

Electronic Supplementary Information

Mechanochemical Reactions of Coordination Polymers by Grinding with KBr

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Materials and Methods

All the chemicals were used as received without further purification. All the solvents used were of reagent grade.

Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer with
20 KBr disk. Elemental analyses were carried out at the Elemental Analysis Lab, CMAC, Department of Chemistry, National University of Singapore. ¹H NMR spectra were recorded on a Bruker ACF 300 spectrometer operating in the quadrature mode at 300 MHz. Powder X-ray diffraction patterns (PXRD) were recorded on a Siemens D500 diffractometer with graphite monochromatised Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) at room temperature (23°C).
25 Water present in the compounds were determined from an SDT 2960 TGA thermal analyzer with a heating rate of 5°C min⁻¹ in a N₂ atmosphere using a 5-10 mg sample per run. The UV irradiation was carried out using a Luzchem-4Z with UVA lamp centred at 320 nm wavelength.

Powder X-ray diffraction (PXRD) measurement for Rietveld structure analysis of **4** was
30 performed at Beam Line X16C of the National Synchrotron Light Source at Brookhaven National Laboratory. The powdered sample was held in an 1.0-mm diameter thin-wall quartz capillary. X-Rays of wavelength 0.700142 Å were selected by a Si(111) channel cut monochromator. Diffracted X-rays were selected by a Ge(111) analyzer and detected by a scintillation counter. The incident intensity was monitored by an ion chamber and used to
35 normalize the measured signal. The TOPAS-Academic program was used to index, solve, and refine the crystal structure.^{1,2,3} **4** was successfully indexed and a space group of *P*-1 tentatively assigned. The structure was solved from the synchrotron powder diffraction data by simulated annealing, confirming the space group selection. From this initial structure solution, the structure was successfully refined (Figure S5).

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Reaction of coordination polymers by grinding with alkali metal halides

The precursors **1**, **2** were synthesized as reported in the literature.

All the reactions were carried out by simple grinding of the precursors in an agate mortar and pestle for a specific time. After every two minutes of grinding, spatula has been used to remove the compounds in the pestle and to mix thoroughly. The elemental analysis of the compounds obtained by grinding (whose PXRD patterns matched with the respective 5 simulated PXRD patterns) were carried out to confirm the purity of the system. A representative procedure has been given below.

[ZnBr₂bpe], 3: [Zn₂(μ-bpe)₂(μ-CH₃CO₂)₂(CF₃CO₂)₂] (0.1 mmol, 0.043 g) and KBr (0.2 mmol, 0.024g) were manually ground for 20 min. After obtaining the PXRD pattern of the complex, it was washed with water to remove the acid and KBr impurities. IR (KBr, cm⁻¹): 10 1613 (m), 1561 (vs), 1503 (m), 1429 (m), 1347 (m), 1301(vw), 1254 (w), 1228(vw),1202(s), 1070 (w), 1026 (vw), 971(m); ¹H NMR (*d*₆-DMSO, 300 MHz, 298 K): δ = 8.60 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 ppm (s, 2H, CH=CH). Elemental analysis (%) calcd. for.C₁₂H₁₀N₂ZnBr₂: C, 35.38; H, 2.47; N, 6.88; Found: C, 35.24; H, 2.22; N, 6.73

15 3 by solution method: A solution of bpe (0.05 mmol, 0.011 g) in DMF (2 mL) was added to a solution of ZnBr₂ (0.05 mmol, 0.0091 g) in DMF (2 mL) in a scintillation vial. The resulting solution was heated at the rate of 5°C per min to 98°C and the temperature was maintained for 4 days and the resulting mixture was cooled to room temperature in 3 h. This colourless rod like crystals obtained were isolated and washed with acetone, and finally dried 20 under vacuum. IR (KBr, cm⁻¹): 1613 (m), 1561 (vs), 1503 (m), 1428 (m), 1347 (m), 1301 (vw), 1254 (w), 1228 (vw), 1202 (s), 1070 (w), 1026 (vw), 971(m); ¹H NMR (*d*₆-DMSO, 300 MHz, 298 K): δ = 8.59 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 (s, 4H, CH=CH). Elemental analysis (%) calcd. for.C₁₂H₁₀N₂ZnBr₂: C, 35.38; H, 2.47; N, 6.88; Found: C, 35.20; H, 2.33; N, 6.76.

25 **[ZnI₂bpe], 4:** KI had been used instead of KBr. IR (KBr, cm⁻¹): 1612 (m), 1555 (vw), 1503 (w), 1429 (m), 1301(vw), 1202(s), 1068 (w), 1025 (vw), 970 (m), 828 (m), 548 (m); ¹H NMR (*d*₆-DMSO, 300 MHz, 298 K): δ = 8.60 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 ppm (s, 2H, CH=CH). Elemental analysis (%) calcd. for.C₁₂H₁₀N₂ZnI₂: C, 28.74; H, 2.01; N, 5.59; Found: 30 C, 28.96.; H, 2.25; N, 5.04.

[CdBr₂bpe], 4 by grinding: [Cd(bpe)(CH₃CO₂)₂(H₂O)] (0.1 mmol, 0.043 g) and KBr (0.2 mmol, 0.024 g) were manually ground for 20 min. After obtaining the PXRD pattern of the complex, it was washed with water to remove the acid and KBr impurities. IR (KBr, cm⁻¹): 35 1604 (s), 1559 (m), 1503 (m), 1429 (m), 1355 (vw), 1303 (vw), 1256 (vw), 1206(w), 1074 (w), 1010 (s), 977 (m) 828 (s), 547 (s); ¹H NMR (*d*₆-DMSO, 300 MHz, 298 K): δ = 8.60 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 ppm (s, 2H, CH=CH). Elemental analysis (%) calcd. for.C₁₂H₁₀N₂CdBr₂: C, 31.71; H, 2.22; N, 6.16; Found: C, 31.69; H, 2.34; N, 6.17.

40 **[CdBr₂bpe], 4 by layering:** CdBr₂ (0.1 mmol, 0.034 g) was dissolved in 4 ml H₂O and 0.2 ml of this solution was added into a fusion tube. 0.7 ml of DMF was layered above as a buffer. Then 0.2 ml of bpe in CH₃OH from the stock solution (0.1 mmol in 4ml MeOH) was layered above the DMF buffer layer. Colorless plate like crystals started to form at the solvent junction within 2 days. Yield: 0.07 g, 26%. IR (KBr, cm⁻¹): 45 1605 (s), 1560 (m), 1504 (m), 1427 (m), 1357 (vw), 1304 (vw), 1256 (vw), 1207 (w), 1076 (w), 1012 (s), 981 (m) 830 (s), 547 (s); ¹H NMR (*d*₆-DMSO, 300 MHz, 298 K): δ=8.60 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 ppm (s, 2H, CH=CH). Elemental analysis (%) calcd. for.C₁₂H₁₀N₂CdBr₂: C, 31.71; H, 2.22; N, 6.16; Found: C, 31.55; H, 2.30; N, 6.24.

4 after photodimerization: Powdered **4** (15 mg) packed in between glass slides was irradiated with UV lamp centred at 320 nm 25 h. IR (KBr, cm^{-1}): 1604 (m). ^1H NMR (d_6 -DMSO, 300 MHz, 298 K): δ = 8.32 (d, 4H, Py-H), 7.22 (d, 4H, Py-H), 4.66 ppm (s, 2H, CH-CH). Elemental analysis (%) calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{CdBr}_2$: C, 31.71; H, 2.22; N, 6.16; Found: C, 31.69; H, 2.34; N, 6.17. ^1H NMR (300 MHz, d_6 -DMSO, 298 K): δ = 8.35 (d, 4H; Py-H), 7.24 (d, 4H; Py-H), 4.68 ppm (s, 4H; CH-CH). Elemental analysis (%) calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{CdBr}_2$: C, 31.71; H, 2.22; N, 6.16; Found: C, 31.82; H, 2.38; N, 5.99.

[CdCl₂bpe], 2-KCl by grinding: $[\text{Cd}(\text{bpe})(\text{CH}_3\text{CO}_2)_2(\text{H}_2\text{O})]$ (0.1 mmol, 0.043 g) and KCl (0.5 mmol, 0.037 g) were manually ground for 20 minutes. After obtaining the PXRD pattern of the complex, it was washed with water to remove the acid and KCl impurities. IR (KBr, cm^{-1}): 1607 (s), 1559 (m), 1503 (m), 1432 (m), 1355 (vw), 1303 (vw), 1258 (vw), 1206(w), 1074 (w), 1010 (s), 977 (m) 828 (s), 547 (s); ^1H NMR (d_6 -DMSO, 300 MHz, 298 K): δ = 8.60 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 ppm (s, 2H, CH=CH). Elemental analysis (%) calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{CdCl}_2$: C, 39.43; H, 2.76; N, 7.66; Found: C, 39.34; H, 2.56; N, 7.17.

[CdI₂bpe], 2-KI by grinding: $[\text{Cd}(\text{bpe})(\text{CH}_3\text{CO}_2)_2 \text{H}_2\text{O}]_n$ (0.1 mmol, 0.043 g) and KI (0.5 mmol, 0.080 g) were manually ground for 20 min. After obtaining the PXRD pattern of the complex, it was washed with water to remove the acid and KI impurities. IR (KBr, cm^{-1}): 1605 (s), 1559 (m), 1503 (m), 1429 (m), 1355 (vw), 1303 (vw), 1256 (vw), 1206(w), 1074 (w), 1010 (s), 977 (m) 828 (s), 547 (s); ^1H NMR (d_6 -DMSO, 300 MHz, 298 K): δ = 8.60 (d, 4H, Py-H), 7.62 (d, 4H, Py-H), 7.55 ppm (s, 2H, CH=CH). Elemental analysis (%) calcd. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{CdI}_2$: C, 26.28; H, 1.83; N, 5.80; Found: C, 26.05; H, 1.62; N, 5.11.

25 The above reactions were conducted three or more times to confirm the reproducibility of the reaction. Some grinding reactions were conducted inside the glove box in order to keep the two compounds dry throughout the grinding process. This is due to the humid laboratory environment which may have had negative impact on the reaction and affected the outcome.

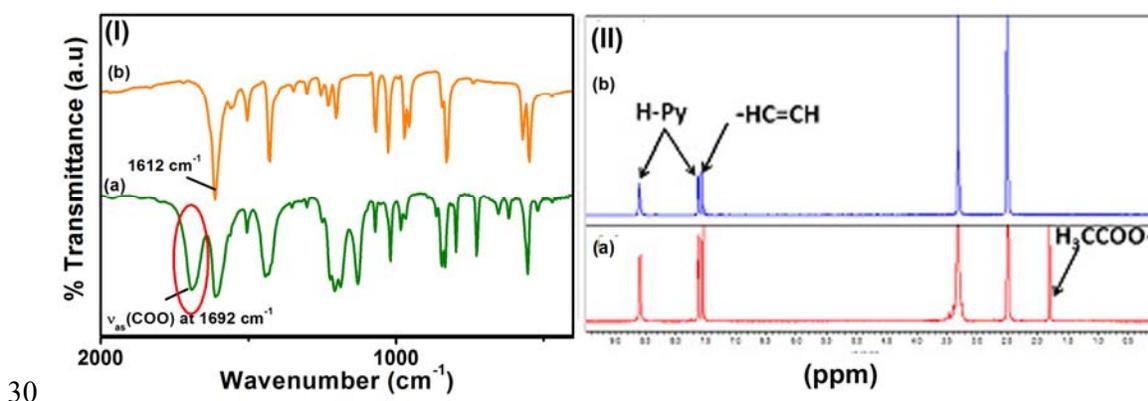


Fig. S1. The IR (I) and ^1H NMR (II) spectra of **1** (a) before and (b) after grinding with KBr.

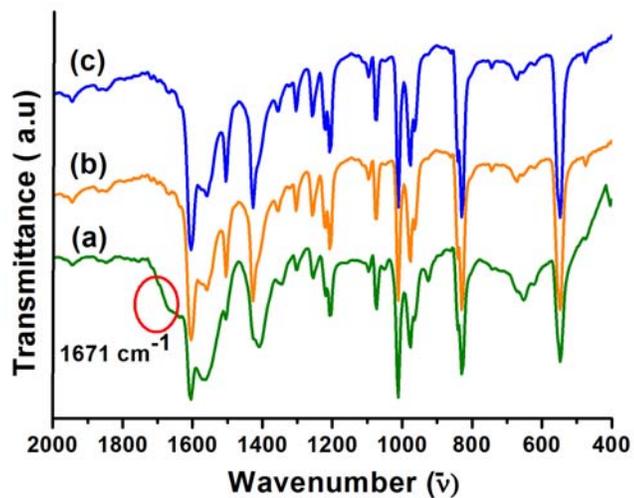


Fig. S2. The IR spectra of (a) **2** after grinding with KBr (b) after washing the ground product (c) **4** obtained by solution method.

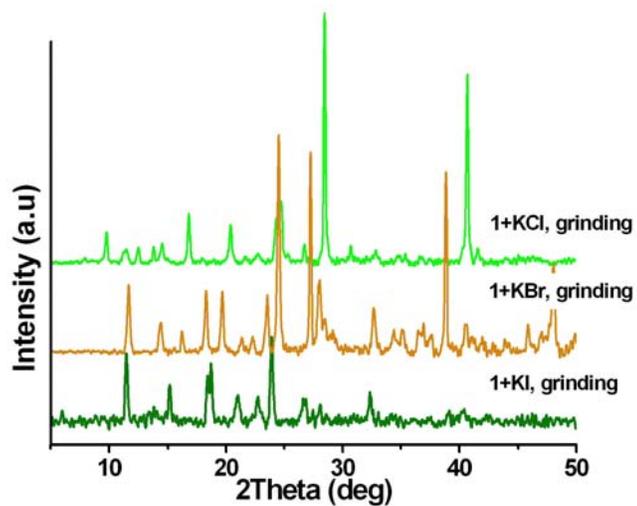


Figure. S3: The PXRD patterns of the products obtained upon grinding **1** with KI, KBr and KCl.

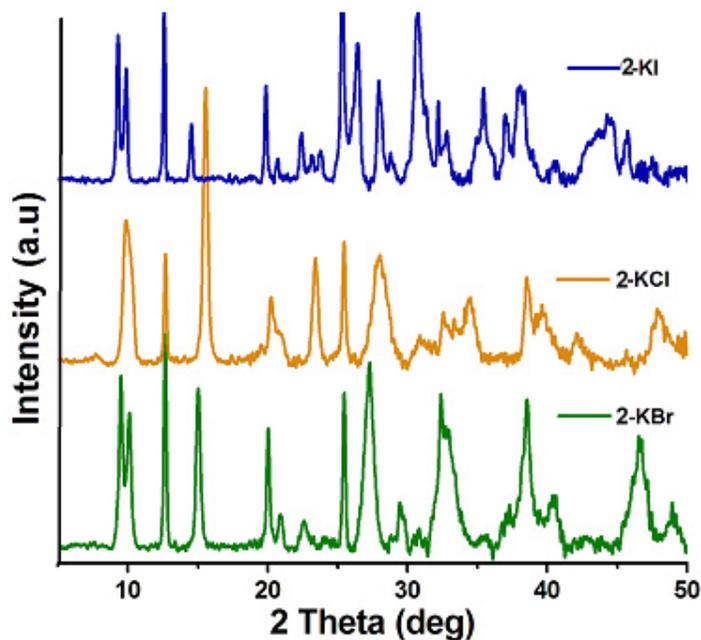
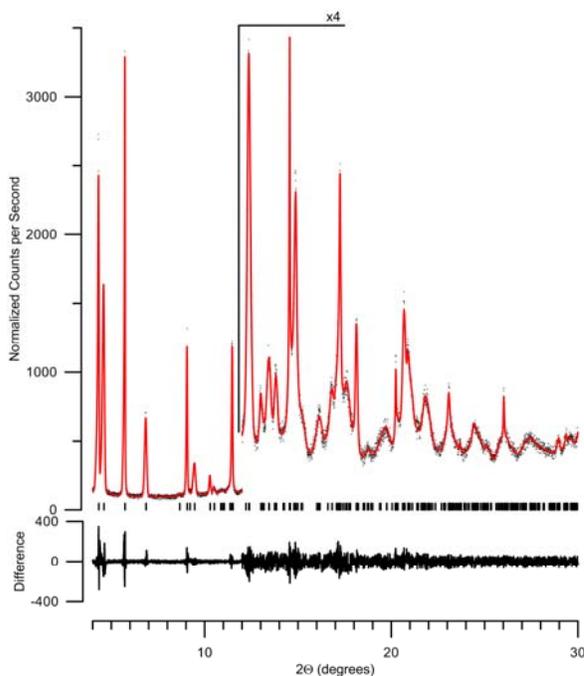


Fig. S4. The PXR D patterns of the products obtained upon grinding 2 with KI, KBr and KCl.



5 Fig. S5. High-resolution synchrotron powder diffraction data (dots) and Rietveld fit of the data for 4. The lower trace is the difference, measured minus calculated, plotted to the same vertical scale.

- (1) Bruker AXS (2005): *TOPAS V4: General profile and structure analysis software for powder diffraction data.* - User's Manual, Bruker AXS, Karlsruhe, Germany.
- (2) a) Coelho, A. A. *J. Appl. Cryst.* **2000**, *33*, 899. b) Coelho, A. A. *J. Appl. Cryst.* **2003**, *36*, 86.
- (3) TOPAS-Academic is available at <http://www.topas-academic.net>.