Supporting Information of

A New Class of N–H Excited-State Intramolecular Proton Transfer (ESIPT) Molecules Bearing Localized Zwitterionic Tautomer

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1. Experimental Section

General.

All chemicals were used as received unless noted otherwise. Spectrophotometric grade solvents were used without further purification. All reported ¹H NMR and ¹³C NMR spectra were collected using 400 or 500 MHz spectrometers. Chemical shifts (δ ppm) were determined using TMS as an internal standard; J values are given in Hz. Melting points were determined using a capillary-type apparatus. Chromatography was performed on silica (230–400 mesh). Mass spectra were obtained via electron impact mass spectrometry with a double focusing sector mass analyzer (EI-MS) or using a time-of-flight spectrometer in positive or negative electrospray ionization mode (TOF MS ES+ or ES-)

Preparation of 2-(2'-nitrophenyl)imidazo[1,2-a]pyridine starting from 2-aminopyridine.[S1]



A sealed tube was charged with 1-(2-nitrophenyl)ethanone (12.0 mmol, 1982 mg), 2-aminopyridine (27.6 mmol, 2.3 eq., 2600 mg) and iodine (14.4 mmol, 1.2 eq., 3655 mg). The reaction mixture was stirred at 110 °C. After 4 h, the mixture was cooled to 70 °C and stirred overnight. The residue was diluted with 5 mL of distilled water, and an excess of aqueous sodium hydroxide (45%) was added. The reaction mixture was stirred at 100°C for 1 h. After cooling to room temperature, the reaction mixture was diluted with 60 mL of ethyl acetate. 10% aqueous HCl was added to the water-organic mixture until a neutral pH was obtained. The mixture was then extracted with ethyl acetate. The organic layer was washed with water, dried over Na₂SO₄, and concentrated under reduced pressure.

The product was isolated by column chromatography (silica, hexanes/ethyl acetate $6:1 \rightarrow$ hexanes/ethyl acetate 2:1). The pure product was obtained as a yellow solid (2210 mg, 77%). Data: mp 153-154 °C (lit. [S2] 151-152 °C); ¹H NMR (500 MHz, DMSO- d_6 , δ) 6.94 (dt, 1H, $J_1 = 6.8$ Hz, $J_2 = 1.12$ Hz), 7.28 (ddd, 1H, $J_1 = 9.2$ Hz, $J_2 = 6.7$ Hz, $J_3 = 1.3$ Hz), 7.55 – 7.60 (m, 2H), 7.73 (td, 1H, $J_1 = 7.7$ Hz, $J_2 = 1.3$ Hz), 7.84 (dd, 1H, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz), 7.93 (dd, 1H, $J_1 = 7.8$ Hz, $J_2 = 1.4$ Hz), 8.28 (s, 1H), 8.59 (dt, $J_1 = 6.8$ Hz, $J_2 = 1.2$ Hz); ¹³C NMR (125 MHz, DMSO- d_6 , δ) 108.7, 112.4, 115.2, 115.6, 116.0, 116.1, 124.5, 126.3, 127.7, 128.4, 143.5, 145.7, 146.6; HR-TOF MS(ES+) obsd 240.0763, calcd exact mass 240.0773 $C_{13}H_{10}N_3O_2 - [M+H]^+$.

2-(imidazo[1,2-a]pyridin-2-yl)aniline.[S1]



Ethanol solution of 2-(2'-nitrophenyl)imidazo[1,2-*a*]pyridine (8.0 mmol, 1910 mg) and $SnCl_2 \cdot 2H_2O$ (32.0 mmol, 4 eq., 7220 mg) was stirred at 100 °C for 12 h under inert atmosphere. After cooling to room temperature, using 5% NaHCO₃ aqueous solution pH of the reaction mixture was made slightly basic (pH 8–9). The resulting suspension was filtered through a pad of Celite, and washed with ethanol. Alcohol was evaporated and the remaining aqueous solution was extracted with ethyl acetate. Combined organic phase was washed with water and brine, dried over Na₂SO₄, and concentrated under reduced pressure. The product was isolated by column chromatography (silica, hexanes/ethyl acetate 3:1). The pure product was obtained as a yellowish solid (820 mg, 49%). Data: mp 126-127

°C (lit. [S1] 126-127 °C); ¹H NMR (500 MHz, DMSO- d_6 , δ) 6.53 – 6.60 (m, 3H), 6.73 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.2 Hz), 6.92 (td, 1H, J_1 = 6.7, J_2 = 1.2 Hz), 6.99 – 7.04 (m, 1H), 7.27 (ddd, 1H, J_1 = 9.1 Hz, J_2 = 6.7 Hz, J_3 = 1.3 Hz), 7.54 – 7.62 (m, 2H), 8.29 (s, 1H), 8.53 (dt, 1H, J_1 = 6.7 Hz, J_2 = 1.2 Hz); ¹³C NMR (125 MHz, DMSO- d_6 , δ) 111.0, 112.7, 116.8, 123.6, 125.5, 126.8, 127.1, 128.9, 130.5, 132.0, 139.8, 144.6, 148.8; HR-TOF MS(ES+) obsd 210.1022, calcd exact mass 210.1031 C₁₃H₁₂N₃ – [M+H]⁺.

N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)acetamide.



To a solution of 2-(imidazo[1,2-*a*]pyridin-2-yl)aniline (0.5 mmol, 105 mg) in dichloromethane (8 ml) was added dropwise acetyl anhydride (0.5 mmol, 1eq., 51 mg) to the mixture over 15 min at ice bath. Then warm to room temperature and stir for about 4 hours. The mixture was washed by water and purified by column chromatography (silica, hexanes/ethyl acetate 3:1). The pure product was obtained as a solid (116 mg, 93%). Data: mp 111-112 °C; ¹H NMR (500 MHz, DMSO- d_6 , δ) 2.19 (s, 3H), 7.01 (dt, 1H, J_1 = 6.79 Hz, J_2 = 1.1 Hz), 7.13 (dt, 1H, J_1 = 7.5 Hz, J_2 = 1.1 Hz), 7.28 – 7.33 (m, 1H), 7.35 (ddd, 1H, J_1 = 9.1 Hz, J_2 = 6.8 Hz, J_3 = 1.2 Hz), 7.70 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.1 Hz), 8.46 (d, 1H, J = 8.3 Hz), 8.49 (s, 1H), 8.60 (dt, J_1 = 6.7 Hz, J_2 = 1.2 Hz), 12.49 (s, 1H); ¹³C NMR (125 MHz, DMSO- d_6 , δ) 25.0, 110.5, 113.2, 116.4, 120.1, 120.5, 123.1, 125.7,

 $126.8, 127.4, 128.3, 136.9, 140.6, 143.5, 168.1; \ \text{HR-TOF} \ \text{MS(ES+)} \ \text{obsd} \ 252.1129, \ \text{calcd} \ \text{exact} \ \text{mass} \ 252.1137 \ C_{15} H_{14} N_3 O - [M+H]^{+}.$

2,2,2-trifluoro-N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)acetamide.



To a dichloromethane solution of 2-(imidazo[1,2-*a*]pyridin-2-yl)aniline (0.5 mmol, 105 mg) and trimethylamine (0.5 mmol, 1eq., 51 mg) TFAA (0.5 mmol, 1eq., 105 mg) was added dropwise to the mixture over 15 min at ice bath. Then warm to room temperature and stir for about 6 hours. The mixture was washed by water and purified by column chromatography (silica, hexanes/ethyl acetate 3:1). The pure product was obtained as a white solid (120 mg, 80%). Data: mp 168-169 °C; ¹H NMR (500 MHz, DMSO-*d*₆, δ) 7.05 (dt, 1H, *J*₁ = 6.8 Hz, *J*₂ = 1.1 Hz), 7.33 (dt, 1H, *J*₁ = 7.6 Hz, *J*₂ = 1.2 Hz), 7.38 – 7.46 (m, 2H), 7.58 (dd, 1H, *J*₁ = 9.0 Hz, *J*₂ = 0.8 Hz), 7.99 (dd, 1H *J*₁ = 9.0 Hz, *J*₂ = 1.5 Hz), 8.47 (dd, 1H, *J*₁ = 8.3 Hz, *J*₂ = 1.0 Hz), 8.61 (s, 1H), 8.63 (dt, 1H, *J*₁ = 6.8 Hz, *J*₂ = 1.1 Hz), 14.62 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆, δ) 110.8, 113.6, 116.0, 120.7, 120.9, 125.5, 126.7, 127.1, 127.4, 128.0, 134.3, 142.6, 143.3, 153.8, 154.1; HR-TOF MS(ES+) obsd 306.0855, calcd exact mass 306.0854 C₁₅H₁₁F₃N₃O – [M+H]⁺.

N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)-4-methylbenzenesulfonamide.[S1]



A mixture of 2-(imidazo[1,2-*a*]pyridin-2-yl)aniline (0.5 mmol, 105 mg) and 4-toluenesulfonyl chloride (0.8 mmol, 153 mg) was mixed in 5 ml of pyridine and stirred for 24h under inert atmosphere at 50 °C. Reaction was quenching by addition of aqueous solution of HCl to reaction mixture. The resulting suspension was diluted with water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The pure product was obtained after crystallization from methanol solution as a white solid (175 mg, 97%). Data: mp 181-182 °C (lit. [S1] 181-182 °C); ¹H NMR (500 MHz, DMSO-*d*₆, δ) 2.24 (s, 3H), 7.04 (td, 1H, *J*₁ = 6.8 Hz, *J*₂ = 1.1 Hz), 7.09 – 7.16 (m, 3H), 7.24 – 7.29 (m, 1H), 7.40 (ddd, 1H *J*₁ = 9.0 Hz, *J*₂ = 6.8 Hz, *J*₃ = 1.3 Hz), 7.48 – 7.54 (m, 3H), 7.72 (dd, 1H, *J*₁ = 9.0 Hz, *J*₂ = 0.7 Hz), 7.74 (dd, 1H, *J*₁ = 7.8 Hz, *J*₂ = 1.5 Hz), 8.37 (s, 1H), 8.57 (dt, 1H, *J*₁ = 6.8 Hz, *J*₂ = 1,1 Hz), 12.68 (s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆, δ) 2.09, 110.4, 113.4, 116.3, 120.2, 121.1, 124.1, 126.3, 126.6, 126.9, 127.5, 128.7, 129.4, 135.5, 136.1, 142.8, 143.3; HR-TOF MS(ES+) obsd 364.1122, calcd exact mass 364.1120 C₂₀H₁₈N₃O₂S – [M+H]⁺.

2,3,4,5,6-pentafluoro-N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)benzenesulfonamide.



A mixture of 2-(imidazo[1,2-*a*]pyridin-2-yl)aniline (0.5 mmol, 105 mg) and pentafluorobenzenesulfonyl chloride (0.8 mmol, 213 mg) was mixed in 5 ml of pyridine and stirred for 6h under inert atmosphere at room temperature. Reaction was quenching by addition of aqueous solution of HCl to reaction mixture. The resulting suspension was diluted with water and extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated under reduced pressure and purified by column chromatography (silica, hexanes/ethyl acetate 3:2). The pure product was obtained as a white solid (138 mg, 63%). Data: mp 216-218 °C; ¹H NMR (500 MHz, C₆D₆, δ) 5.98 (td, 1H, *J*₁ = 6.8 Hz, *J*₂ = 0.8 Hz), 6.44 (m, 1H), 6.75 (s, 1H), 6.85 (td, 1H, *J*₁ = 7.5 Hz, *J*₂ = 1.0 Hz), 6.91 (d, 1H, *J* = 6.7 Hz), 7.05 (m, 1H), 7.14 (d, 1H, *J* = 9.1 Hz), 7.30 (dd, 1H, *J*₁ = 7.8 Hz, *J*₂ = 1.5 Hz), 8.25 (d, 1H, *J* = 8.4 Hz), 14.25 (broad s, 1H); ¹³C NMR (125 MHz, DMSO-*d*₆, δ) 110.6, 113.6, 114.6, 116.0, 121.7, 122.7, 125.6, 126.7, 127.0, 128.0, 129.0, 133.8, 136.1, 138.2, 142.0, 142.4, 142.9, 143.3, 145.0; HR-TOF MS(ES+) obsd 440.0506, calcd exact mass 340.0492 C₁₉H₁₁N₃O₂F₅S – [M+H]*.

Computational details.

Geometry optimizations were performed to explore minimum energy structures for ground state using density functional theory (DFT) with the PBE1PBE[S3] (hereafter also termed PBE0, its usual name in the literature) hybrid functional. This functional provides a good description of hydrogen bond interactions. [S4, S5] Pople's 6-311++G(d,p) triple- ξ quality basis set[S6] with polarization and diffused functions was employed. Normal mode vibrational frequencies were also calculated in each case to confirm the presence of the local minimum, at the same level of theory. To simulate the effect of solvent, the geometries of selected conformers were optimized using a self-consistent reaction field (SCRF) approach coupled with integral equation formalism of the polarizable continuum model (IEFPCM).[S7, S8] For the thermodynamics of ESIPT, the geometries of the ground states were optimized by the density functional theory (DFT) with a B3LYP hybrid function method and the first excited-state structures were optimized by the time-dependent density functional theory (TDDFT) methodology with a CAM-B3LYP hybrid function in combination with a polarizable continuum model (PCM) in toluene. The 6-311++G(d,p) basis set was employed for all atoms. Single-point excited-state energies were also calculated using the TD-B3LYP theory with a 6-311++G(d,p) basis set under the structures optimized at the TD-CAM-B3LYP/6-311++G(d,p) level. All calculations were carried out using the Gaussian 09 program.[S9]

Spectroscopic measurements

Steady-state absorption spectra were recorded using a Hitachi U-3310 spectrophotometer, and emission spectra were obtained using an Edinburgh FS920 fluorimeter. Detailed time-resolved spectroscopic measurements have been reported previously.[S10] In brief, nanosecond time-resolved experiments were performed by using an Edinburgh FLS920 time-correlated single photon-counting (TCSPC) system with a pulsed hydrogen-filled lamp as the excitation source. Data were fitted with the sum of exponential functions using a nonlinear least-squares procedure in combination with a convolution method. Sub-nanosecond to nanosecond time-resolved studies were performed using another TCSPC system (OB-900 L lifetime spectrometer, Edinburgh) with an excitation light source from the second-harmonic generation (SHG, 360 nm) of pulse selected femtosecond laser pulses at 720 nm (Tsunami, Spectra-Physics). The fluorescence was collected at a right angle with respect to the pump beam path and passed through a polarizer, which was loca ted in front of the detector. The polarization was set at a magic angle (54.7°) with respect to the pump polarization direction to eliminate anisotropy. Similar data analysis and fitting procedures were applied. The temporal resolution, after partial removal of the instrumental time broadening, was ~20 ps.

Ultrafast spectroscopic study of the titled compounds was performed by a femtosecond photoluminescence up-conversion (uPL) system. The femtosecond oscillator (Tsunami, Spectra-Physics) mentioned in the previous paragraph was used with the central output wavelength at 720 nm. In this measurement, fluorescence from a rotating sample cell was focused in a BBO crystal, and its frequency was summed along with an interrogation gate pulse at a designated delay time with respect to the pump pulse. A half-wave plate was used to set the pump polarization at a magic angle (54.7°) with respect to the gate pulse to prevent the fluorescence anisotropy contributed by solute reorientation. Fluorescence up-conversion data were fitted to the sum of exponential functions convoluted with the instrument response function (IRF). The IRF was determined from the Raman scattering signal, and its profile was fitted to a Gaussian function with a full width at half- maximum of ~150 fs.

Scheme S1. Homodesmotic reaction used for the estimation of hydrogen bond strength.



Figure S1. Scaled stacked ¹H NMR spectra of C₆F₅Sulf-NHPIP in various solvents.



Figure S2. NOESY spectrum (left), ¹H NMR (bottom right) and selective NOE NMR (top right) spectra of 2-(imidazo[1,2-a]pyridin-2-yl)aniline in DMSO- d_6 solution.



Figure S3. The absorption (black line) and excitation spectra of (a) H-NHPIP (b) CH₃CO-NHPIP, (c) CH₃C₆H₄Sulf-NHPIP (d) C₆F₅Sulf-NHPIP and CF₃CO-NHPIP (blue and red line that monitored at normal and tautomer peak, respectively.



Figure S4. Decay kinetic acquired by pico-nanosecond time correlated single photon counting (TCSPC) for $CH_3C_6H_4Sulf-NHPIP$ in toluene. The data points (blue and red) shown are with monitored at normal and tautomer emission, respectively. Solid lines depict the best biexponential fits. The fitting parameters are summarized in Table 2. λ_{ex} =360nm.

(a) H-NHPIP



(b) CH₃CO-NHPIP



Figure S5. Geometrical structures of N*, TS* and T* species of compounds (a) H-NHPIP and (b) CH₃CO-NHPIP



(b)





Figure S6. Potential energy diagram for singlet excited-state transitions of (a) H-NHPIP and (b) CH₃CO-PIP.

Equilibrium constant of chemical reaction related to the standard Gibbs free energy is shown in eq. S1. Taking into account that calculated Gibbs free energy of reaction can be expressed by eq. S3, where $\varepsilon_0 + G_{corr}$ is sum of electronic and thermal Free Energies and also in view of two-component character of mixture, a concentration of the conformer **H-NHPIP** can be found following eq. S4. Relation between concentration of **H-NHPIP**(r) and concentration of **H-NHPIP** is shown by eq. S2.

$$\exp\left\{-\frac{\Delta_r G(298K)}{RT}\right\} = \frac{[\mathrm{H-NHPIP}(r)]}{[\mathrm{H-NHPIP}]}$$
(S1)

$$[H - NHPIP(r)] = 1 - [H - NHPIP]$$
(S2)

$$\Delta_r G(298K) = \left(\varepsilon_0 + G_{corr}\right)_{\mathrm{H-NHPIP}(r)} - \left(\varepsilon_0 + G_{corr}\right)_{\mathrm{H-NHPIP}}$$
(S3)

$$[\mathrm{H} - \mathrm{NHPIP}(\mathbf{r})] = \left[\exp\left\{ -\frac{\left(\varepsilon_0 + G_{corr}\right)_{\mathrm{H} - \mathrm{NHPIP}(\mathbf{r})} - \left(\varepsilon_0 + G_{corr}\right)_{\mathrm{H} - \mathrm{NHPIP}}}{RT} \right\} + 1 \right]^{-1} \quad (S4)$$

Table S1. Sum of electronic and thermal free energies, reaction Gibbs free energy and concentrations of H-NHPIP and H-NHPIP(r)conformers calculated for the gas phase and dimethyl sulfoxide (DMSO) medium described by polarizable continuum model.

Solvent	Gas phase	DMSO	
Sum of electronic and thermal free energies (ε ₀ +G _{corr}) for H-NHPIP , Hartree	-665.484292	-665.496155	
Sum of electronic and thermal free energies (ϵ_0+G_{corr}) for $\mbox{H-NHPIP(r)},$ Hartree	-665.478906	-665.492516	
Reaction Gibbs free energy, kcal/mol	3.380	2.283	
[H-NHPIP] in mixture, %	99.66	97.90	
[H-NHPIP(r)] in mixture, %	0.34	2.10	

cpds in toluene	λ _{cal.abs} /nm (ƒ)	λ _{cal.em} /nm (ƒ) ^[a]	НОМО	LUMO
H-NHPIP	378 (0.2908) 338 (0.2759)*	N: 409 (0.392) T: 688 (0.217)		
CH₃CO-NHPIP	340 (0.3781)	N: 379 (0.472) T: 649 (0.181)		
CH₃C₀H₄Sulf- NHPIP	330 (0.3376)	N: 373 (0.426) T: 572 (0.230)		
C ₆ F₅Sulf-NHPIP	331 (0.0447)	N: 367 (0.425) T: 509 (0.294)		
CF₃CO-NHPIP	331 (0.4404)	N: 370(0.477) T: 520(0.243)		

 Table S2. Computed absorption/emission wavelengths and oscillator strengths (f) of the first singlet excitation/relaxation in their normal or tautomer forms and the frontier orbitals for the titled compounds in their normal form involved in the first singlet excitation.

^[a] N = normal emission; T = tautomer (ESIPT) emission. * H-NHPIP (r)



2-(2-nitrophenyl)imidazo[1,2-a]pyridine









¹³C NMR in DMSO- d_6



2-(imidazo[1,2-a]pyridin-2-yl)aniline



S17





¹³C NMR in DMSO- d_6



N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)acetamide



¹H NMR in DMSO-d₆









2,2,2-trifluoro-N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)acetamide













N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)-4-methylbenzenesulfonamide







S30







2,3,4,5,6-pentafluoro-N-(2-(imidazo[1,2-a]pyridin-2-yl)phenyl)benzenesulfonamide



 ^1H NMR in C_6D_6



¹H NMR in C₆D₆ (detailed)







¹H NMR in CDCl₃ (detailed)







¹H NMR in (CD₃)₂CO (detailed)









¹³C NMR in DMSO- d_6

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