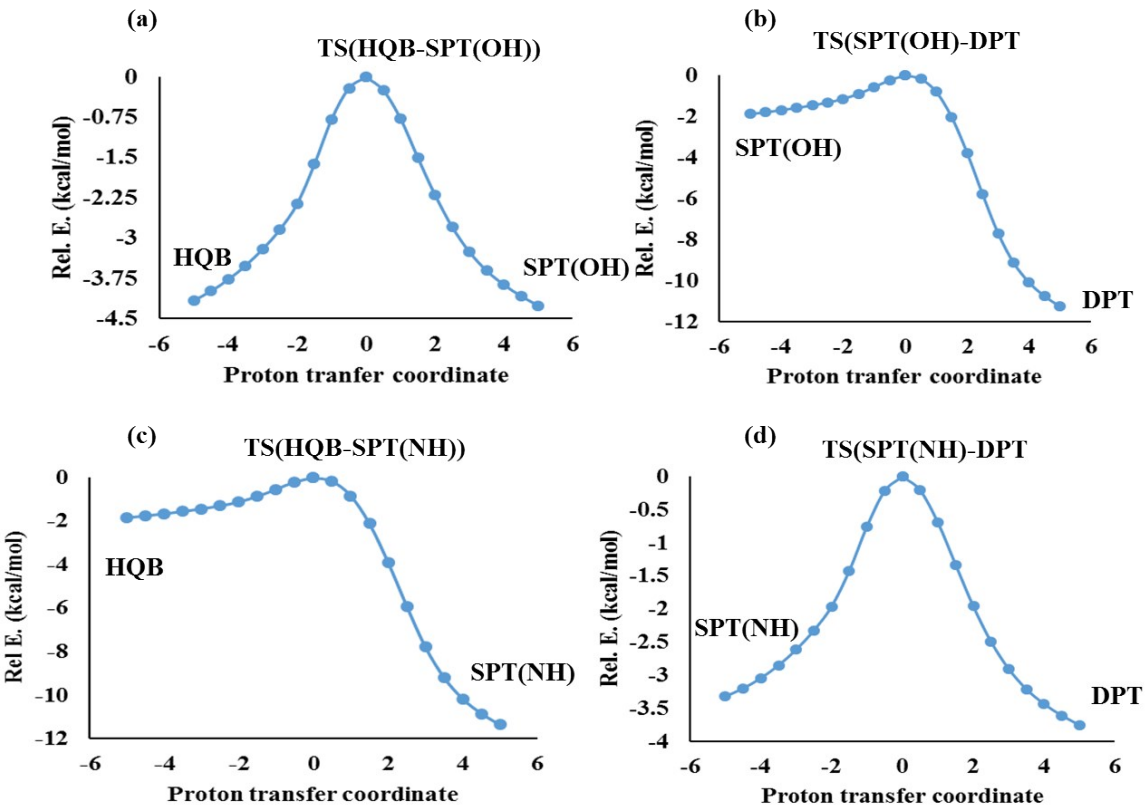

Figure S7. Energy profile of the excited state IRC for the stepwise proton transfer for the path I/ II (HQB → SPT(OH/NH) → DPT) in CH_3CN.

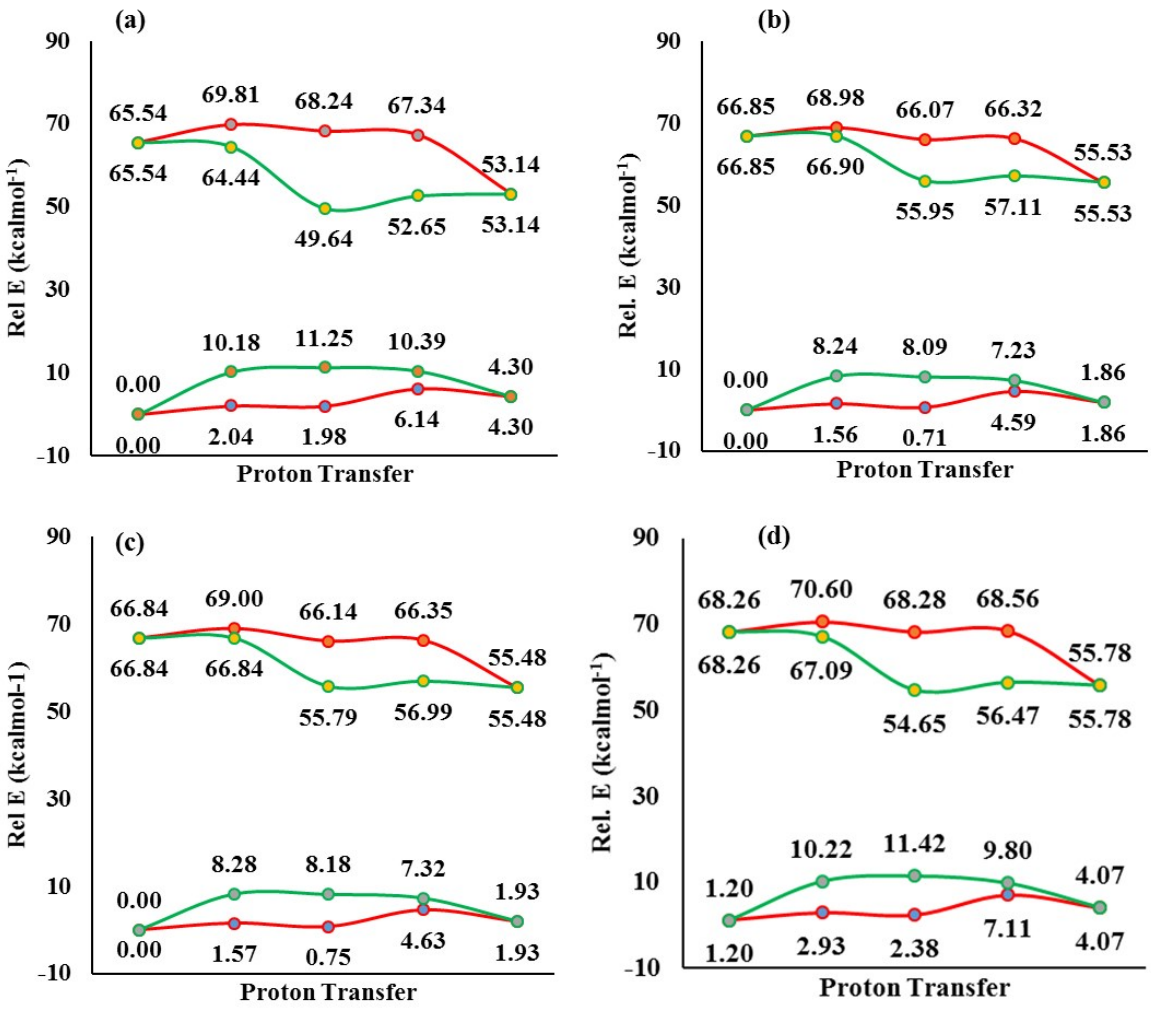

Figure S8 Energy profile of **HQB** in different solvents (a) cyclohexane (b) DMSO, (c) CH_3OH and (d) $CHCl_3$