Electronic Supplementary Material (ESI) for New Journal of Chemistry.

ESI

Synthesis and Acid-Base Property of Proton-Bridged Biaryl Compound Based on Pyridylazulene

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1. vis-NIR spectra

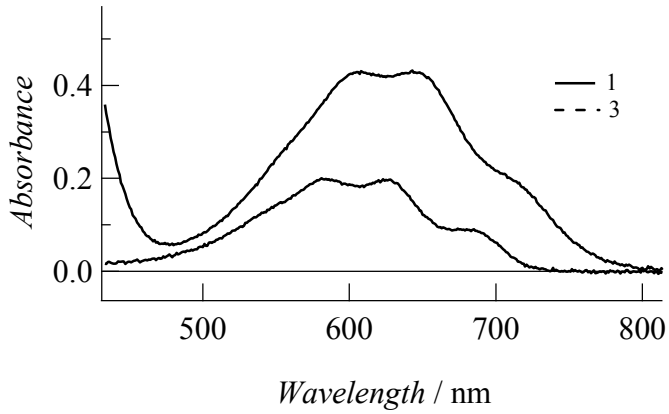


Figure S1. vis-NIR spectra of **1** and **3** in acetonitrile (0.5 mM)

2. DFT calculations

N–H distance dependences of the potential energy difference (ΔE) and molecular orbitals were calculated by the B3LYP/6-31G(d, p) level of theory. The initial structure was taken from the crystal structure where proton is positioned so as to N-H-N angle at 180 degree. The Δd is differential distance from a center between two N atoms and ΔE at Δd =0 is set to 0 eV. Potential energies were calculated for only Py rings where other azulene skeleton was deleted.

(i) Potential energy; ΔE with Δd

see figure 4 in main text

(ii) Molecular orbital with Δd

The situation of Δd = 0 is corresponded to transition state for proton hopping. DFT calculation showed that LUMO and LUMO+1 (as well as HOMO and HOMO-1) were almost degenerated at Δd = 0. Displacement from Δd = 0 slightly lowered HOMO-LUMO energy gaps. This is ascribed by decreased energy level of LUMO by stronger hydrogen bond between N and proton.

(iii-a) **1H$^+$-a**

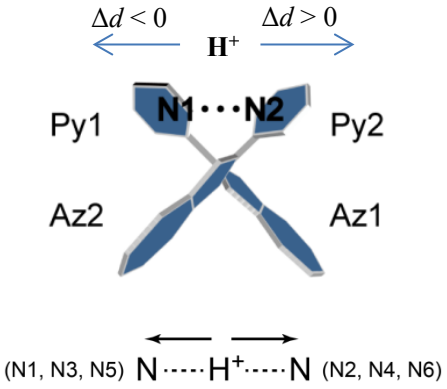
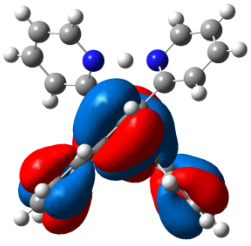
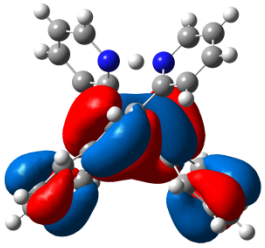
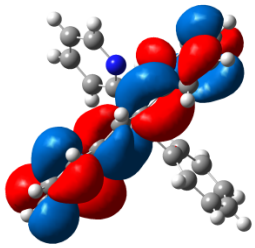
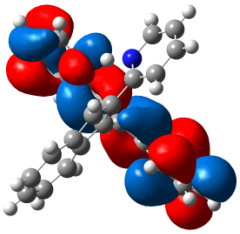
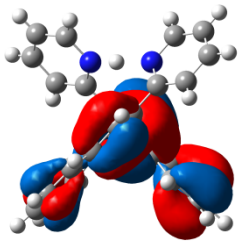
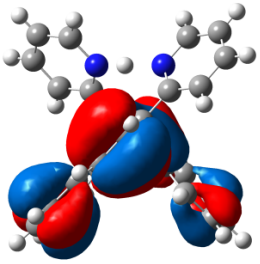
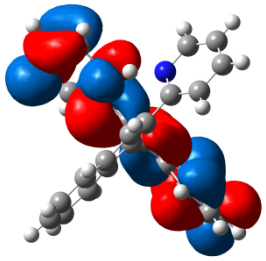
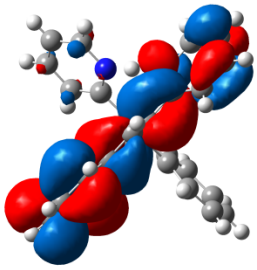
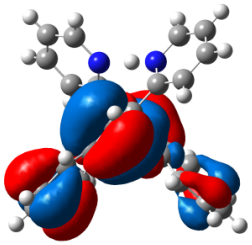
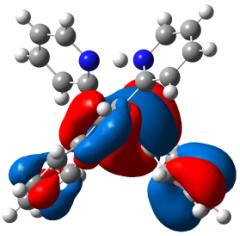
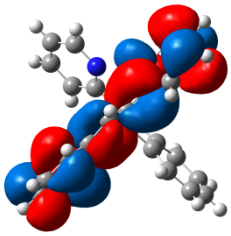
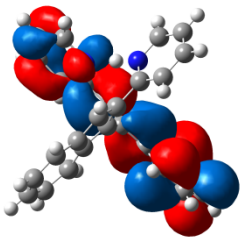


Figure S3-3-1. Molecular orientation with atomic number for table S3-3-1 to S3-3-3.

Table S3-3-1. Molecular orbitals and energies for **1H$^+$-a**.

Δd	HOMO-1(106)	HOMO (107)	LUMO (108)	LUMO+1(109)
0	-8.163 eV 	-8.027 eV 	-5.061 eV 	-4.898 eV 
-0.20	-8.163 eV 	-8.027 eV 	-5.252 eV 	-4.898 eV 
+0.20	-8.191 eV 	-8.027 eV 	-5.279 eV 	-4.871 eV 

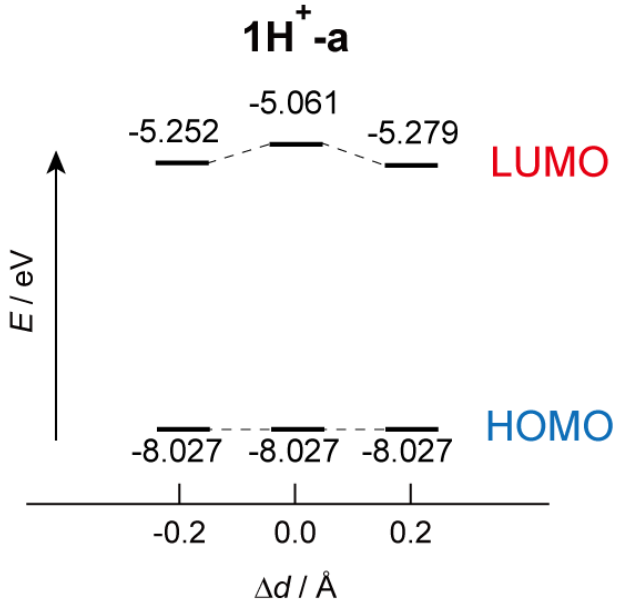
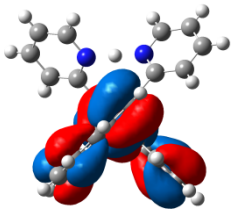
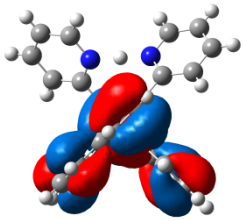
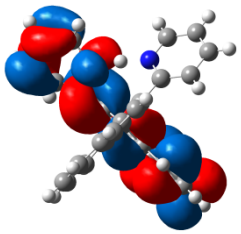
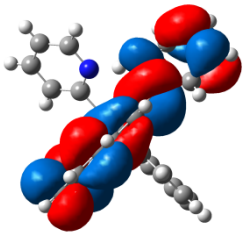
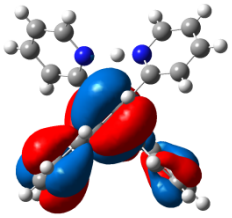
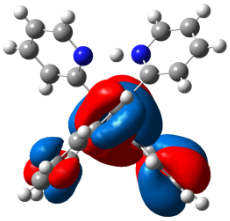
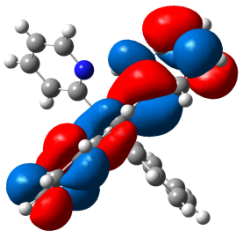
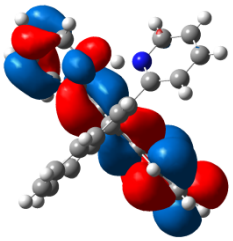


Figure S3-3-2. Energy diagram of **1H$^+$-a**.

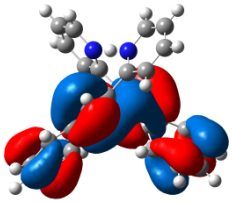
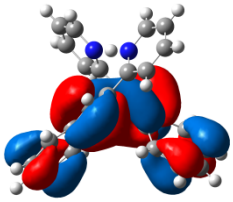
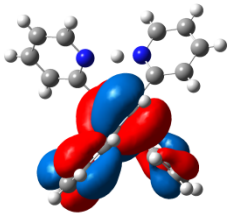
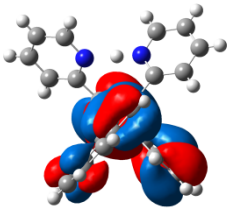
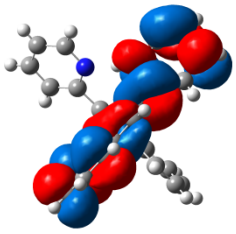
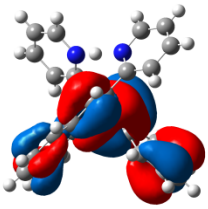
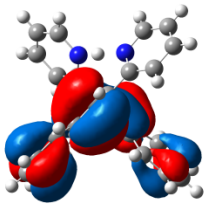
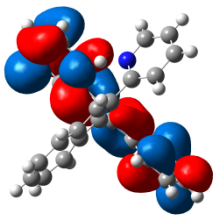
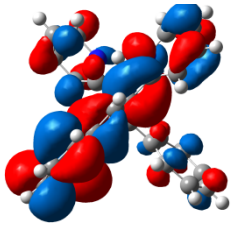
(b) **1H$^+$-b**

Table S3-3-2. Molecular orbitals and energies for **1H$^+$-b**.

Δd	HOMO-1(106)	HOMO (107)	LUMO (108)	LUMO+1(109)
0	-8.191 eV 	-8.082 eV 	-5.034 eV 	-5.007 eV 
(±)0.20	-8.218 eV 	-8.055 eV 	-5.252 eV 	-4.871 eV 

c) **1H$^+$-c**

Table S3-3-3. Molecular orbitals and energies for **1H$^+$-c**.

Δd	HOMO-1(106)	HOMO (107)	LUMO (108)	LUMO+1(109)
0	-8.218 eV 	-8.055 eV 	-5.034 eV 	-4.980 eV 
-0.20	-8.245 eV 	-8.055eV 	-5.197 eV 	-4.871eV 
+0.20	-8.128 eV 	-8.055 eV 	-5.306 eV 	-4.844 eV 

3. NMR

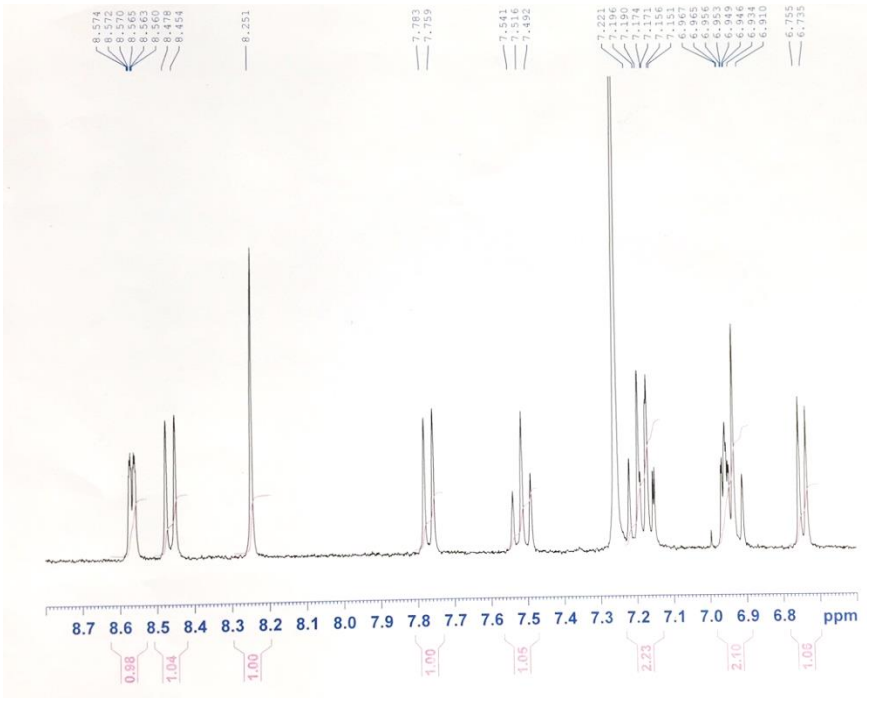


Figure S3-1. ^{1}H-NMR of **1**

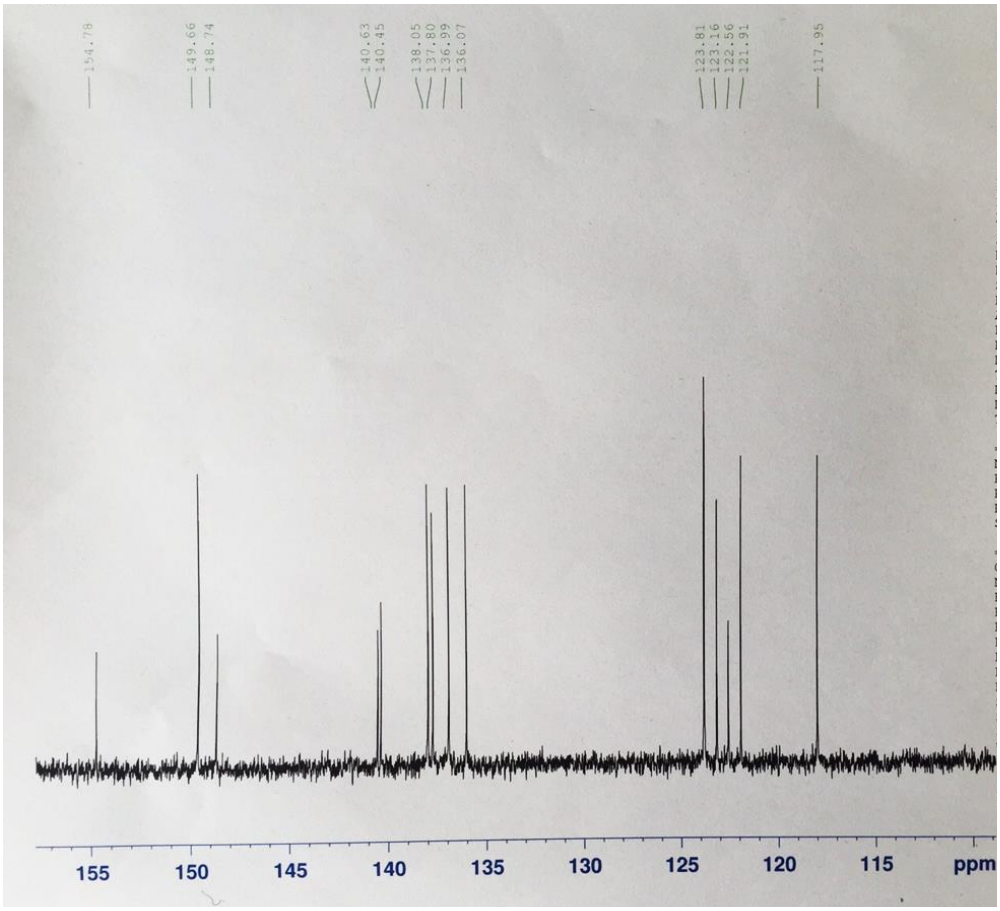


Figure S3-2. ^{13}C-NMR of **1**

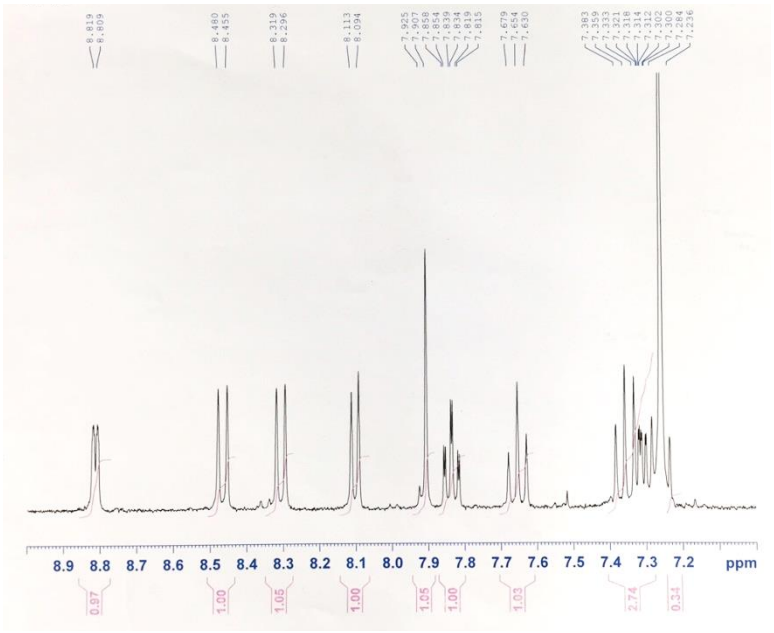


Figure S3-3. ^{1}H-NMR of **4**

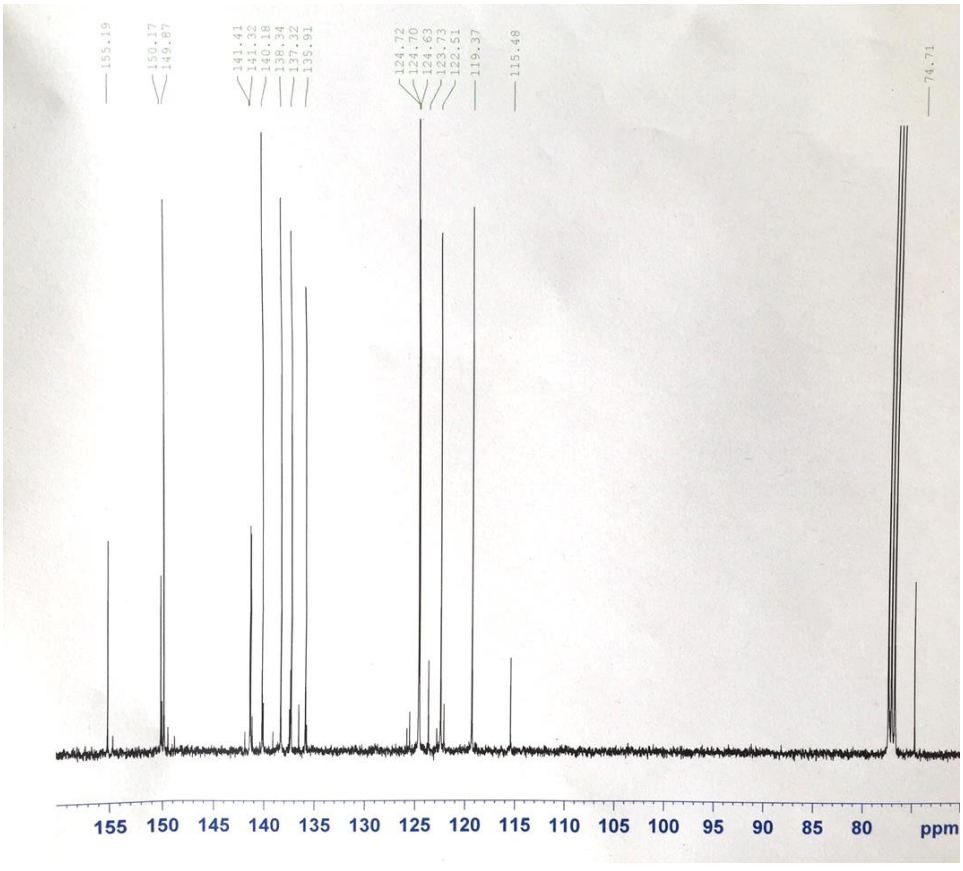


Figure S3-4. ^{13}C-NMR of **4;** Peaks at 115.5 and 123.7 are assigned to peaks by unseparated compound **3** (see ref 26).

4. Acid-base titration

We estimated concentration during titration according to following

$[1H] = (A-A_0)/(A_\infty-A_0)\times[1]_0$

where A, A_∞ and A_0 are absorbance (606 nm) during titration, at after titration (saturated) and before titration, respectively. $[1]_0$ is initial concentration of **1** (0.5 mM). By similar way, concentration of **3H** was estimated, but using absorbance at 700 nm. We have confirmed that corresponding results were obtained using absorbance at several different wavelengths.

Titration using HBF_4 resulted in similar changes (Figure S4). Peaks observed after protonation are almost corresponded. However, first and second protonation are almost overlapped. And spectra changes are saturated at 4 eq of acid. This is accounted for by stronger acidity of HBF_4 (p*K*a -0.4) than TFA (p*K*a 0.23).

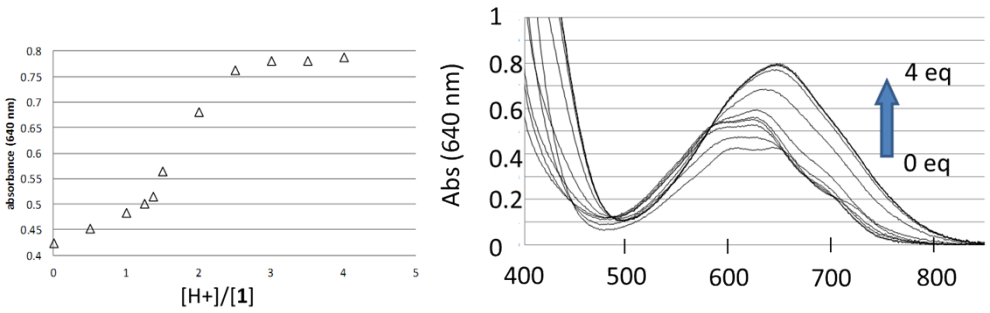


Figure S4. Plot of absorbance at 640 nm against proton concentration per concentration of **1** (left) and original UV-VIS spectra during titration upto 4 eq of proton against **1** (right).