Electronic Supplementary Information

Stabilizing and color tuning of pyrazine radical by coordination for photochromism

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1. Experimental Section

1.1 Materials.

All chemicals in AR grade were purchased commercially and used without any further purification. Water was deionized and distilled before use.

1.2 Methods.

1) TD-DFT and thermochemical calculations

All calculations were carried out using the Gaussian 09 program (Revision D.01).[1] The ground-state geometries of prz, Me-prz$^+$, and Me-prz-Me^{2+} were optimized at the B3LYP/6-31+g(d,p) level. The widely used exchange correlation functional B3LYP[2] was chosen in view of its good compromise between accuracy and computational cost. Vibrational analyses were conducted to confirm each stationary point to be a minimum, and at the same time offered the thermochemical results. TD-DFT calculations[3] were performed on the basis of the ground-state geometry using the same functional and basis set.

2) Density of states (DOS) calculations

The calculation models were built directly from the single-crystal X-ray diffraction data. Plane wave-based DFT calculations of the total and partial densities of states were performed using the Cambridge Sequential Total Energy Package (CASTEP) code.[4] The exchange-correlation energy was described by the Perdew−Burke−Eruzerhof (PBE) functional within the generalized gradient approximation (GGA).[5] The norm conserving pseudopotentials were chosen to modulate the electron−ion interaction. The orbital electrons of C 2s22p2, H 1s1, N 2s22p3, O 2s22p4, and Zn 3d104s2 were treated as valence electrons. The number of plane waves included in the basis was determined by a cutoff energy of 750 eV, and the numerical integration of the Brillouin zone was performed using a Monkhorst−Pack-point sampling of 4 × 2 × 3 for compound **1** and 3 × 3 × 2 for compound **2**. Other parameters used in the calculations were set by default.

3) Elemental analyses

Elemental analyses of C, H, and N were performed on an Elementar Vario EL III microanalyzer.

4) X-ray powder diffraction (PXRD)

PXRD patterns were collected at room temperature on a Rigaku MiniFlex II diffractometer using Cu *K*α radiation (λ = 1.5406 Å). The simulated PXRD patterns were derived from the free Mercury software (http://www.ccdc.cam.ac.uk/solutions/csd-system/components/mercury/).

5) Ultraviolet–visible (UV–vis) absorption

UV–vis absorption spectra were measured in the reflectance mode at room temperature on a Perkin-Elmer Lambda 900 UV/vis/NIR spectrophotometer with an integrating sphere attachment and $BaSO_4$ as a reference. The absorption spectra were converted by the Kubelka–Munk function, $F(R) = \alpha/S = (1-R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient that is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance.

6) FT-IR Spectroscopy

A PerkinElmer Spectrum One FT-IR spectrophotometer was used to measure the IR data for compounds **1** and **2** over the scope 4000−400 cm^{-1} with the pure KBr pellets as the matrixes.

7) Electron spin resonance (ESR)

ESR spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in the X band.

8) Thermo gravimetric (TG) analysis

TG analyses of compounds **1** and **2** were done on a NETZSCH STA 449C simultaneous thermal analyzer with Al_2O_3 crucibles under N_2 atmosphere (20 $mL\cdot min^{-1}$) at a heating rate of 10 $K\cdot min^{-1}$.

9) X-ray photoelectron spectroscopy (XPS)

XPS studies were performed with a ThermoFisher ESCALAB250 X-ray photoelectron spectrometer (powered at 150 W) using Al K_α radiation (λ = 8.357 Å; spot size, 500 μm). To compensate for surface charging effects, all XPS spectra were referenced to the C 1s neutral carbon peak at 284.6 eV.

10) Light source

A PLSSXE300C 300 W xenon lamp system equipped with an IR filter was used to illuminate samples for achieving various spectra, and the distances between these samples and the Xe lamp were around 30 cm.

1.3 Synthesis

1.3.1 Synthesis of $[Zn_2(H_2O)_2(malonate)_2(prz)]_n$ (1; prz = pyrazine)

Compound **1** was synthesized by the reported procedure.[6] The phase purity of its crystalline samples was checked by PXRD (Fig. S1) and elemental analyses. Anal. Calcd for **1**: C, 26.63; H, 2.70; N, 6.21%. C 26.69, H 2.87, N 6.29%. A TG analysis showed that **1** is stable up to ca. 163 ºC (Fig. S9a).

1.3.2 Synthesis of $[Zn_7(\mu_4\text{-}O)_2(acetate)_{10}(prz)_2]$ (2; prz = pyrazine)

Compound **2** was synthesized by the reported procedure.[7] The phase purity of its crystalline samples was checked by PXRD (Fig. S2) and elemental analyses. Anal. Calcd for **2**: C, 27.10; H, 3.06; N, 4.50%. Found: C, 27.03; H, 3.06; N, 4.39%. A TG analysis showed that **2** is stable up to ca. 135 ºC (Fig. S9b).

2. Graphics.

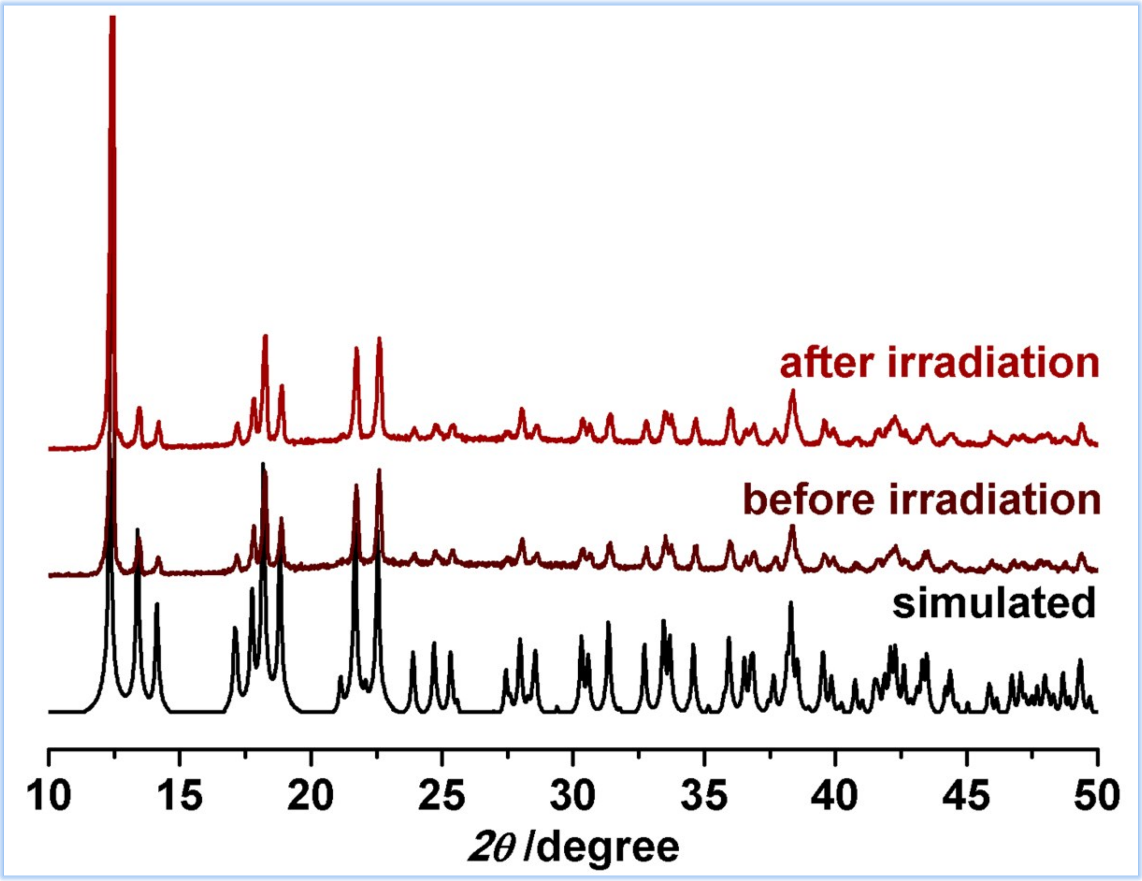

Fig. S1. PXRD patterns for **1**. For comparison, the simulated result from the single-crystal diffraction data is also shown.

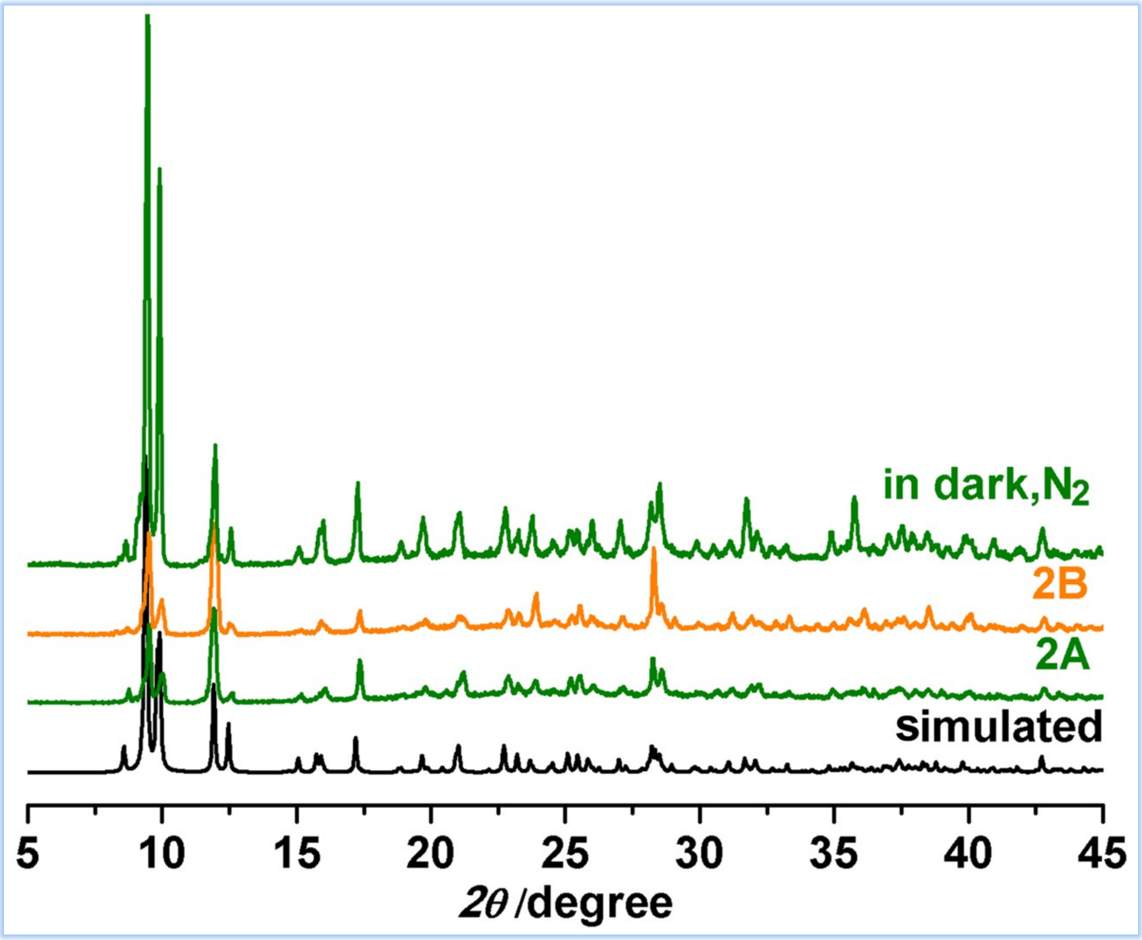

Fig. S2. PXRD patterns for **2** upon sequential processing. For comparison, the simulated result from the single-crystal diffraction data is also shown.

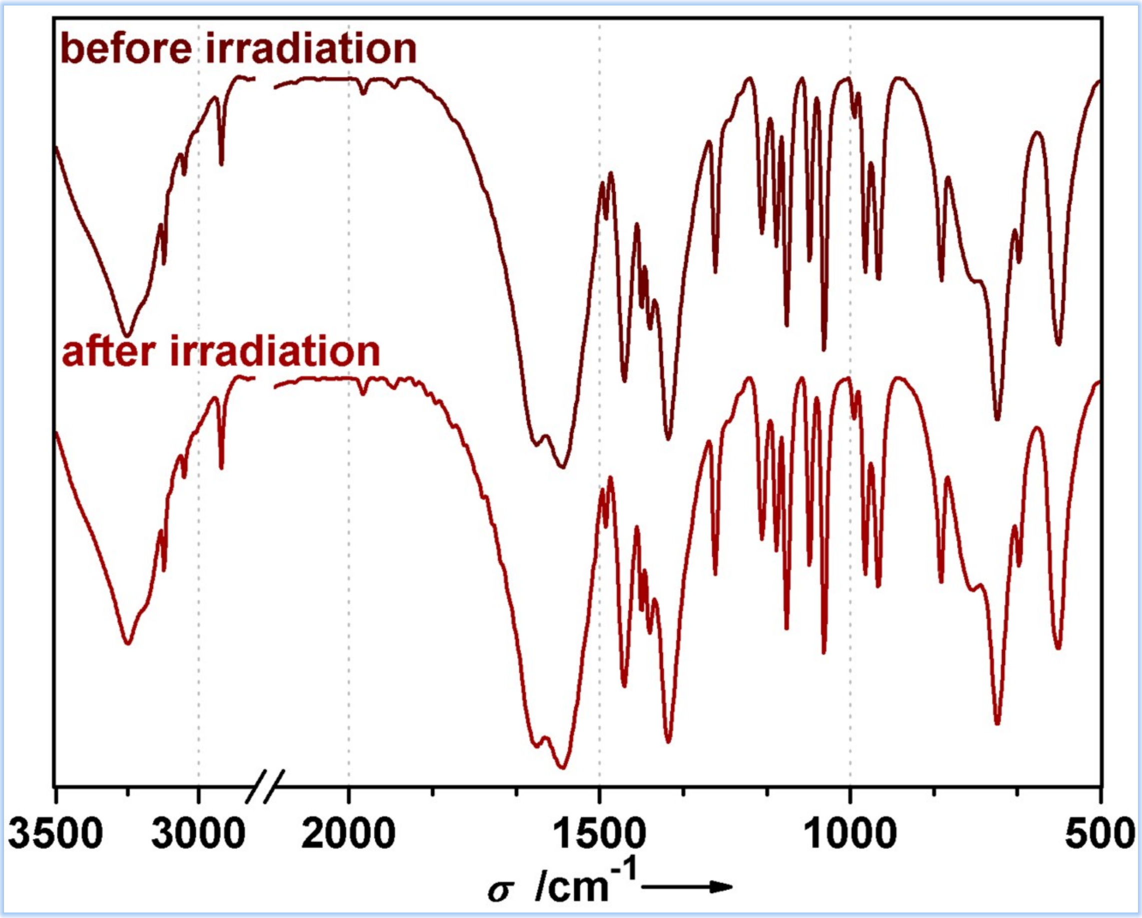

Fig. S3. IR spectra of **1** in the KBr matrix.

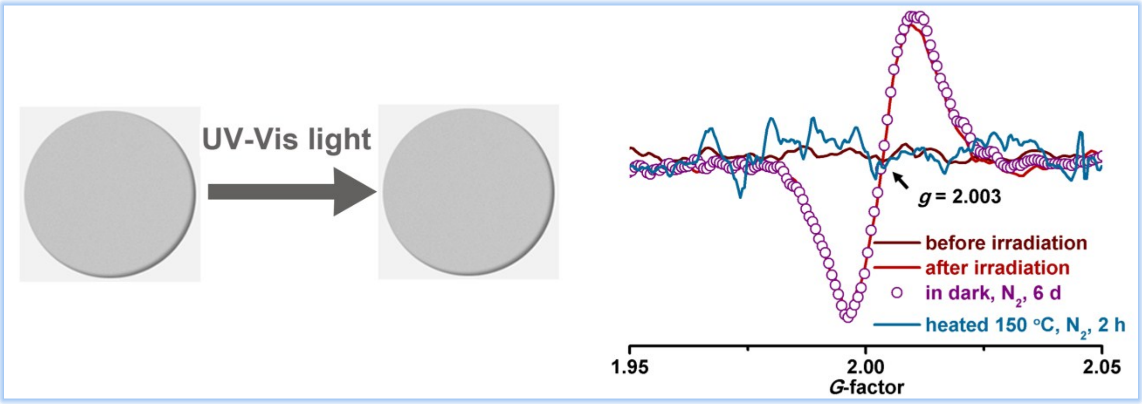

Fig. S4. For **1**: (left) photographs of the samples before and after irradiation; (right) ESR spectra upon sequential processing.

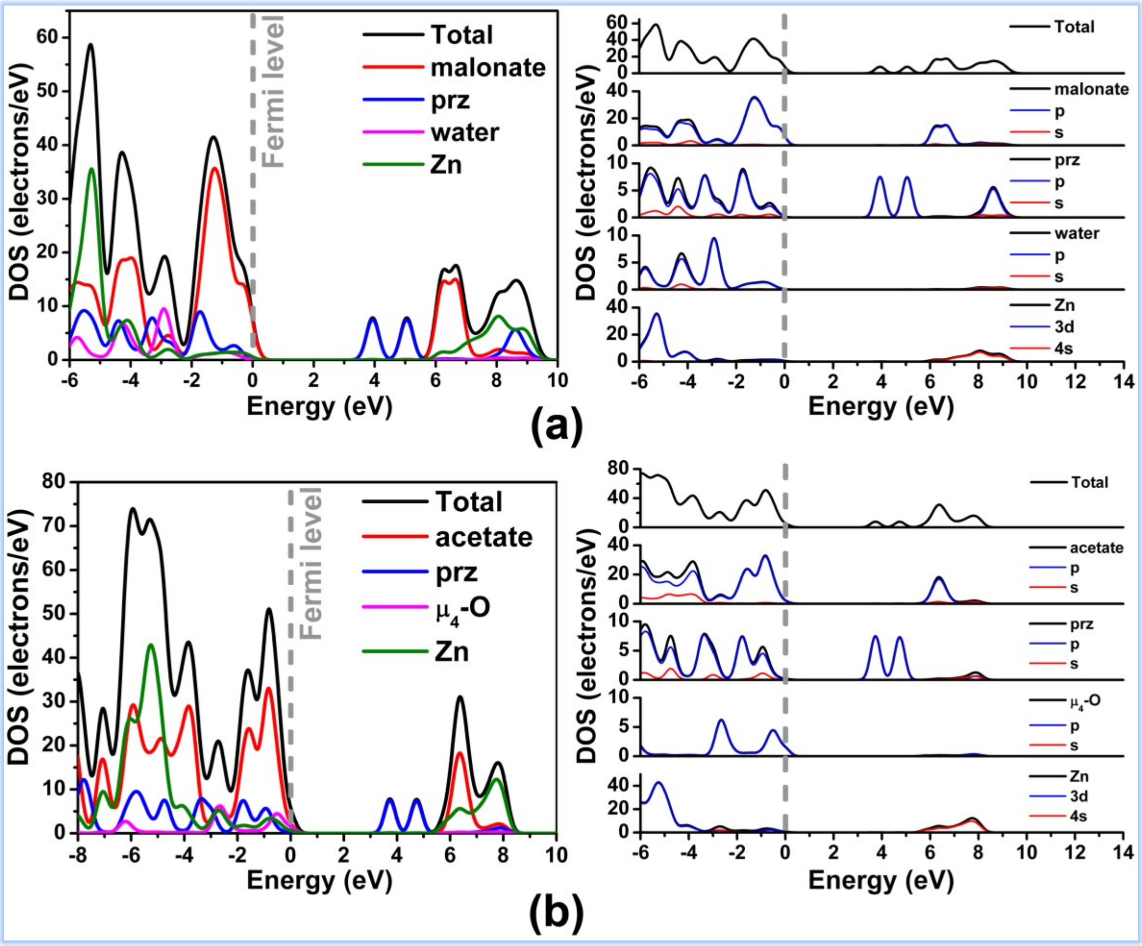

Fig. S5. Total and partial density of states (DOS) of **1** (a) and **2** (b)**.** The Fermi level is set at 0 eV by default.

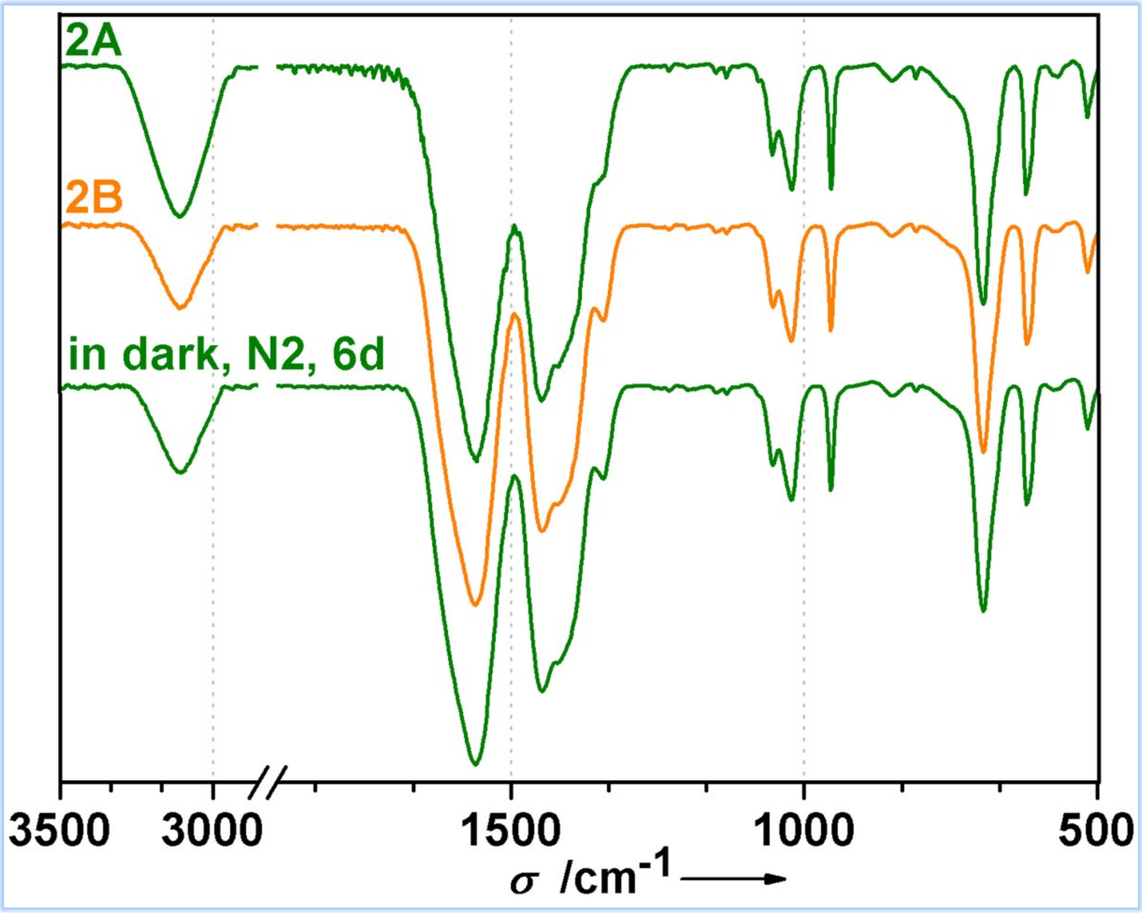

Fig. S6. IR spectra of **2** in the KBr matrix.

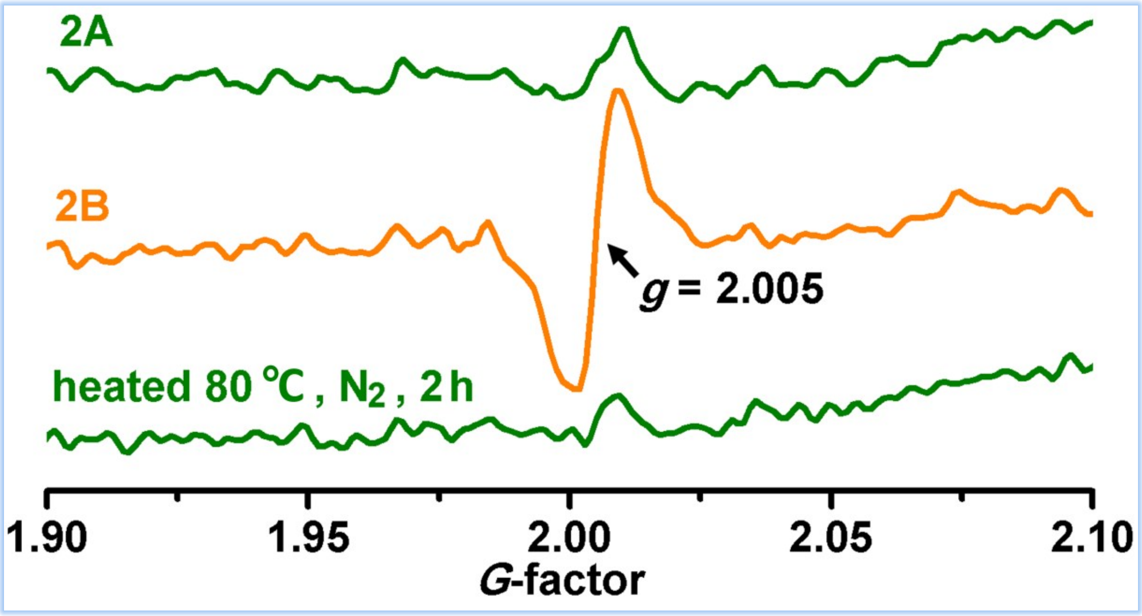

Fig. S7. ESR spectra of **2** before irradiation (**2A**), after irradiation (**2B**) at room temperature and then annealed at 80 ºC under N_2 for 2 h.

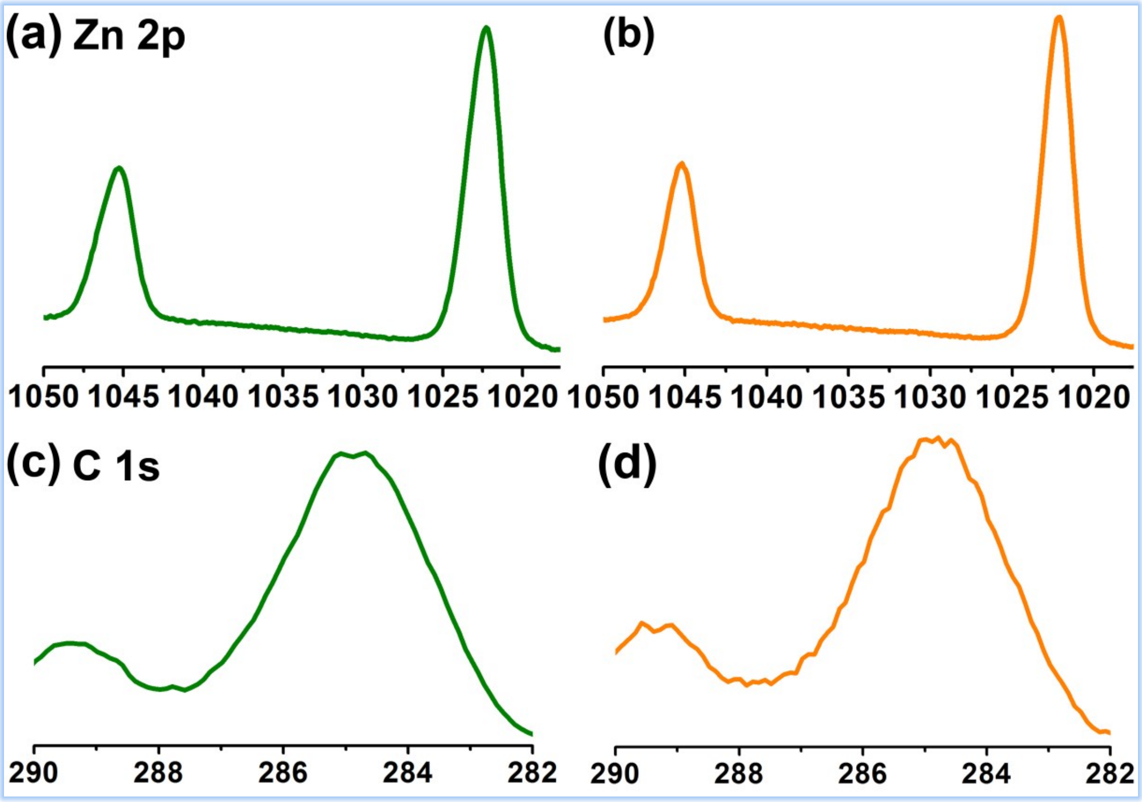

Fig. S8. Zn 2p (a,b) and C 1s (c,d) XPS (Al-K_{α}) core-level spectra of **2** before and after irradiation. The horizontal axes represent binding energies (eV).

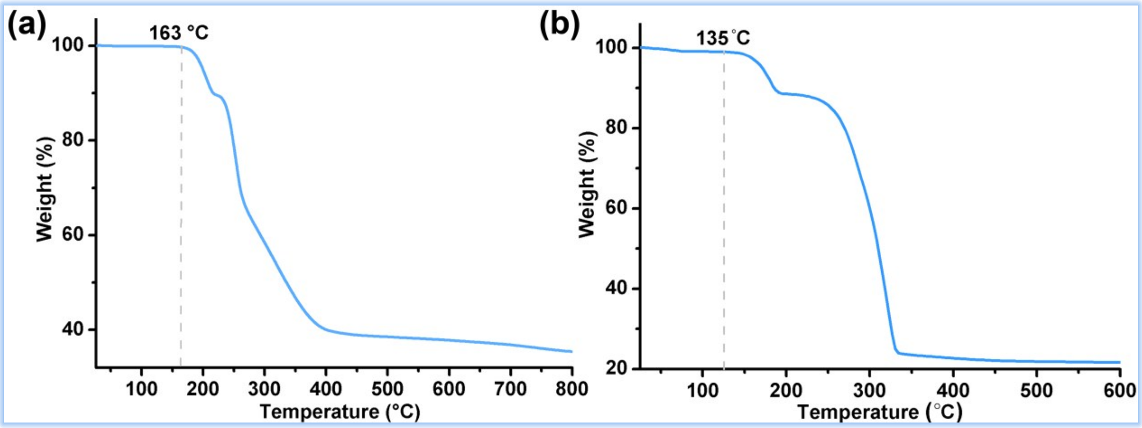

Fig. S9. TG curves of **1** (a) and **2** (b) under N_2.

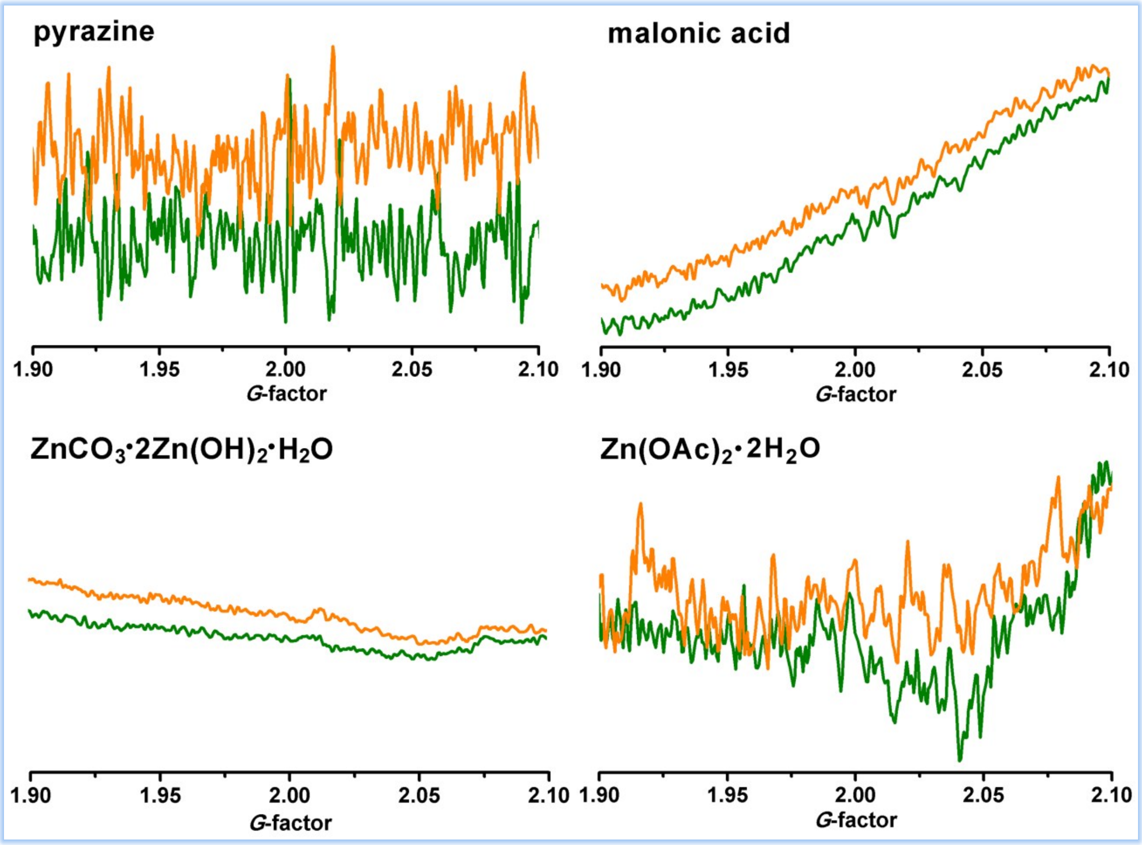

Fig. S10. ESR spectra of the starting reactants before irradiation (olive) and after irradiation (orange).

References:

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