

## Highly stable photoresponsive complex framework formation involves unusual selective hydrogenation of a pyridine derivative

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### General Methods

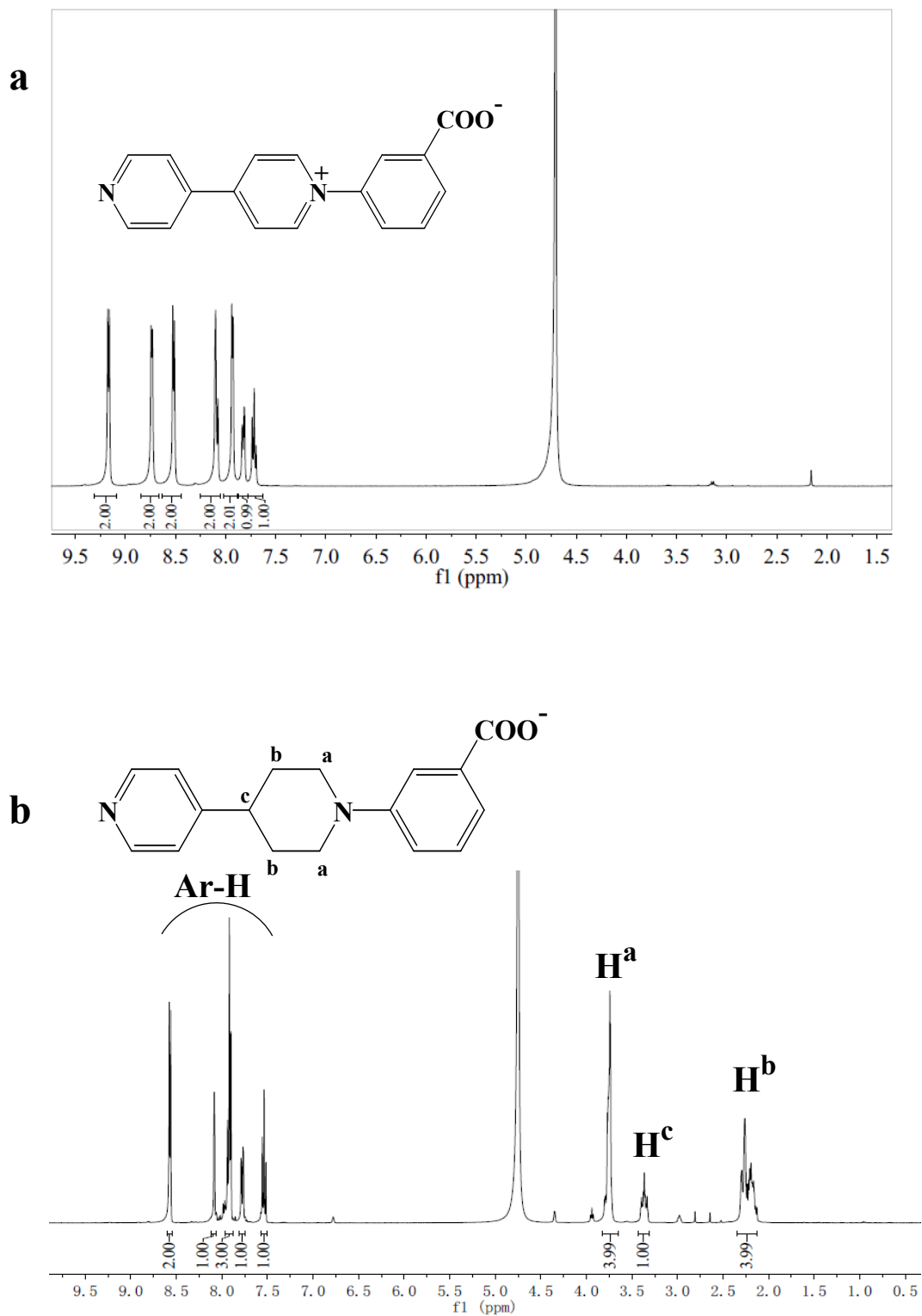
A TA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N<sub>2</sub> at a rate of 10°C min<sup>-1</sup>. UV-Visible spectral measurements were carried out using a HITACHI U-3010 spectrometer. The ESR spectra were recorded at room temperature with a Bruker EMX-10/12 Electron Spin Resonance Spectrometer. IR spectra were characterized by a Bruker Tensor 27 FTIR spectrometer in the range of 4000-400 cm<sup>-1</sup> using a KBr disk. <sup>1</sup>HNMR spectrum was recorded on a Bruker Ultrashield 400 Plus using a solution prepared by acid digesting 20mg of crystal sample in a D<sub>2</sub>O/DCl mixture. XPS measurements were carried on an ESCALAB 250 X-ray Photoelectron spectrometer with a monochromatized AlK $\alpha$  X-ray source (1486.6 eV photons) at a pass energy of 20 eV. The anode voltage was set at 15 kV (150W). The pressure in the analysis chamber was maintained at 2 $\times$ 10<sup>-9</sup> mbar during each measurement.

**Preparation of 1:** N-(3-carboxyphenyl)-4,4'-bipyridinium chloride (0.0624g, 0.2mmol) was added to a mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.2975g, 1mmol) and 2-aminoterephthalic acid (0.0724g, 0.4mmol) in DMF/H<sub>2</sub>O (1:1, 10ml). The mixture was sealed in a 25ml Teflon-lined steel bomb and heated at 120°C for 48h. Yellow needle-like crystals were collected by filtration, washed by water and dried at room temperature (0.035g, 56% yield based on N-(3-carboxyphenyl)-4,4'-bipyridinium chloride). <sup>1</sup>HNMR (400 MHz, D<sub>2</sub>O/DCl) :  $\delta$  = 2.13-2.30 (m, 4H, H<sup>b</sup>),  $\delta$  = 3.33-3.40 (m, 1H, H<sup>c</sup>),  $\delta$  = 3.74-3.77 (m, 4H, H<sup>a</sup>),  $\delta$  = 7.52-8.58 (m, 8H, Ar-H). IR (cm<sup>-1</sup>,KBr pellet): 2960 m, 2885 m, 1615 s, 1560 vs, 1420 s, 1382 vs, 1214s, 1079 m, 986 s, 957 m 760 s, 520 m.

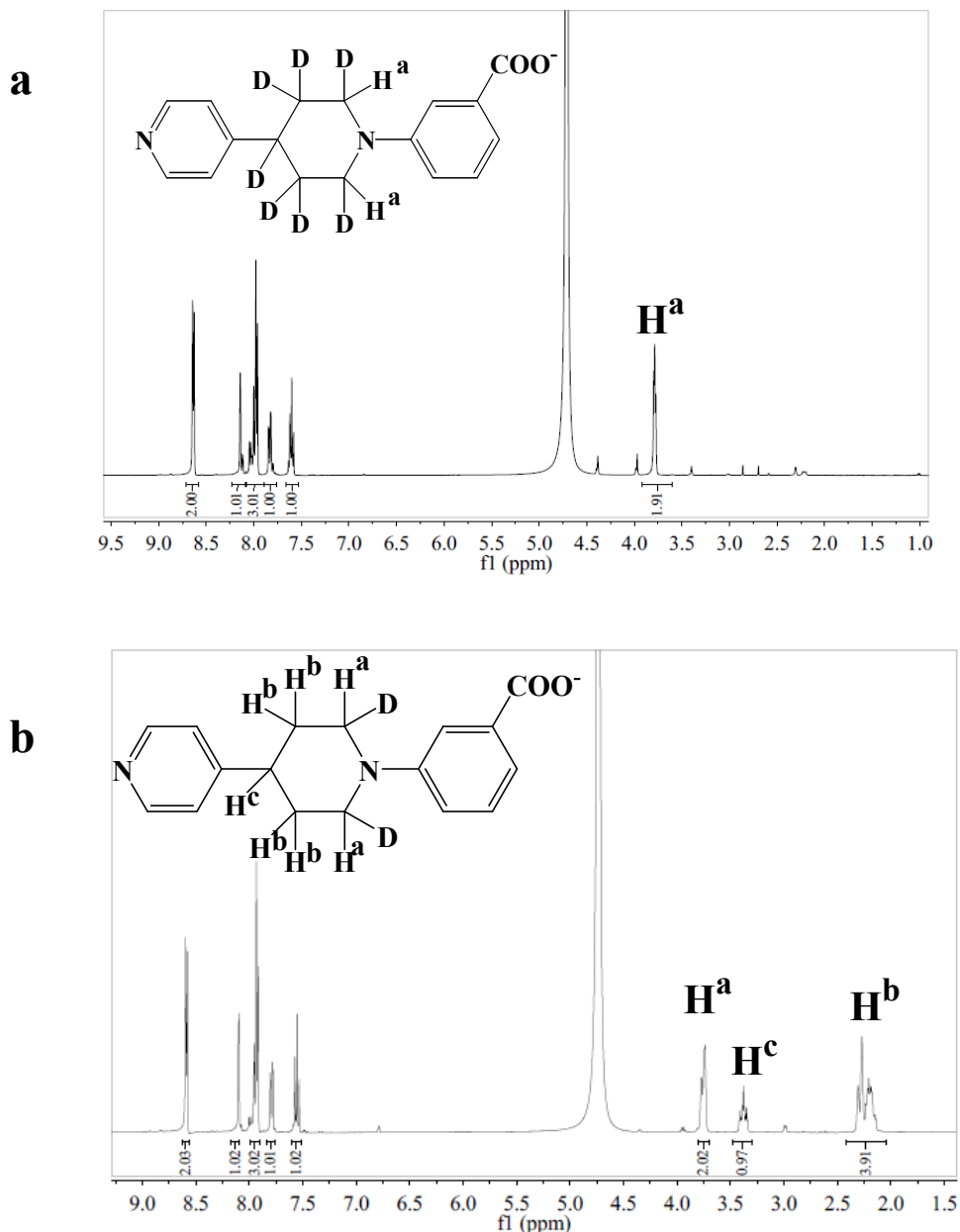
**Crystal data for 1a (before irradiation):** C<sub>34</sub>H<sub>34</sub>N<sub>4</sub>O<sub>4</sub>Zn,  $f_w$ = 628.02 g·mol<sup>-1</sup>, Orthorhombic, space group Fdd2,  $a$ = 21.494(4) Å,  $b$ = 36.481(7) Å,  $c$ = 7.2800(13) Å,  $V$ = 5708.6(18) Å<sup>3</sup>,  $Z$ =8,  $\rho_{\text{calcd}}$ =1.461 g·cm<sup>-3</sup>, final  $R_I$ = 0.0376 and  $wR_2$ = 0.0847 for 2160 independent reflections [ $I > 2\sigma(I)$ ].

Crystal data for **1b (after irradiation)**:  $C_{34}H_{34}N_4O_4Zn$ ,  $f_w = 628.02 \text{ g}\cdot\text{mol}^{-1}$ , Orthorhombic, space group Fdd2,  $a = 21.497(4) \text{ \AA}$ ,  $b = 36.708(7) \text{ \AA}$ ,  $c = 7.2655(14) \text{ \AA}$ ,  $V = 5733.4(19) \text{ \AA}^3$ ,  $Z = 8$ ,  $\rho_{\text{calcd}} = 1.455 \text{ g}\cdot\text{cm}^{-3}$ , final  $R_1 = 0.0388$  and  $wR_2 = 0.0825$  for 2134 independent reflections [ $I > 2\sigma(I)$ ].

The data were measured on a Bruker Nonius KappaCCD area detector with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 110K. The structures were solved by direct methods and refined by full-matrix least-squares methods with SHELXL. CCDC 838047 and 863588 contains the supplementary crystallographic data for compound **1a** and **1b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



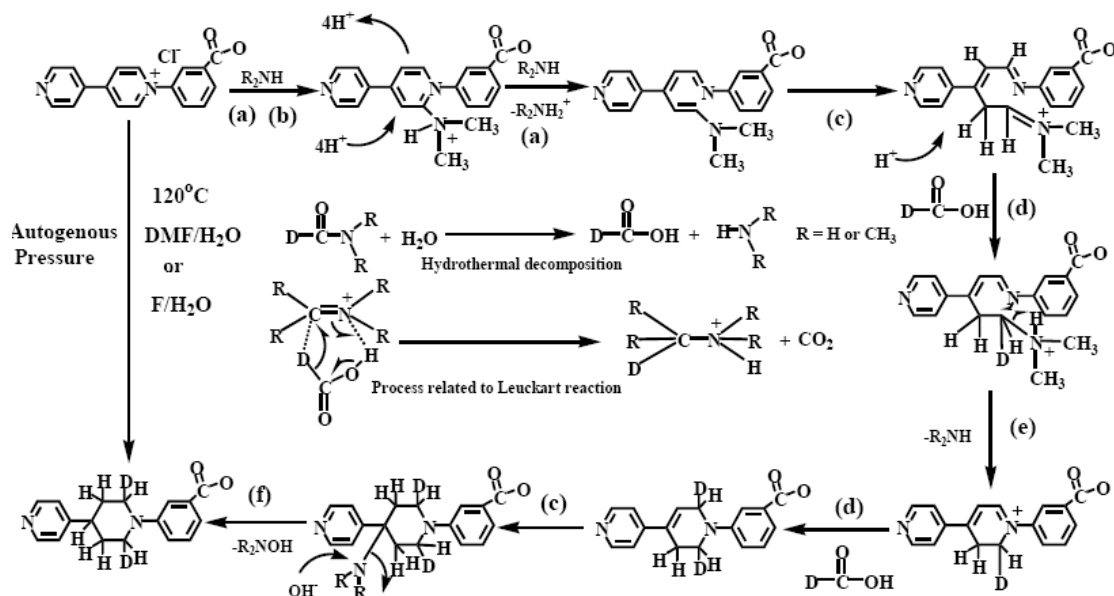
**Fig. S1** (a) NMR observation of *N*-(3-carboxyphenyl)-4,4'-bipyridinium chloride; (b) NMR observation of the hydrogenation product PYPDB in compound **1**, 2.13-2.30 (m, 4H, CH<sub>2</sub>), 3.33-3.40 (m, 1H, CH), 3.74-3.77 (m, 4H, N-CH<sub>2</sub>), 7.52-8.58 (m, 8H, Ar-H).



**Fig. S2** (a) NMR observation of the hydrogenation product PYPDB with  $D_2O$  and DMF as solvent. 3.74–3.77 (m, 2H, N- $CH_2$ ), 7.52–8.58 (m, 8H, Ar-H); (b) NMR observation of the hydrogenation product PYPDB with  $H_2O$  and DMF- $d_7$  as solvent. 2.13–2.30 (m, 4H,  $CH_2$ ), 3.33–3.40 (m, 1H, CH), 3.74–3.77 (m, 2H, N- $CH_2$ ), 7.52–8.58 (m, 8H, Ar-H).

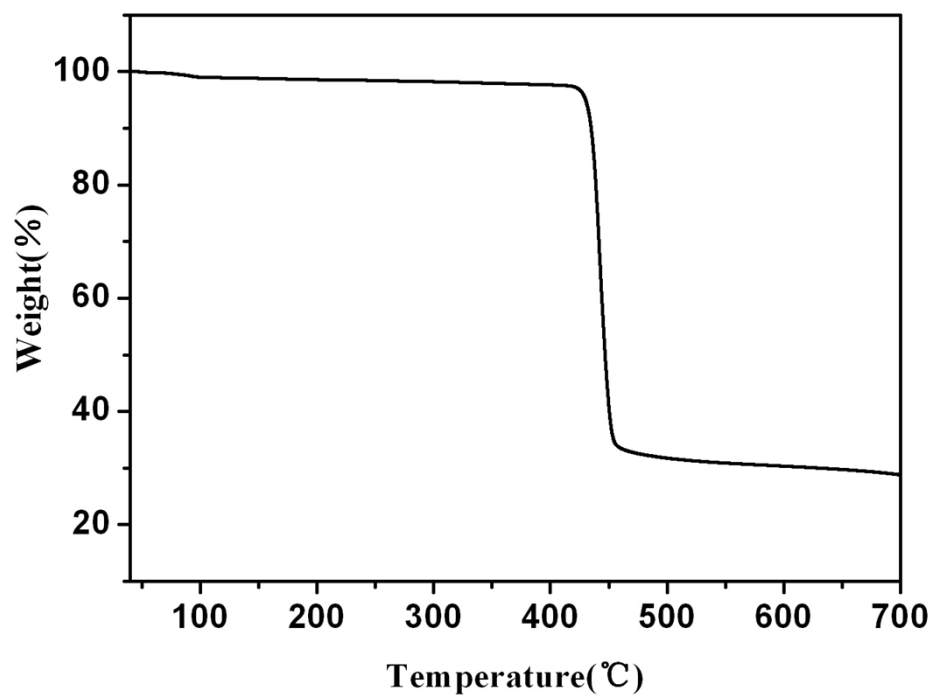
By comparison with Fig. S1b, the peaks disappear in Fig. S2a (2.13–2.30 (m, 4H,  $CH_2$ ), 3.33–3.40 (m, 1H, CH), 3.74–3.77 (m, 2H, N- $CH_2$ )) and the peaks disappear in Figure S2b (3.74–3.77 (m, 2H, N- $CH_2$ )), indicate the following conclusions:

- Two hydrogen atoms coming from the DMF molecule are added to the carbon atoms (C8, C10) next to the N2 atom.
- The four original hydrogen atoms of the central ring are removed among the reductive process.
- Seven hydrogen atoms for addition come from water solvent.

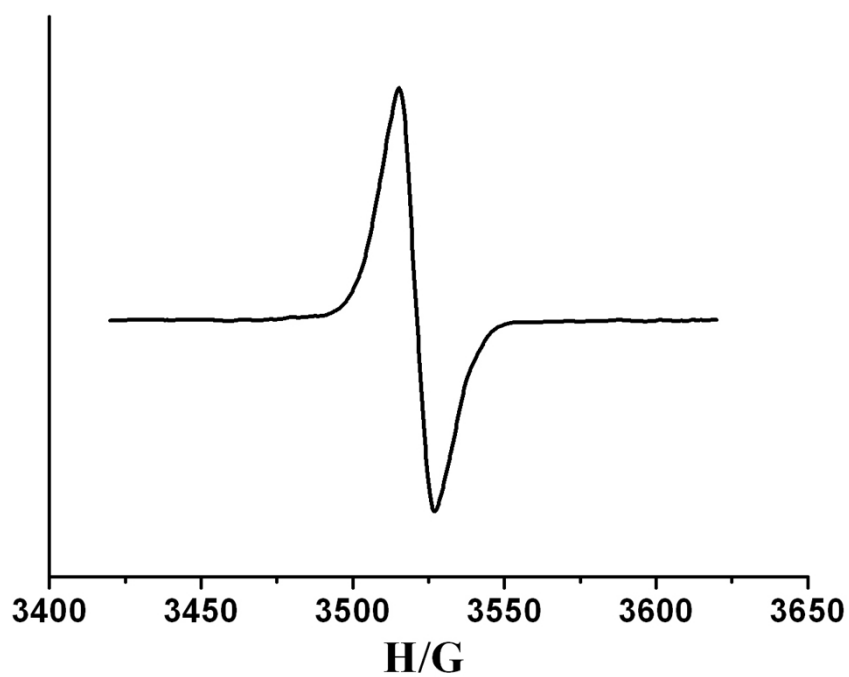


**Fig. S3** Proposed mechanism for the hydrogenation of the central pyridinium ring: (a) The ANRORC mechanism of zinc salt; (b) Proton exchange reaction; (c) Electrophilic addition; (d) Process related to Leuckart reaction; (e) Substitution reaction; (f) Substitution and elimination reaction.

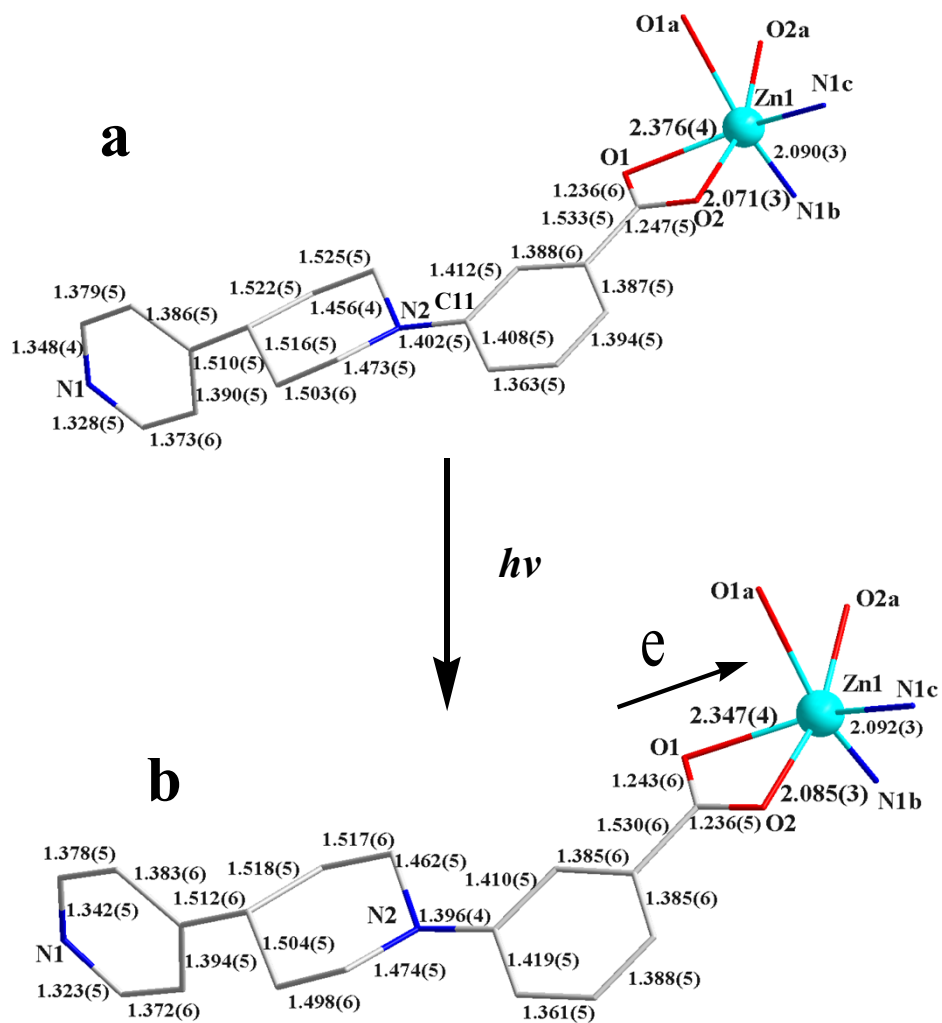
A proposed hydrogenation mechanism is depicted in Fig. S3 based on the experimental data. It is well known that DMF is hydrolyzed gradually to form formic acid and dimethylamine, especially at elevated temperatures. The presence of both acid and base reagents in a mixture under hydrothermal condition (the neutral hydrolysis has been proposed as gas-phase processes operate) led to the formation of a new type of reaction system: acid and base can react with organic substrates at the same time. To begin with, the in-situ generated amine attacks the central pyridinium ring. Its addition leads to ring opening of **1a**, a kind of aryl-substituted zinc salt. Hydrogen exchange is reported for benzo-substituted heterocycles in neutral water at elevated temperatures. Then, the reaction apparently involves a polar mechanism. The electrophilic atom  $H^+$  adds to the alkene and an iminium group is formed. Furthermore, the hydrogen atom originated from the formic acid enters the unsaturated amine via a process related to the Leuckart reaction. After the processes of nucleophilic attack, ring closing, amine elimination and the repeated reduction of the formic acid, a central tetrahydropyridine ring is formed. It is known that the attached pyridine ring can enhance the stability of the side chain intermediate in para substituted position. Finally, the following electrophilic addition, substitution and elimination reactions complete the last hydrogenation process.



**Fig. S4** Thermal gravimetric curve of compound 1.

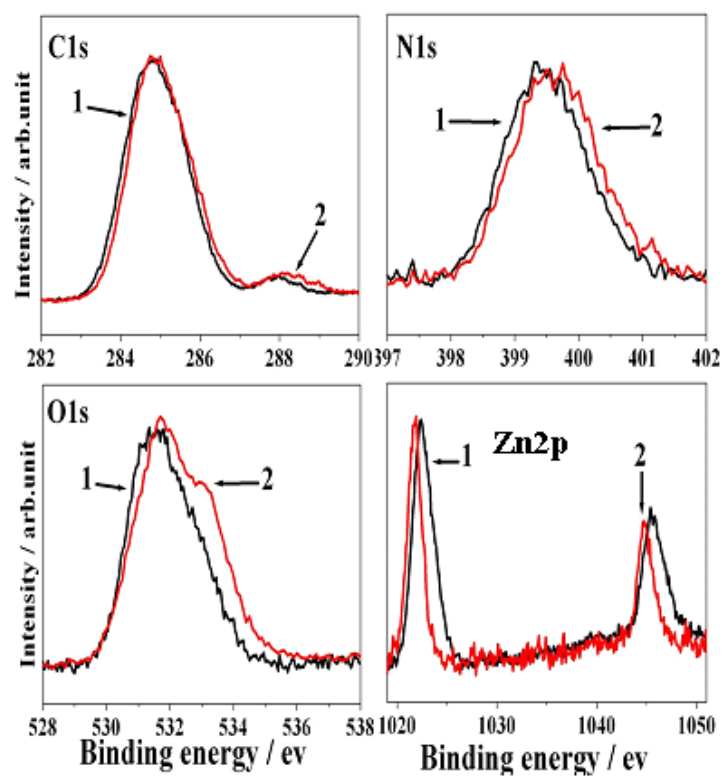


**Fig. S5** ESR spectrum of **1** after photoirradiation for 10 min.

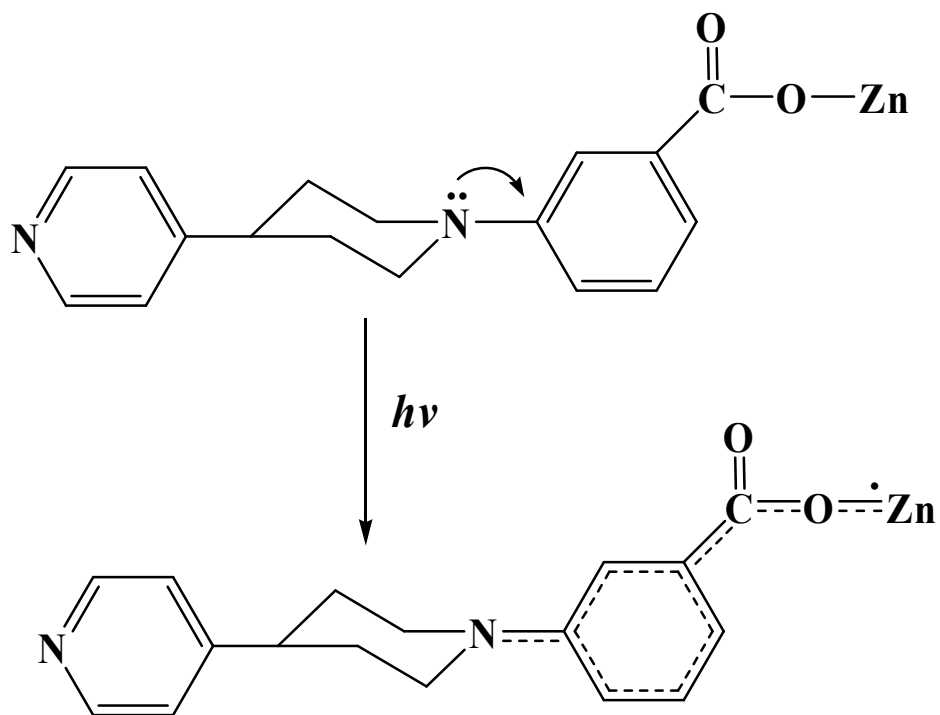


**Fig. S6** Structural unit variations between the two crystal forms of **1** before (a) and after (b) photoirradiation. For clarity, hydrogen atoms are omitted and only the independent unit is shown.





**Fig. S7** C1s, N1s, O1s and Zn2p XPS core-level spectra of crystal before (1) and after (2) photoirradiation



**Fig. S8** Photoinduced electron transfer in the donor-bridge-acceptor system of compound **1**.