

Electronic Supplementary Information

Stacking-induced broadband near-infrared absorption beyond 2500 nm and deep-red phosphorescence from purely organic radicals

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Materials and physical measurements:

All reagents were commercially available and used without further purification. The FT-IR spectra (KBr disk, 4000–400 cm^{-1}) were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were obtained on Micromass GCT-MS instrument operating in electron impact (EI) mode and time of flight (TOF) mass detector. The solution (10^{-4} M DMF) and solid-state UV/Vis/NIR absorption spectra were recorded at room temperature on a DUV-3700 UV/vis/NIR spectrometer. The solution (10^{-4} M DMF) photoluminescence (PL) spectra, and solid-state PL spectra and the decay lifetimes were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The solid-state quantum yields were measured also on a Fluorolog-3-TAU fluorescence spectrophotometer equipped with a BaSO_4 -coated integrating sphere. The quantum yields of solution state were measured at room temperature in a 10^{-4} M DMF solution using quinine sulfate ($\Phi = 0.54$) as a reference. Corrections were made due to the change in solvent refractive indices.^{S1} The EPR spectra were recorded on a JES-FA 200 ESR spectrometer at X-band. Thermogravimetric analyses were performed under N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ with a Shimadzu TGA-50H thermogravimetric analyzer.

The X-ray diffraction measurements were performed on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) using graphite monochromated Cu-K α radiation ($\lambda = 1.54184\text{ \AA}$). The structures were 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), 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 .

Synthesis of 3-formyl-2,3'-biimidazo[1,2-*a*]pyridin-2'-one derivatives 1 and 2:

3-Formyl-2,3'-biimidazo[1,2-*a*]pyridin-2'-one (Hfbipo⁻) was synthesized according to previous procedure.^{S2} KOH (2.24 g, 40 mmol) were added into 25 mL ethanol containing Hfbipo⁻ (0.556 g, 2 mmol), and then acetophenone (1.4 mL, 10 mmol) was added. The reaction mixture was stirred at room temperature for 12 h, giving rise to the deep-green viscous solution, which was poured into 200 mL of water. The resulting deep-green suspension solution was acidified to pH 7 by acetic acid, leading to the orange suspension solution. After filtrated and washed with water, recrystallization of solid from DMF/H₂O (v/v, 2:1) afforded orange solid of **1**. Yield: 0.68 g (1.79 mmol, 89.5 %). IR (KBr, cm⁻¹): 3425(vs), 1647(vs), 1610(vs), 1556(s), 1518(s), 1487(s), 1353(m), 1335(m), 1282(s), 1245(m), 1218(s), 1175(m), 1110(w), 1040(m), 1014(m), 964(w), 890(w), 842(w), 811(w), 743(s), 697(m). HRMS (EI, m/z, [M]⁺): Calc. for C₂₃H₁₆N₄O₂: 380.25, Found: 380.

KOH (2.24 g, 40 mmol) were added into 25 mL ethanol containing Hfbipo⁻ (0.556 g, 2 mmol), and then 4-acetylpyridine (0.60 g, 5 mmol) was added. The reaction mixture was stirred at room temperature for 8 h, giving rise to the brown viscous solution, which was poured into 200 mL of water. The resulting brown suspension solution was acidified to pH 7 by acetic acid, leading to the red suspension solution. After filtrated and washed with water, recrystallization of solid from DMF/H₂O (v/v, 5:3) afforded red solid of **2**. Yield: 0.36 g (0.94 mmol, 47.0 %). IR (KBr, cm⁻¹): 3319(vs), 1650(vs), 1609(vs), 1562(m), 1519(s), 1487(m), 1359(m), 1337(w), 1286(s), 1243(s), 1228(s), 1050(w), 957(m), 805(w), 751(m), 698(w), 646(w), 610(m). HRMS (EI, m/z, [M]⁺): Calc. for C₂₂H₁₅N₅O₂: 381.28, Found: 381.

Orange block crystals of **1**•2(H₂O) and red block crystals of **2**•2(H₂O) suitable for X-ray diffraction analysis were obtained by slowly decreasing temperature (from 65 °C to room temperature) during recrystallization procedure.

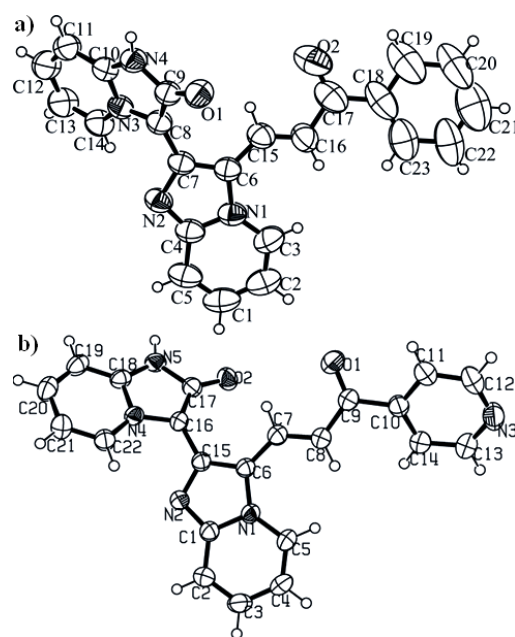


Fig. S1 ORTEP drawing of molecular structures of **1**(a) and **2** (b) with ellipsoids drawn at 50% probability.

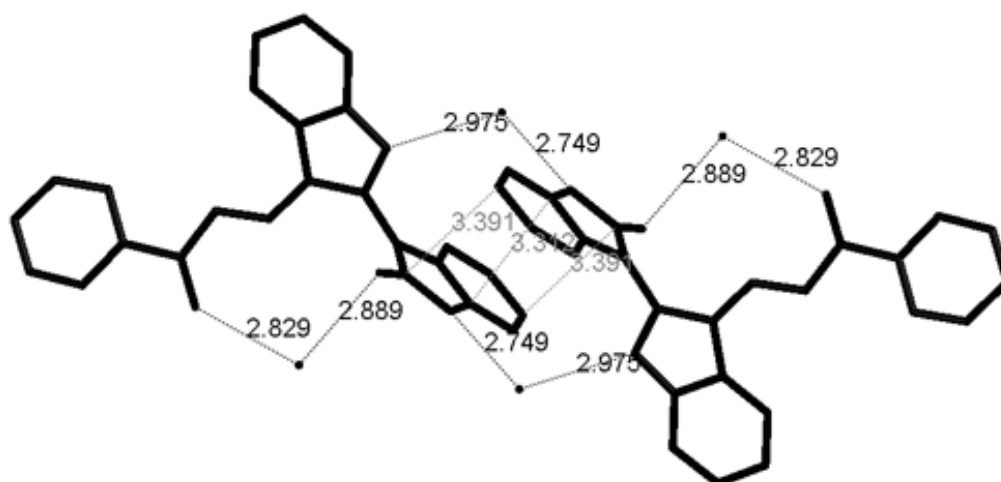


Fig. S2 The dimer structure of **2** formed by the hydrogen bonds (black dashed lines) and intermolecular π - π interactions (grey dashed lines).

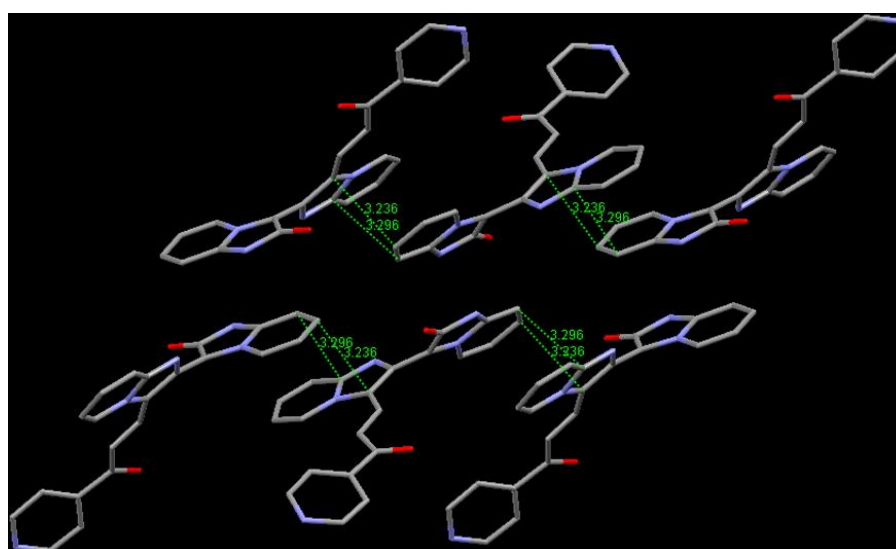


Fig. S3 1D chain structure of **2** formed by intermolecular close contacts.

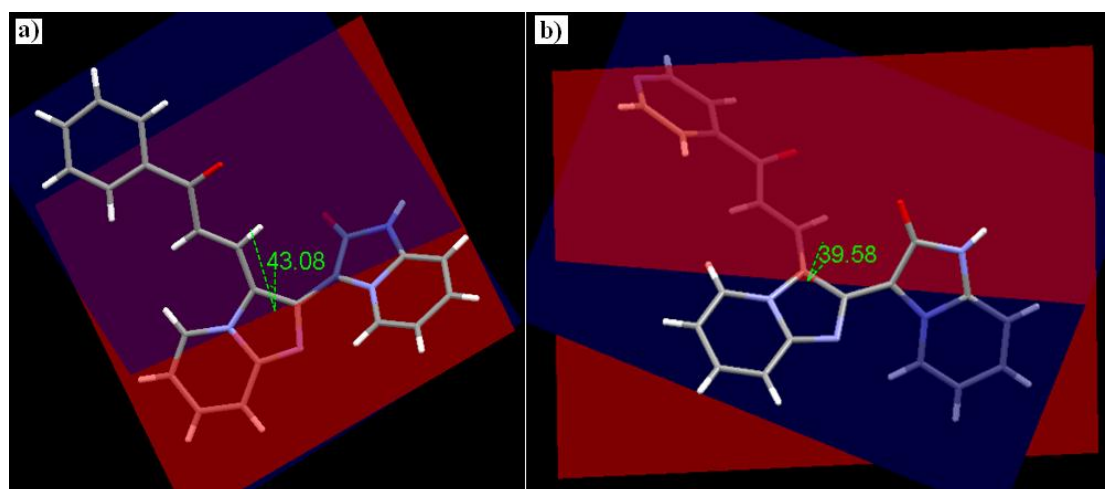


Fig. S4 Dihedral angle between two imidazo[1,2-*a*]pyridine rings for **1** (a) and **2** (b).

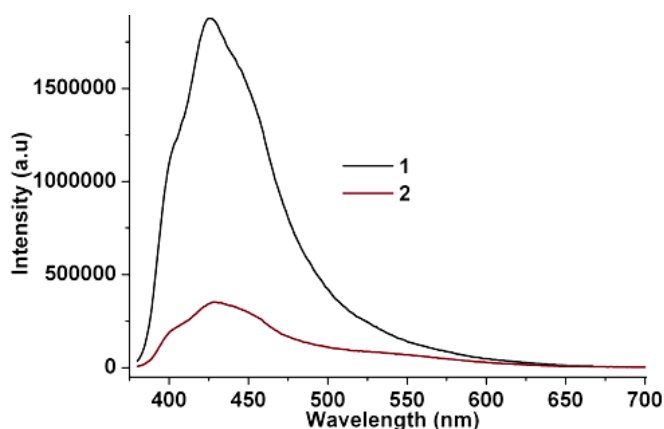


Fig. S5 Room-temperature PL spectra of **1** and **2** in 10^{-4} M DMF solution, upon excitation at 365 nm.

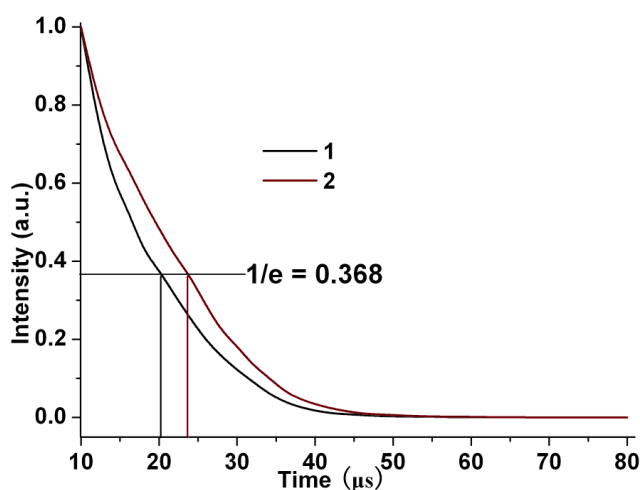


Fig. S6 The decay lifetime curves of **1** and **2** at emission peak of 583 and 665 nm, respectively in the solid state. The lifetime (τ) is defined as the time in which the emission intensity decays to $1/e$ of the initial intensity (I_0), where e is the natural log constant and is equal to 2.718. ($I = I_0 e^{-(t/\tau)} \Rightarrow \tau = t \Rightarrow I = (1/e) I_0$).^{S3}

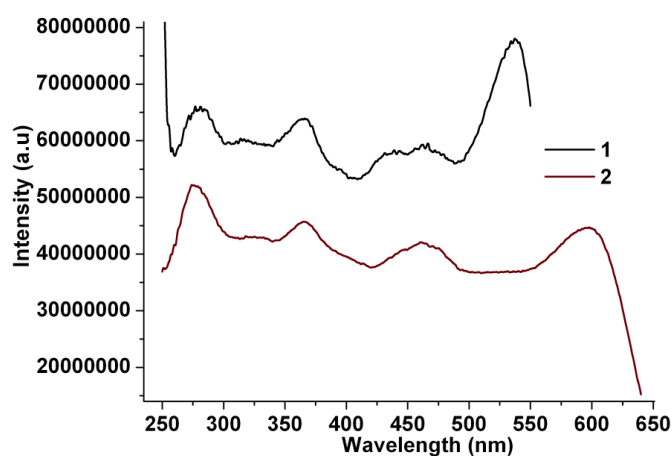


Fig. S7 Room-temperature solid-state excitation spectra of **1** and **2** under emission wavelengths of 583 and 665 nm, respectively.

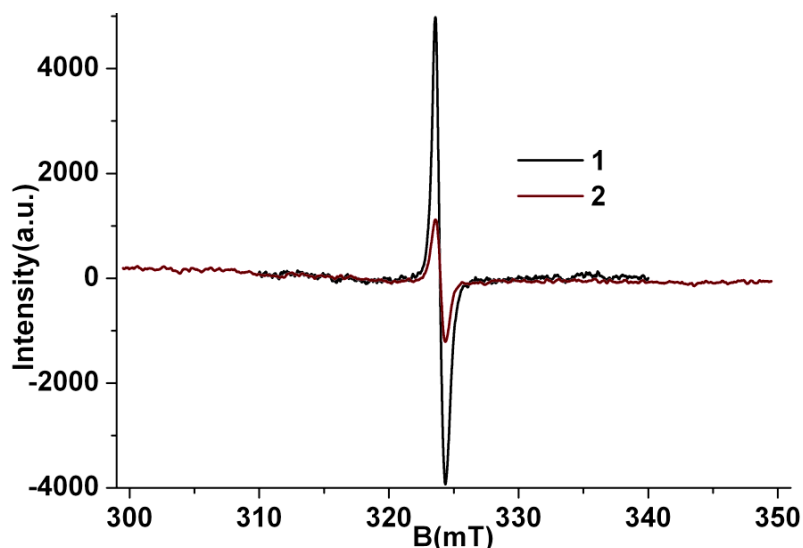


Fig. S8 Solid-state EPR spectra of **1** and **2** at room temperature.

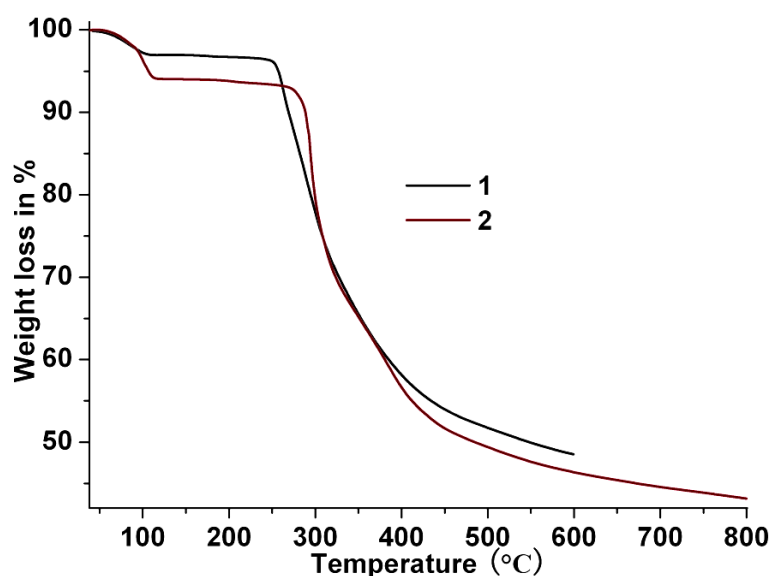


Fig. S9 TGA curves of **1** and **2**.

Because one guest water molecule only forms weak hydrogen bonds with **1** ($C23 \cdots O4 (H_2O) = 3.093 \text{ \AA}$ and $C3 \cdots O4 = 2.989 \text{ \AA}$), as described in crystal structure, this water molecule could easily be lost. As a result, TGA curve of microcrystal sample of **1** only reveals the loss of one guest water molecule, however, microcrystal sample of **2** exhibits the loss of two guest water molecules from TGA curve which is consistent with crystal structure.

Reference

- S1 C. F. Li, G. P. Yong and Y. Z. Li, *Inorg. Chem. Commun.*, 2010, **13**, 179–182.
S2 Y. Z. Li, G. P. Yong, Y. M. Zhang, C. F. Li and W. L. She, *Synth. Met.*, 2011, **161**, 713–717.
S3 K. C. Stylianou, R. Heck, S.Y. Chong, J. Bacsá, J. T. A. Jones, Y. Z. Khimyak, D. Bradshaw and M. J. Rosseinsky, *J. Am. Chem. Soc.*, 2010, **132**, 4119–4130.