Electronic Supplementary Information

Stimuli-responsive switching of magnetic properties and solid-state colors for 2, 3'-biimidazo[1,2-a]pyridin-2'-one radical derivatives

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Physical measurements

FT-IR spectra were recorded using a Bruker EQUINOX55 FT-IR spectrophotometer. The solid-state $^{13}$C NMR spectra were obtained on Bruker Avance 400 MHz NMR spectrometers. The solution (10$^{-4}$ M DMF or acetone), and the solid-state photoluminescence (PL) spectra and the decay lifetimes were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The quantum yields were measured also on a Fluorolog-3-TAU fluorescence spectrophotometer equipped with a BaSO$_4$-coated integrating sphere, upon excitation at 365 nm. Powder X-ray diffraction (PXRD) patterns were collected on a Philips X’pert PRO SUPER diffractometer operating with nickel-filtered Cu-Kα radiation ($\lambda = 1.540598$ Å). The EPR spectra were recorded on a JES-FA 200 ESR spectrometer at X-band. Temperature dependence of magnetic susceptibilities was measured for the microcrystalline samples using a SQUID magnetosusceptometer (Quantum Design MPMS).

The X-ray diffraction measurements were performed on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) using graphite monochromated Cu-Kα radiation ($\lambda = 1.54184$ Å). The structure was solved by direct method (SHELXL 97) and completed by difference Fourier method (SHELXL 97). Refinement was performed against $F^2$ by weighted full-matrix least-squares (SHELXL 97),$^{91}$ and empirical absorption correction (SCALE3 ABSPACK) was applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. The C−H hydrogen atoms were placed in geometrically calculated positions; the N−H and O−H hydrogen atoms were located in the difference Fourier map and kept fixed in that position. Weighted $R$ factor ($R_w$) and all goodness of fit S are based on $F^2$, conventional $R$ factor ($R$) is based on $F$.

The determination of Cl$^-$ amount from HCl gas treated 1 (1•(HCl)$_n$)

After 1 (0.19 g, 0.50 mmol) was exposed to HCl gas for 30 min, the resulting 1•(HCl)$_n$ sample was immersed in deionized water and treated 30 min by ultrasound.
After filtration, the AgNO₃ aqueous solution was dropwise added to the filtrate till no precipitate was produced, then the resulting precipitate was centrifugally separated and washed several times with dilute HNO₃ aqueous solution and ethanol, and then white AgCl solid was dried at 75 °C under vacuum condition for 8 h. Hereafter, the dried AgCl solid was weighed. The average 0.65 mmol Cl⁻ from three times repeated experiments was obtained.

The determination of NH₄Cl stoichiometry from HCl/NH₃ treated 1 (cycled 1)
After 1 (0.19 g, 0.5 mmol) was exposed to HCl gas for 30 min and then ammonia atmosphere for 5 min, resultant solid sample was again exposed to HCl gas for 30 min and then ammonia atmosphere for 5 min. After 5 such cycles, the resulting cycled 1 sample was immersed in deionized water and treated 30 min by ultrasound. After filtration, the AgNO₃ aqueous solution was dropwise added to the filtrate till no precipitate was produced, then the resulting precipitate was centrifugally separated and washed several times with dilute HNO₃ aqueous solution and ethanol, and then white AgCl solid was dried at 75 °C under vacuum condition for 8 h. Hereafter, the dried AgCl solid was weighed. The average 4.2 mmol Cl⁻ from three times repeated experiments was obtained. When NaOH aqueous solution was dropwise added to the settled solution from centrifugalization, the odour of ammonia gas was produced and such gas can make pH test strips become blue, indicating the existence of NH₄⁺ ion.

The determination of HCl stoichiometry from HCl gas treated 2 (2•(HCl)ₙ)
After 2 (0.19 g, 0.50 mmol) was exposed to HCl gas for 30 min, the resulting 2•(HCl)ₙ sample was immersed into saturated NaHCO₃ aqueous solution until no bubble was observed. After filtration, the AgNO₃ aqueous solution was dropwise added to the filtrate till no precipitate was produced, then the resulting precipitate was centrifugally separated and washed several times with dilute HNO₃ aqueous solution and ethanol, and then white AgCl solid was dried at 75 °C under vacuum condition for 8 h. Hereafter, the dried AgCl solid was weighed. The average 1.45 mmol Cl⁻ from three times repeated experiments was obtained.

Table S1 Selected bond angles (º) for 1a•2ClO₄⁻ and 2a•3ClO₄⁻•H₂O

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>1a•2ClO₄⁻</th>
<th>2a•3ClO₄⁻•H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(3)-C(17)-C(16)</td>
<td>112.9(2)</td>
<td></td>
</tr>
<tr>
<td>N(3)-C(17)-C(18)</td>
<td>101.35(19)</td>
<td></td>
</tr>
<tr>
<td>C(16)-C(17)-C(18)</td>
<td>114.2(2)</td>
<td></td>
</tr>
<tr>
<td>N(3)-C(17)-H(17)</td>
<td>109.4</td>
<td></td>
</tr>
<tr>
<td>C(16)-C(17)-H(17)</td>
<td>109.4</td>
<td></td>
</tr>
<tr>
<td>C(18)-C(17)-H(17)</td>
<td>109.4</td>
<td></td>
</tr>
<tr>
<td>O(2)-C(18)-N(4)</td>
<td>127.7(3)</td>
<td></td>
</tr>
<tr>
<td>O(2)-C(18)-C(17)</td>
<td>126.1(3)</td>
<td></td>
</tr>
<tr>
<td>N(4)-C(18)-C(17)</td>
<td>106.2(2)</td>
<td></td>
</tr>
</tbody>
</table>
Fig. S1 ORTEP diagrams of molecular structure of 1 (a) and 1a (b) with ellipsoids drawn at 50% probability.

Fig. S2 Dihedral angle between two imidazo[1,2-α]pyridine rings for 1 (a) and 1a (b).

Fig. S3 ORTEP diagrams of molecular structure of 2 (a) and 2a (b) with ellipsoids drawn at 50% probability.

Fig. S4 Dihedral angle between two imidazo[1,2-α]pyridine rings for 2 (a) and 2a (b).
**Fig. S5** IR spectra of 1a and 2a.

**Fig. S6** The 1D chain structure of 1 formed by the hydrogen bonds and intermolecular π-π interactions.

**Fig. S7** The dimer structure of 2 formed by the hydrogen bonds (black dashed lines) and intermolecular π-π interactions (grey dashed lines).

**Fig. S8** 1D double-stranded chain structure of 2 formed by intermolecular close contacts.
Fig. S9 The 2D network of 1a formed by anion-π interactions.

Fig. S10 Room-temperature PL spectra of 1, 2, 1a and 2a in $10^{-4}$ M DMF solution upon excitation at 365 nm.

Fig. S11 Room-temperature PL spectra of 1a (a) and 2a (b) in $10^{-4}$ M acetone solution with addition of various amounts of triethylamine upon excitation at 365 nm.
Fig. S12 Photographs of acid-induced phosphorescent color changes taken under illumination with a 365-nm mercury lamp.

Fig. S13 The decay lifetime curves of 1 (a), 1a (b) and 1•(HCl)n (c) at emission peak of 583, 524 and 540 nm, respectively in the solid state. The lifetime (τ) is defined as the time in which the emission intensity decays to 1/e of the initial intensity (I₀), where e is the natural log constant and is equal to 2.718. (I = I₀e⁻(t/τ) \Rightarrow τ = t \Rightarrow I = (1/e) I₀).

Fig. S14 Solid-state X-Band EPR spectra of 1a and 2a (the inset) at room temperature.
**Fig. S15** The PXRD patterns of 1 (a), 1•(HCl)$_n$ (b) and 1a (c).

**Reference**

S1 G. M. Sheldrick, *SHELX-97, Programs for the Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen (Germany), 1997.