

Electronic Supplementary Information

Stacking-induced white-light and blue-light phosphorescence from purely organic radical materials

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Materials and physical measurements:

All reagents were commercially available and used without further purification. Microanalytical data (C, H, N) were collected on an Elementar Vario EL III microanalyzer. The FT-IR spectra (KBr disk, 4000–400 cm^{-1}) were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer. The solution (10 μM H_2O and DMSO) photoluminescence (PL) spectra, and solid PL spectra and the decay lifetime were determined at room temperature on a Fluorolog-3-TAU fluorescence spectrophotometer. The solid quantum yield was measured on an Edinburgh FLS920 fluorescence spectrometer equipped with a BaSO_4 -coated integrating sphere, a 450-W Xe lamp, and a R928P PMT detector using the single-photon counting mode. The CIE-1931 chromaticity coordinates were calculated using a ColorCoordinate.exe program. The same results can also be obtained using a gocie.exe program from <http://www.geocities.com/krjustin/gocie.html>. Reflectance diffusion spectra were recorded in the solid state at room temperature on a DUV-3700 UV/vis/NIR spectrometer. The EPR spectra were recorded on a JES-FA 200 ESR spectrometer at X-band.

The X-ray diffraction measurement was performed on a Gemini S Ultra CCD diffractometer (Oxford diffraction Ltd.) using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). 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), 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 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxo-N-(pyridin-2-yl)acetamide:

m-Chloroperoxybenzoic acid (4.8 g, 24 mmol) was added into an ice-bath cooling DMF (120 mL) solution of Hbipo $^{\ominus}$ (5.5 g, 22 mmol), leading to a dark red solution. The reaction mixture was stirred for 2 h, giving rise to the yellow solid, which was collected by filtration and washed with water and methanol, recrystallization from ethanol afforded yellow solid of 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxo-N-(pyridin-2-yl)acetamide. Yield: 2.66 g (10 mmol, 45.5 %). IR (KBr, cm^{-1}): 3364(s), 3156(w), 3108(w), 3044(w), 1708(s), 1669(vs), 1639(m), 1589(w), 1577(w), 1521(vs), 1472(w), 1440(s), 1306(w), 1154(w), 1125(w), 1055(w),

1044(w), 763(m). Anal. Calc. (%) for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.90; H, 3.91; N, 21.21. The proposed mechanism for this *m*-chloroperoxybenzoic acid promoted ring-opening reaction under mild conditions is shown in Scheme S1.

Synthesis of compound 1a:

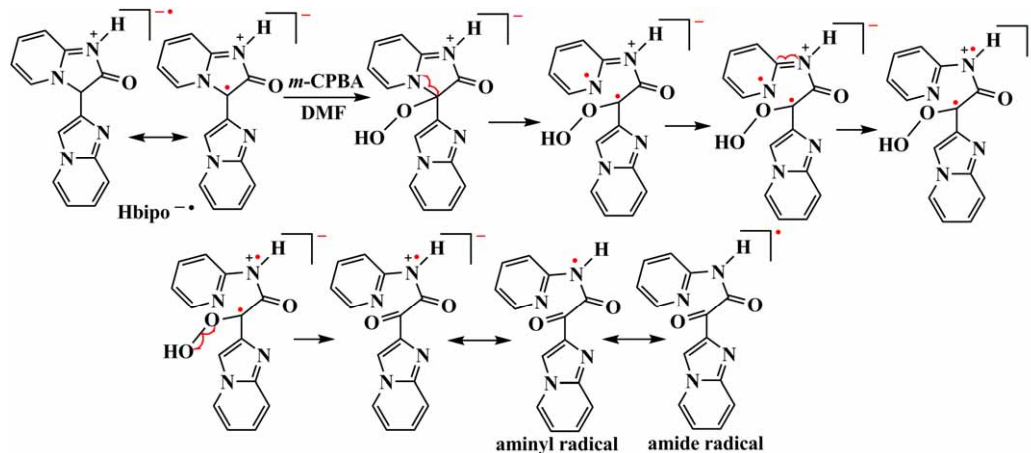
To a solution of 2-(imidazo[1,2-*a*]pyridin-2-yl)-2-oxo-*N*-(pyridin-2-yl)acetamide (0.50 g, 1.88 mmol) and ethanol (20 mL) was added 0.5 mL 7 mol L⁻¹ NaOH aqueous solution, and then the solution was refluxed for 48 h at 50 °C. The resulting white solid (**1a**) was collected by filtration and washed with ethanol, and then was recrystallized from ethanol. Yield: 0.32 g (1.5 mmol, 79.8%). IR (KBr, cm⁻¹): 3178(m), 3082(m), 3050(m), 1660(vs), 1613(vs), 1531(w), 1475(w), 1409(m), 1367(w), 1321(w), 1280(w), 1253(w), 1163(m), 1126(w), 1055(w), 939(w), 918(w), 848(w), 813(w), 766(w), 752(m), 723(m), 693(w). Anal. Calc. (%) for $C_9H_5NaN_2O_3$: C, 50.95; H, 2.37; N, 13.20. Found: C, 49.25; H, 2.36; N, 12.82. The calculated composition of **1a** is in good agreement with EA data. No IR bands in the range of 1760–1680 cm⁻¹ indicate **1a** is a carboxylate salt.

Synthesis of compound 1:

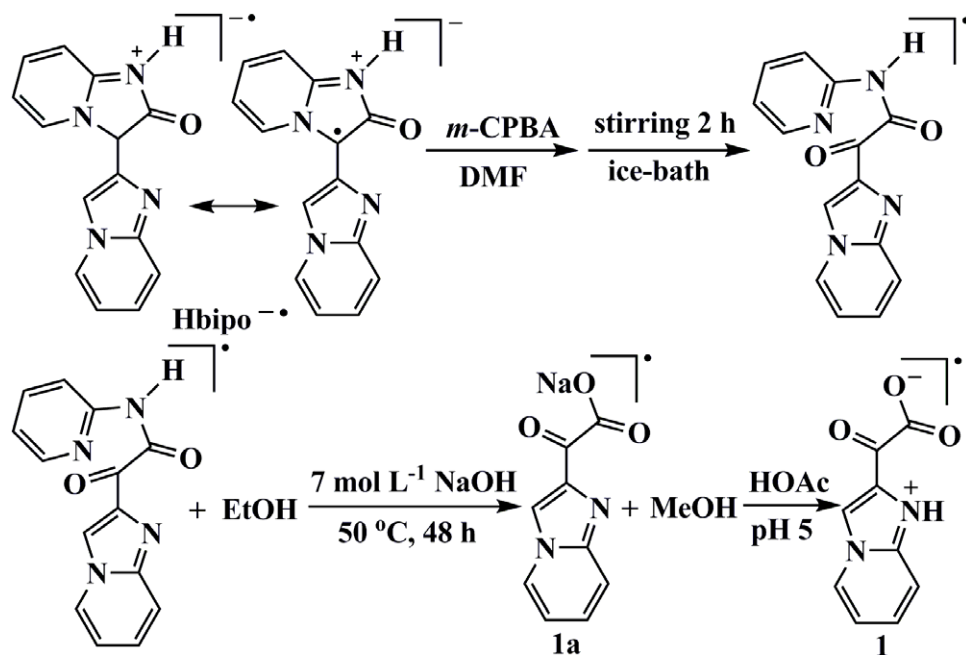
To a suspension of **1a** (0.32 g, 1.5 mmol) and methanol (20 mL) was added HOAc until pH 5. The resulting solid was collected by filtration and washed with methanol, and then recrystallized from ethanol, affording white solid **1**. Yield: 0.228 g (1.2 mmol, 80 %). IR (KBr cm⁻¹): 3173(m), 3107(w), 3083(m), 3033(m), 1656(vs), 1618(vs), 1534(s), 1476(w), 1458(w), 1407(s), 1371(m), 1358(m), 1324(m), 1282(m), 1260(w), 1172(s), 1132(s), 1058(s), 940(m), 918(w), 852(w), 815(m), 792(m), 774(m), 752(s), 722(m). Anal. Calc. (%) for $C_9H_6N_2O_3$: C, 56.84; H, 3.16; N, 14.74. Found: C, 56.27; H, 3.32; N, 14.25. Colorless block crystals of **1**·(H₂O) suitable for X-ray single-crystal diffraction analysis were prepared by diffusion of acetone into the aqueous solution of **1**.

The detailed synthetic steps for carboxylic acid radical and its sodium salt from Hbipo^{-•} are presented in Scheme S2.

It should be indicated that the structures of **1** and **1a** characterized by ¹H- and ¹³C-NMR were unsuccessful, since they are radicals.



Scheme S1 Proposed mechanism for *in situ* *m*-CPBA promoted ring-opening reaction of Hbipo^{-•}.



Scheme S2 Synthetic steps for carboxylic acid radical and its sodium salt from Hbipo $^{\cdot-}$.

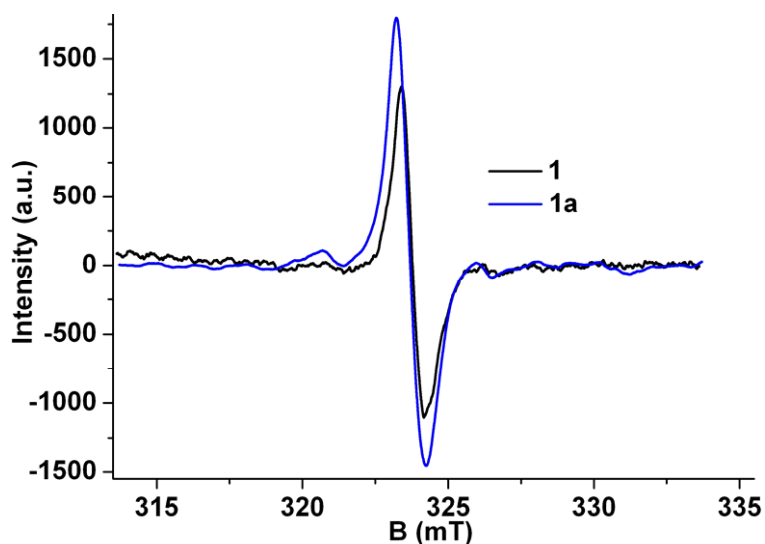


Fig. S1 Solid-state EPR spectra of 1 and 1a at room temperature.

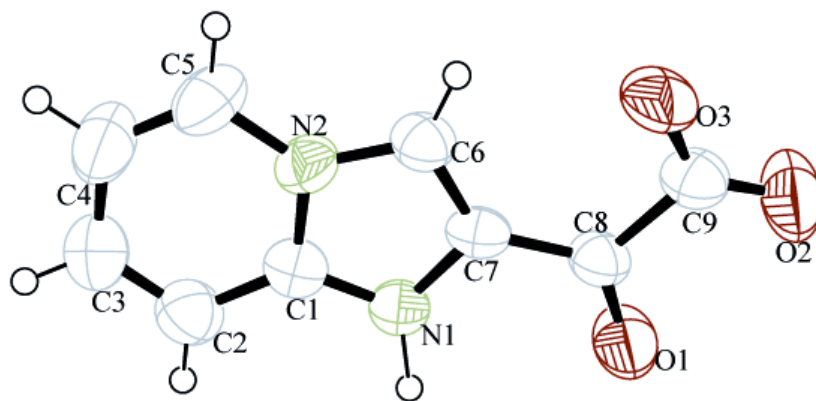


Fig. S2 ORTEP diagram of internal salt of 1 with ellipsoids drawn at 50% probability.

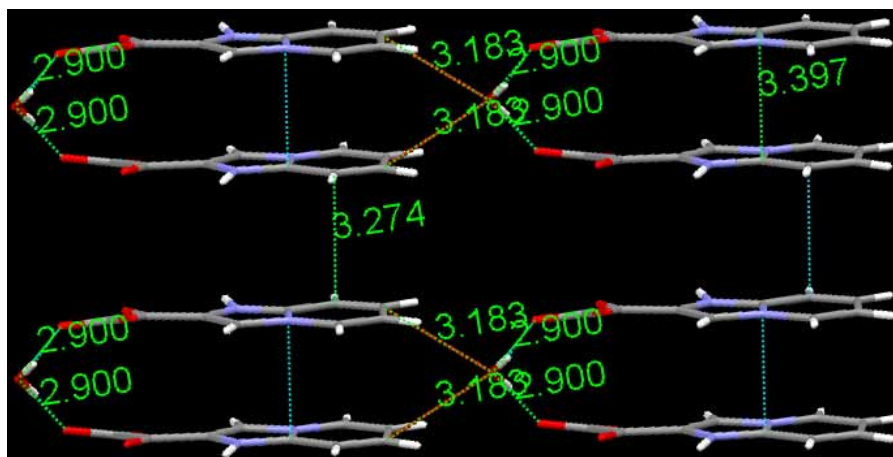


Fig. S3 The 2D supramolecular network of **1**•(H₂O) assembled by hydrogen bonds.

The guest water molecule links two chains through double O4 (H₂O)–H···O2 hydrogen bonds (O4···O2 = 2.900 Å), and double C3–H···O4 hydrogen bonds, leading to short C3'···O4 contacts of 3.183 Å.

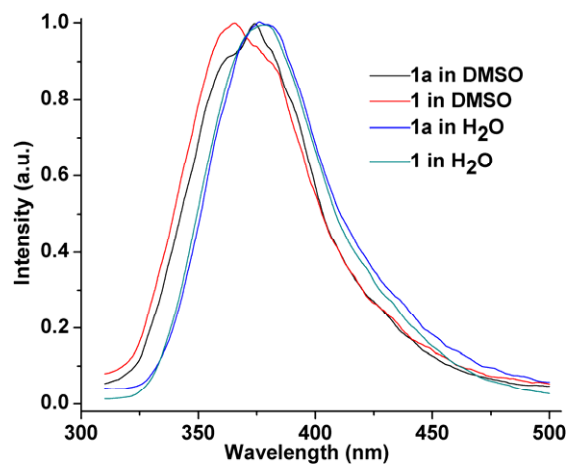


Fig. S4 PL spectra of **1** and **1a** in the dilute H₂O and DMSO solution.

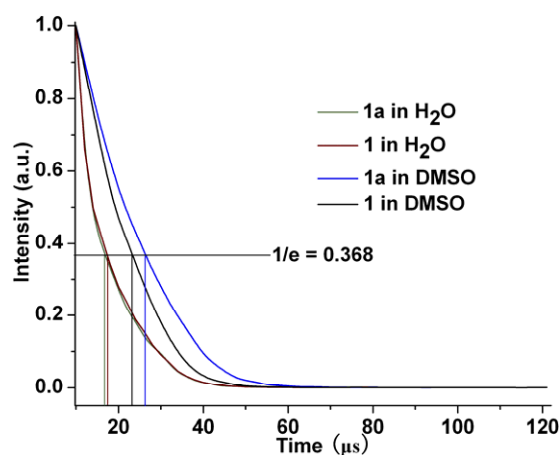


Fig. S5 The decay lifetime curves of **1** and **1a** in the dilute H₂O and DMSO solution. The lifetime (τ) is defined as the time in which the emission intensity decays to $1/e$ of the initial intensity (I_0), where e is the natural log constant and is equal to 2.718. ($I = I_0 e^{-(t/\tau)} \Rightarrow \tau = t \Rightarrow I = (1/e) I_0$).^{S1}

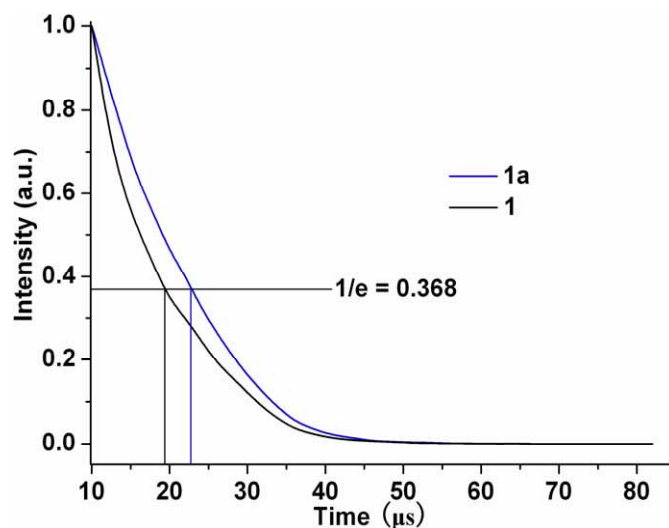


Fig. S6 The decay lifetime curves of **1** and **1a** in the solid state. The lifetime (τ) is defined as the time in which the emission intensity decays to $1/e$ of the initial intensity (I_0), where e is the natural log constant and is equal to 2.718. ($I = I_0 e^{-(t/\tau)} \Rightarrow \tau = t \Rightarrow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

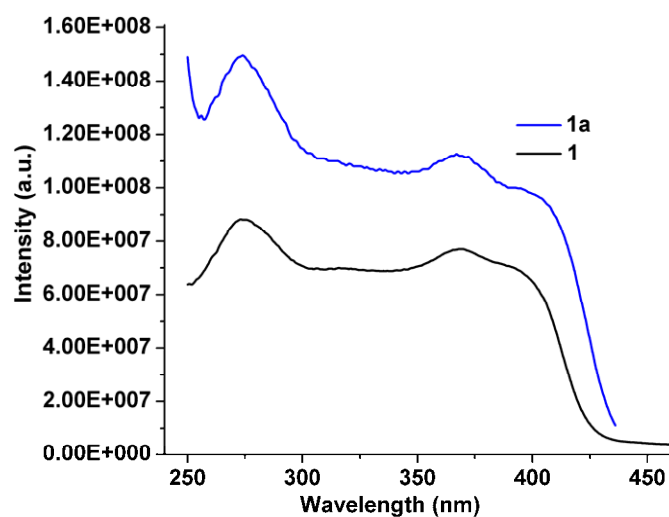


Fig. S7 Solid excitation spectra of **1** and **1a** at room temperature.

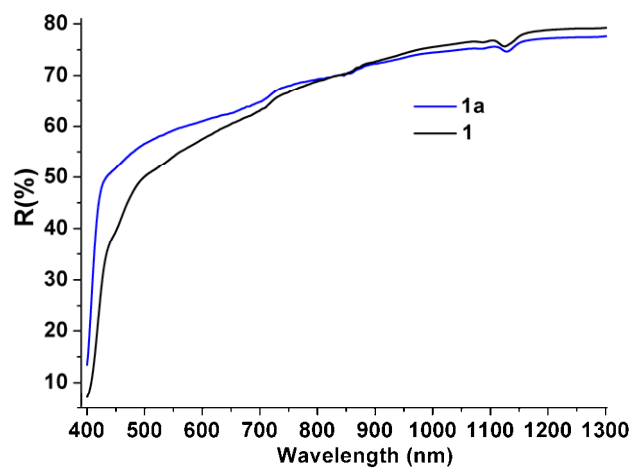


Fig. S8 The diffuse reflective spectra of **1** and **1a** at room temperature.

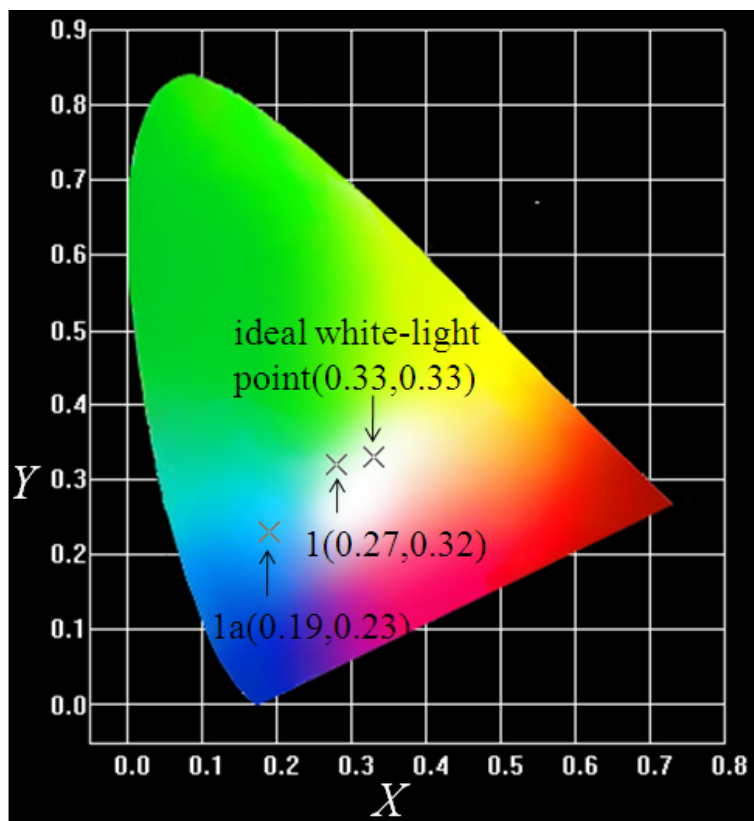


Fig. S9 CIE chromaticity diagram for **1** and **1a** upon excitation at 365 nm.

Reference

S1 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.