Supporting Information

A Genuine Intramolecular Proton Relay System Undergoing Excited-state Double Proton Transfer Reaction

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Synthetic Details

All reactions were performed under nitrogen. Solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Merck pre-coated glass plates (0.20 mm with fluorescent indicator UV254) and were visualized with UV light irradiation at 254/366 nm. Flash column chromatography was carried out with use of silica gel from Merck (230-400 mesh). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) or fast atom bombardment (FAB) mode. The ^{1}H and ^{13}C NMR spectra were obtained on Bruker spectrometers operating at frequencies as indicated for each compound. FT-IR spectra were recorded on a Nicolet magna-IR 550 series II. Melting points were uncorrected.
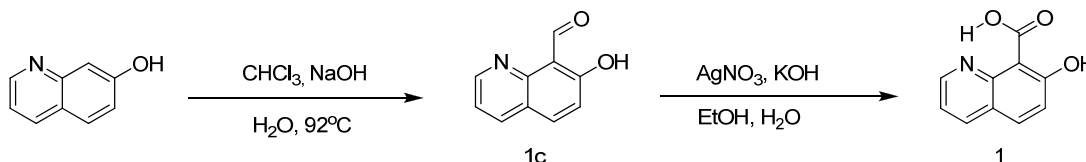
7-Hydroxyquinoline-8-carbaldehyde (**1c**)***.*** Chloroform (15 mL) was added to a mixture of 7-hydroxyquinoline (1.00 g, 6.9 mmol) in a solution of NaOH (7.00 g in 8 mL water). The reaction was stirred at 92 ^{o}C for 20 h. After cooling, the reaction was filtered, washing with water, and the filtrate was extracted into chloroform, which was separated and evaporated to give a residue that was purified by column chromatography (1:1 EtOAc/hexane) to give 7-hydroxyquinoline-8-carbaldehyde (0.38g, 32%) as a yellow solid: ^{1}H NMR (400 MHz, CDCl$_3$):δ 13.13 (s, 1H), 11.22 (s, 1H), 8.87-8.86 (m, 1H), 8.07-8.05 (m, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.37-7.34 (m, 1H), 7.20 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$):δ 197.4, 165.9, 153.7, 148.3, 137.2, 136.3, 120.6, 120.0, 118.8, 112.6. ESI-MS: *m/z* 174 (M+H)$^+$

***7-Hydroxyquinoline-8-carboxylic acid* (1).** To a stirred solution of 7-hydroxyquinoline-8-carbaldehyde (**1c**, 0.40 g, 2.3 mmol) in EtOH (6 mL), a solution of AgNO$_3$ (0.95g, 5.6 mmol) in distilled water (12 mL) was added slowly followed by the addition of a solution of KOH (1.26 g, 22.5 mmol) in water (25 mL) during 1 h. The reaction mixture was stirred at room temperature for an additional 8 h. It was filtered, aqueous layer washed with ether (2×15 mL) and neutralized with dil. HCl and extracted into ether (3 x 30 mL). Organic layer was washed with water, dried (Na$_2$SO$_4$), evaporated solvent and residue purified by column chromatography (Silica Gel, hexane:EtOAc, 6:4) to give **1** (0.27 g, 62%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d6):δ17.66 (s, 1H), 16.51 (s, 1H), 8.93 (d, *J* = 6.0 Hz, 1H), 8.82 (d, *J* = 6.0 Hz, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 7.66-7.63 (m, 1H), 7.30 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6): δ 173.31, 172.22, 144.27, 142.90, 141.91, 133.48, 125.54, 122.42, 117.20, 100.19. ESI-MS: *m/z* 190 (M+H)$^+$
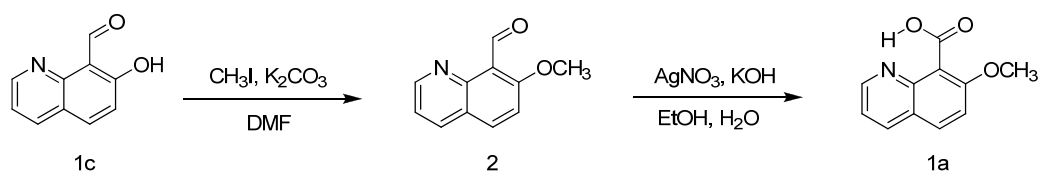
***7-Methoxyquinoline-8-carbaldehyde* (2).** 7-Hydroxyquinoline-8-carbaldehyde (**1c**, 0.35 g, 2.0 mmol) and K$_2$CO$_3$ (0.35 g, 2.5 mmol) were dissolved in 10 mL DMF. The CH$_3$I was added to the mixture under confined condition, and the reaction was stirred overnight at room temperature. The CH$_3$I was removed by evaporation. The reaction mixture was diluted by the 50ml water and extracted with EtOAc. The organic layer was dried over MgSO$_4$ and moved by evaporation. The crude material was purified by column chromatography using EtOAc/petroleum (1:1) to yield 0.30g (80%) of **2**. ^{1}H NMR (400 MHz, CDCl$_3$):δ 11.22 (s, 1H), 8.87(m, 1H), 8.07-8.05(m, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.37-7.34(m, 1H), 7.17(d, *J* = 8.4 Hz, 1H), 4.02(s, 3H). ESI-MS: *m/z* 188 (M+H)$^+$

***7-Methoxyquinoline-8-carboxylic acid* (1a).** To a stirred solution of 7-methoxyquinoline-8-carbaldehyde (**2**) (0.37 g, 2.0 mmol) in EtOH (5 mL), a solution of AgNO$_3$ (0.68 g, 4.0 mmol) in distilled water (12 mL) was added slowly followed by the addition of a solution of KOH (0.90 g, 16.0 mmol) in water (25 mL) during 1 h. The reaction mixture was stirred at room temperature for an additional 8 h. It was filtered, aqueous layer washed with ether (2×15 mL) and neutralized with dil. HCl and extracted into ether (3×30 mL). Organic layer was washed with water, dried (Na$_2$SO$_4$), evaporated solvent and

residue purified by column chromatography (Silica Gel, hexane : EtOAc,1:1) to give **1a**.^{1}H NMR (400 MHz, CDCl$_3$):δ 8.92-8.91 (m, 1H), 8.09-8.07 (m, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.37-7.3 (m, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H). ESI-MS: *m/z* 204 (M+H)[+]
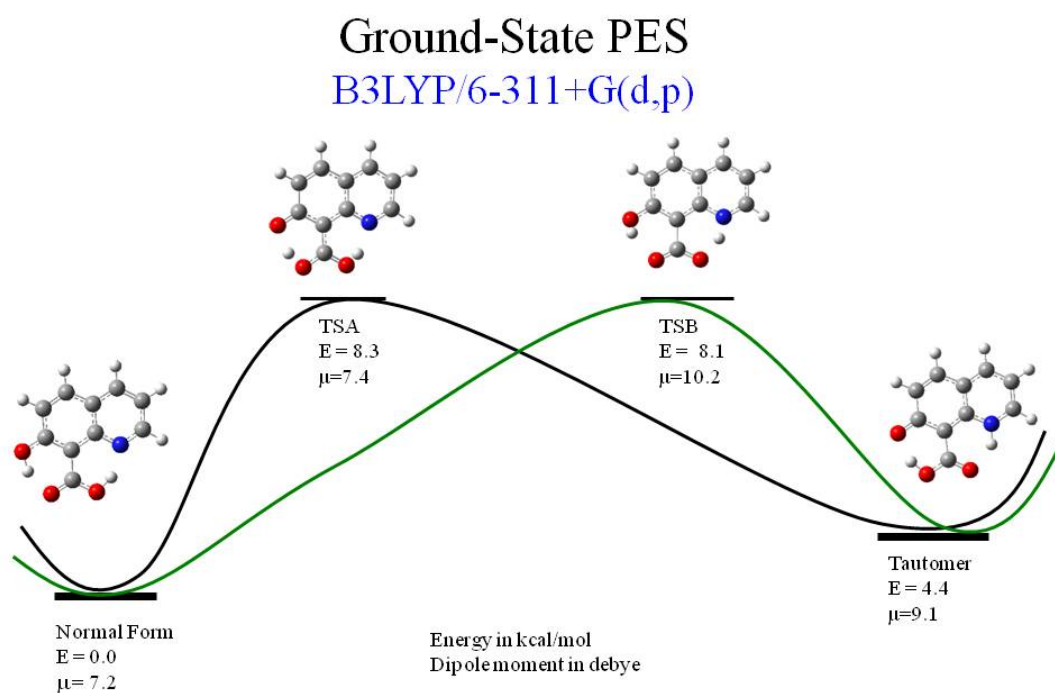
Computational Details

The structures, energies, and vibrational frequencies of the normal form, tautomer forms, and transition states of the double-proton transfer system of compound **1** in the gas phase were calculated using the B3LYP/6-311+G(d,p) method on the ground electronic state and using CIS/6-311+G(d,p) method on the first excited state. Time-dependent DFT with the B3LYP functional (TD-B3LYP) and 6-311+G(d,p) basis set was also used to calculate the structures of normal form and tautomer form of compound **1** on the first excited state. Single-point excited state energies were also calculated using the TD-B3LYP theory and the EOM-CCSD theory with the 6-311+G(d,p) basis set at the structures calculated at CIS/6-311+G(d,p) level. The vertical excitation energies of compound 1 at ground-state geometry was calculated using the TD-B3LYP/ 6-311+G(d,p) method. The vertical emission energy of the tautomer from the first excited state geometry was also predicted by TD-B3LYP/ 6-311+G(d,p) method. The EOM-CCSD calculation was performed using the Molpro 2009.1 program,[S1] and all other electronic structure calculation was performed usng the Gaussian 09 program.[S2]

References

(S1) MOLPRO, version 2009.1, designed by H.-J. Werner and P. J. Knowles, 2009.

(S2) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

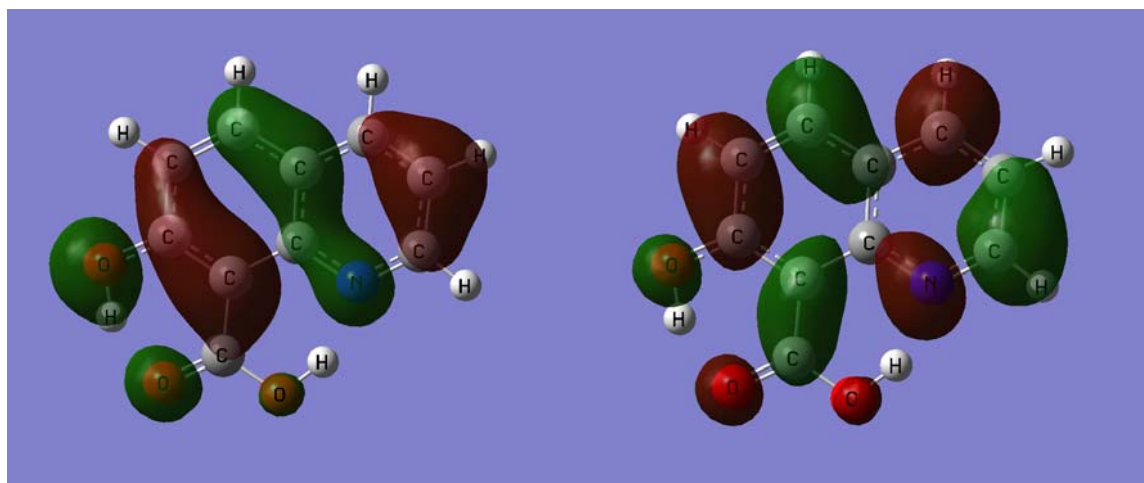**Scheme S1.** Ground-State Energetics Calculated by the B3LYP/6-311+G(d,p) Method

Ground-State PES
B3LYP/6-311+G(d,p)

TSA
E = 8.3
μ=7.4

TSB
E = 8.1
μ=10.2

Normal Form
E = 0.0
μ= 7.2

Tautomer
E = 4.4
μ=9.1

Energy in kcal/mol
Dipole moment in debye

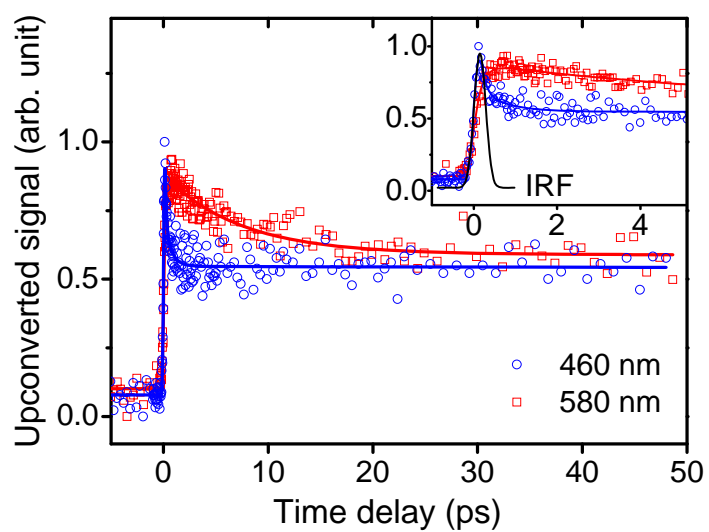**Figure S1.** Frontier orbitals of **1**. HOMO (left) and LUMO. (right)

Figure S2. Time-resolved femtosecond fluorescence up-conversion of deuterated compound **1** monitored at 460 nm (blue open circles, ○) and 580 nm. (red open squares, □) Solid lines depict corresponded fitting curves (blue and red) and instrument response function.(black) Inset: The depiction of relaxation dynamics within 5 ps.