Coordination-Driven Fast Self-Assembly of Charge-Transfer Hydrogel with Reversible Photochromism

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1. Materials and Physical Measurements

All chemicals were obtained from commercial sources and used as received without further purification. NMR spectra were recorded with a Bruker Avance III 400MHz NMR spectrometer. Elemental analyses of C, H, N and S were carried out with a Vario EL III elemental analyzer. Powder X-ray diffraction (PXRD) were collected on Rigaku desktop MiniFlex 600 diffractometer with Cu Kα radiation (λ=1.5418 Å) or Mo Kα radiation (λ=0.71073 Å). FT-IR spectra were recorded in the range 4000–400 cm^{-1} on a Bruker FT-IR spectrum VERTEX70 spectrometer with pressed KBr pellets. Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. The **gel-Pb** samples were sandwiched between quartz plates. ESR spectra were recorded on a Bruker BioSpin E500 ESR spectrometer with a 100 kHz magnetic field modulation at 100 K for hydrogel (**gel-Pb**) and at room temperature for **cryst-Mg** or **cryst-Co**, respectively. Thermal analyses were performed on a TGA/DSC 1 STAR^e system from room temperature to 800°C with a heating rate of 10 K/min under nitrogen. Electron micrographs: Scanning electron microscopy (SEM) images were taken by Zeiss SEM. Transmission electron microscopy (TEM) images were carried out by using Hitachi TEM HT7700.

2. Crystallographic Data Collection and Refinement

Suitable single crystal of **cryst-Mg** or **cryst-Co** was mounted on loop for the X-ray measurement. Diffraction data was collected on SuperNova (Dual source) diffractometer equipped with the CrysAlis^{pro} X-ray crystallography data systems. The measurement was made by using graphic monochromatic Cu Kα radiation (λ=1.54184 Å) at 100 K under a cold nitrogen stream. Using Olex2[1], the structure was solved with the ShelXT[2] structure solution program using Intrinsic Phasing and refined with the ShelXL[3] refinement package using Least Squares minimisation. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1554369-1554370. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

3. Experimental Section

Synthesis of N, N'-di(ethanesulfonic acid)-1,4,5,8-naphthalenediimide (H_2TauNDI): A mixture of 1,4,5,8-naphthalene-tetracarboxylic dianhydride (1.41 g, 5.26 mmol) and taurine (1.316 g, 10.52 mmol) in DMF (65 mL) was heated under 423K for ~19 h. When the reaction mixture reached room temperature, a light yellow solid precipitated out, which was collected by filtration. ^{1}H NMR (400 MHz, D_2O) δ 8.63 (s, 4H), 4.67-4.37 (m, 4H), 3.38-3.19 (m, 4H). ^{13}C NMR (101 MHz, D_2O) δ 163.91, 130.95, 126.13, 47.72, 36.03. ESI-HRMS m/z calcd for $C_{18}H_{14}N_2O_{10}S_2$: 482.01; found: 481.00 $[M-H]^-$. FT-IR (KBr, cm^{-1}): 3449(m), 3089(w), 2779(w), 1707(m), 1667(s), 1579(m), 1455(m), 1378(m), 1348(m), 1246(m), 1220(s), 1182(s), 1037(s), 1009(s), 908(w), 817(m), 769(m), 635(m), 534(s).

Synthesis of gel-Pb: To H_2TauNDI (72 mg, 0.15 mmol) in water (1 mL), $Pb(NO_3)_2$ (49.6 mg, 0.15 mmol) in water (1 mL) was added. The hydrogel is formed about 10 s upon standing in ambient temperature. The xerogel can be obtained by freeze drying overnight (Freeze drier: Marin Christ Alphal-2). FT-IR for freeze dried sample (KBr, cm^{-1}): 3432(m), 3079(w), 1764(w), 1704(m), 1669(s), 1579(w), 1456(m), 1382(s), 1348(s), 1246(m), 1219(s), 1187(s), 1037(s), 1010(s), 909(w), 822(m), 769(s), 635(m), 535(s).

Controlled experiments: To H_2TauNDI (72 mg, 0.15 mmol) in water (1 mL), $Co(NO_3)_2{\cdot}6H_2O$ (43 mg, 0.15 mmol) in water (1 mL) was added. Replace nitrates with $Cu(NO_3)_2{\cdot}3H_2O$ (36 mg, 0.15 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (60 mg, 0.15 mmol), $Cd(NO_3)_2{\cdot}4H_2O$ (46.2 mg, 0.15 mmol), $Cr(NO_3)_3{\cdot}9H_2O$ (60 mg, 0.15 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (44.7 mg, 0.15 mmol), $Ba(NO_3)_2$ (39.1 mg, 0.15 mmol), $Sr(NO_3)_2$ (31.6 mg, 0.15 mmol) and $Mg(NO_3)_2{\cdot}6H_2O$ (38.4 mg, 0.15 mmol), respectively. Among them, after adding the $Ba(NO_3)_2$ or $Sr(NO_3)_2$ solution, whitish suspension were obtained, filtered and dried in air, white powders were obtained; while after adding $Co(NO_3)_2{\cdot}6H_2O$ or $Mg(NO_3)_2{\cdot}6H_2O$ solution, tiny **cryst-Co** and **cryst-Mg** were obtained, followed by placing several days in room temperature, suitable size of the crystals were collected and dried in air; the mixture remains transparent by adding the rest of nitrates. FT-IR for **cryst-Mg** (KBr, cm^{-1}): 3535(m), 3401(s), 3272(w), 1713(m), 1659(s), 1573(m), 1460(m), 1386(m), 1348(s), 1246(m), 1177(s), 1037(s), 1010(m), 881(w), 822(s), 769(m), 631(w), 534(m). Anal. Calcd for $Mg(H_2O)_6{\cdot}(C_{18}H_{12}N_2O_{10}S_2)$: C 35.28, H 3.94 N 4.57, S 10.46%. Found: C 35.28, H 3.79, N 4.56, S 10.63%. FT-IR for **cryst-Co** (KBr, cm^{-1}): 3395(m), 3079(w), 1707(m), 1664(s), 1579(w), 1450(m), 1386(m), 1348(s), 1241(s), 1219(s), 1182(s), 1037(s), 1010(m), 881(w), 817(s), 769(m), 631(w), 534(m). Anal. Calcd for $Co(H_2O)_6{\cdot}(C_{18}H_{12}N_2O_{10}S_2)$: C 33.39, H 3.73 N 4.33, S 9.91%. Found: C 33.31, H 3.59, N 4.32, S 10.03%.

4. Crystal Data for Cryst-Mg and Cryst-Co

Table S1. Crystal Data and Structure Refinement Parameters for **cryst-Mg** and **cryst-Co.**

Complex	**cryst-Mg**	**cryst-Co**
Empirical formula	$C_{18}H_{24}MgN_2O_{16}S_2$	$C_{18}H_{24}CoN_2O_{16}S_2$
Formula weight	612.82	647.44
Temperature/K	100.0	99.99(17)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	8.1898(5)	8.1585(7)
b/Å	8.9388(6)	8.9229(7)
c/Å	16.7878(10)	16.8650(18)
α/°	87.381(5)	87.674(8)
β/°	80.708(5)	80.395(8)
γ/°	83.888(5)	83.892(7)
Volume/Å^3	1205.47(13)	1203.33(19)
Z	2	2
ρ_{calc}g/cm^3	1.688	1.787
μ/mm^{-1}	3.052	8.008
F(000)	636.0	666.0
Crystal size/mm^3	0.2 × 0.18 × 0.06	0.2 × 0.2 × 0.08
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.956 to 152.9	9.972 to 144.844
Index ranges	-10 ≤ h ≤ 7, -11 ≤ k ≤ 10, -21 ≤ l ≤ 18	-10 ≤ h ≤ 7, -10 ≤ k ≤ 10, -20 ≤ l ≤ 19
Reflections collected	8127	7237
Independent reflections	4876 [R_{int} = 0.0319, R_{sigma} = 0.0327]	4486 [R_{int} = 0.0674, R_{sigma} = 0.0779]
Data/restraints/parameters	4876/0/403	4486/29/451
Goodness-of-fit on F^2	1.057	1.053
Final R indexes [I>=2σ (I)]	R_1[a] = 0.0386, wR_2[b] = 0.1064	R_1[a] = 0.0770, wR_2[b] = 0.2124
Final R indexes [all data]	R_1[a] = 0.0411, wR_2[b] = 0.1084	R_1[a] = 0.1081, wR_2[b] = 0.2379
Largest diff. peak/hole / e Å^{-3}	0.37/-0.66	0.83/-1.27

[a] $R_1=\sum||F_o| - |F_c|| / \sum|F_o|$. [b] $wR_2 =[\sum w(F_o^2 \_ F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

Table S2 Hydrogen-bond Geometry (Å, °) for **cryst-Mg**.

D—H···A[#]	[Symmetry code]	d(D—H)	d(H···A)	d(D···A)	∠DHA
O11—H11C···O6^{i}	[1-x, 1-y, 1-z]	0.86	1.94	2.8049	174
O11—H11D···O7^{ii}	[x, -1+y, z]	0.83	1.98	2.7977	168
O12—H12B···O2^{ii}	[x, -1+y, z]	0.83	2.24	3.0565	171
O12—H12A···O8^{iii}	[-1+x, -1+y, z]	0.82	2.06	2.8765	174
O13—H13A···O14^{iv}	[-1+x, y, z]	0.86	2.06	2.8632	154
O13—H13B···O1	-	0.81	1.96	2.7678	177
O14—H14B···O6^{i}	[1-x, 1-y, 1-z]	0.79	1.94	2.7225	170
O14—H14A···O2^{i}	[1-x, 1-y, 1-z]	0.90	1.87	2.7684	175
O15—H15B···O10	-	0.81	1.98	2.7815	168
O15—H15A···O7^{ii}	[x, -1+y, z]	0.83	1.90	2.7301	176
O16—H16B···O3^{v}	[-x, 1-y, 1-z]	0.86	1.93	2.7921	178
O16—H16B···O1	-	0.83	1.89	2.7223	173
C2—H2A···O10^{iv}	[-1+x, y, z]	0.97	2.52	3.4826	170
C2—H2B···O5	-	0.97	2.41	2.7394	100
C10—H10A···O9	-	0.97	2.56	3.0797	114
C11—H11A···O3^{vi}	[1+x, y, z]	0.97	2.44	3.3397	154
C11—H11A···O10	-	0.97	2.33	2.7360	104
C17—H17···O9^{vii}	[1-x, 2-y, -z]	0.93	2.55	3.2038	127

[#] D = Donor, A = Acceptor.

Table S3 Hydrogen-bond Geometry (Å, °) for **cryst-Co**.

D—H···A[#]	[Symmetry code]	d(D—H)	d(H···A)	d(D···A)	∠DHA
O11—H11C···O6^{i}	[1+x, -1+y, z]	0.84	2.00	2.7952	158
O11—H11D···O8^{ii}	[1-x, 1-y, 1-z]	0.84	1.98	2.7931	163
O12—H12A···O15^{iii}	[-x, 1-y, 1-z]	0.84	2.05	2.8471	159
O12—H12B···O2	-	0.84	1.93	2.7622	169
O13—H13A···O7^{iv}	[x, -1+y, z]	0.84	2.05	2.8792	170
O13—H13B···O1^{iv}	[x, -1+y, z]	0.84	2.20	3.0092	164
O14—H14A···O2^{ii}	[1-x, 1-y, 1-z]	0.84	1.93	2.7148	154
O14—H14B···O3	-	0.84	1.97	2.7950	167
O15—H15A···O1^{v}	[-1+x, y, z]	0.84	1.93	2.7623	169
O15—H15B···O8	-	0.84	1.92	2.7241	161
O16—H16A···O10	-	0.84	1.96	2.7735	162
O16—H16B···O6^{ii}	[x, -1+y, z]	0.84	1.89	2.7236	171
C2—H2A···O10	-	0.97	2.53	3.4947	176
C8—H8···O5	-	0.93	2.51	2.8393	101
C10—H10B···O9	-	0.97	2.53	3.0901	117
C11—H11B···O3	-	0.91	2.50	3.3476	154
C11—H11B···O10	-	0.91	2.29	2.7362	110
C18—H18···O9^{vi}	[-x, 2-y, -z]	0.93	2.51	3.1932	130

[#] D = Donor, A = Acceptor.

5. Related Data and Figures

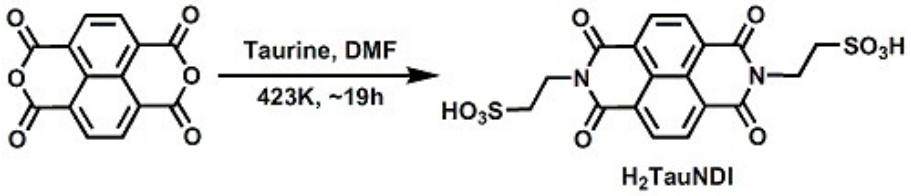

Figure S1. Synthesis of H_2TauNDI.

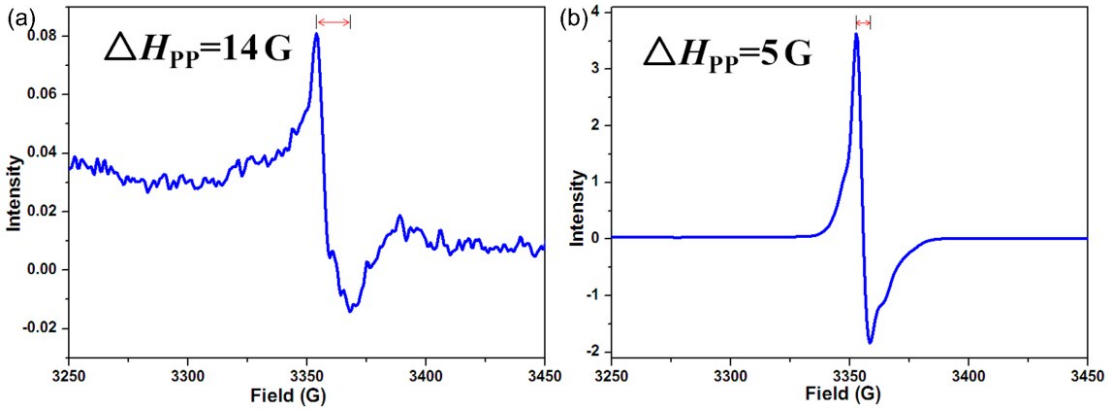

Figure S2. Peak-to-peak line width for **gel-Pb** hydrogel at 100K a) before irradiation, b) after irradiation.

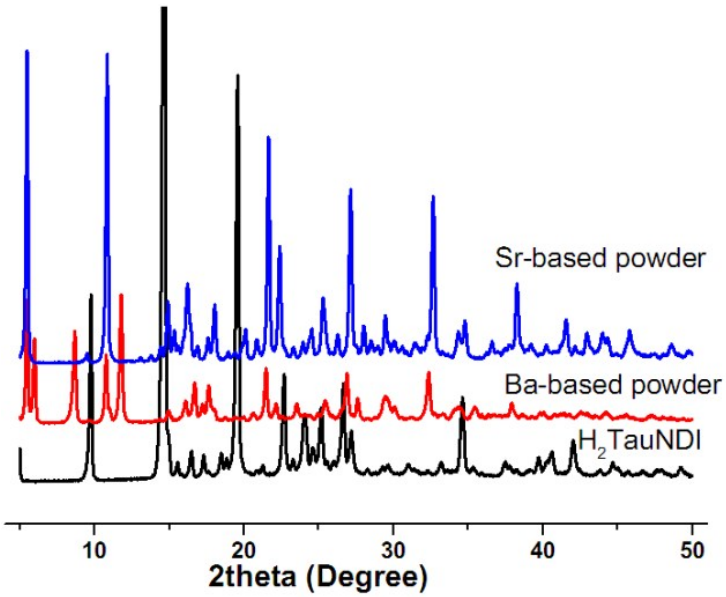

Figure S3. (a)The simulated PXRD pattern based on the H_2TauNDI powders; (b) PXRD pattern of the as-synthesized Ba-based powders; (c) PXRD pattern of the as-synthesized Sr-based powders.

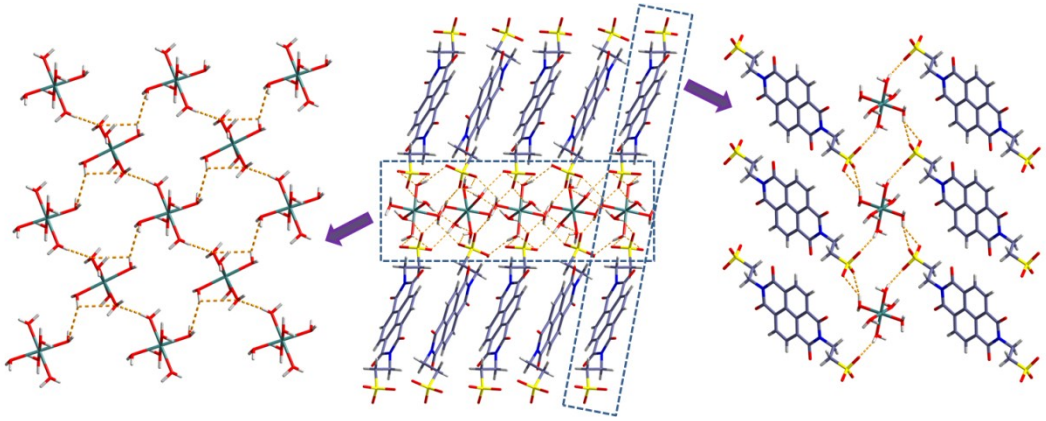

Figure S4. Hydrogen bonds in **cryst-Mg**.

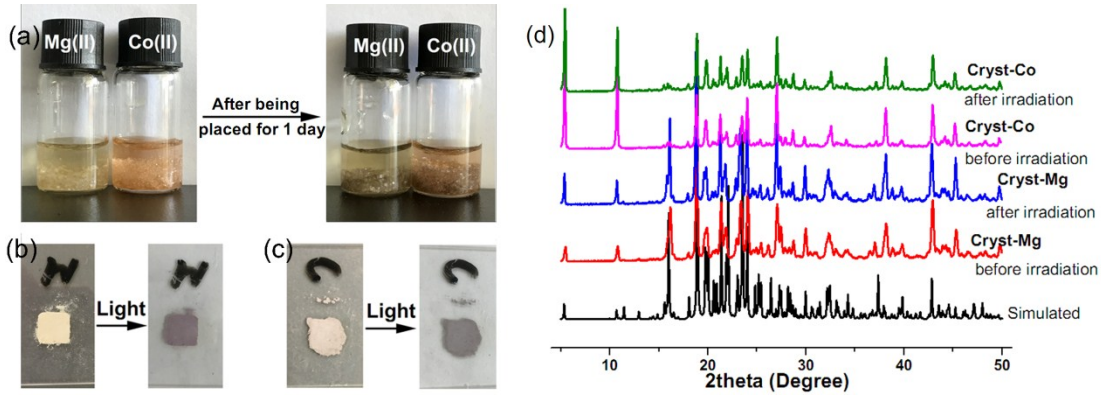

Figure S5. (a-c) The photograph of **cryst-Mg** and **cryst-Co** shows their photochromism (b: discoloration effect of **cryst-Mg**; c: discoloration effect of **cryst-Co**; both irraditon by LED light with 460-465 nm for 3 min); (d) The PXRD patterns of **cryst-Mg** and **cryst-Co** (before or after irradiation by LED light with 460-465 nm for 3 min).

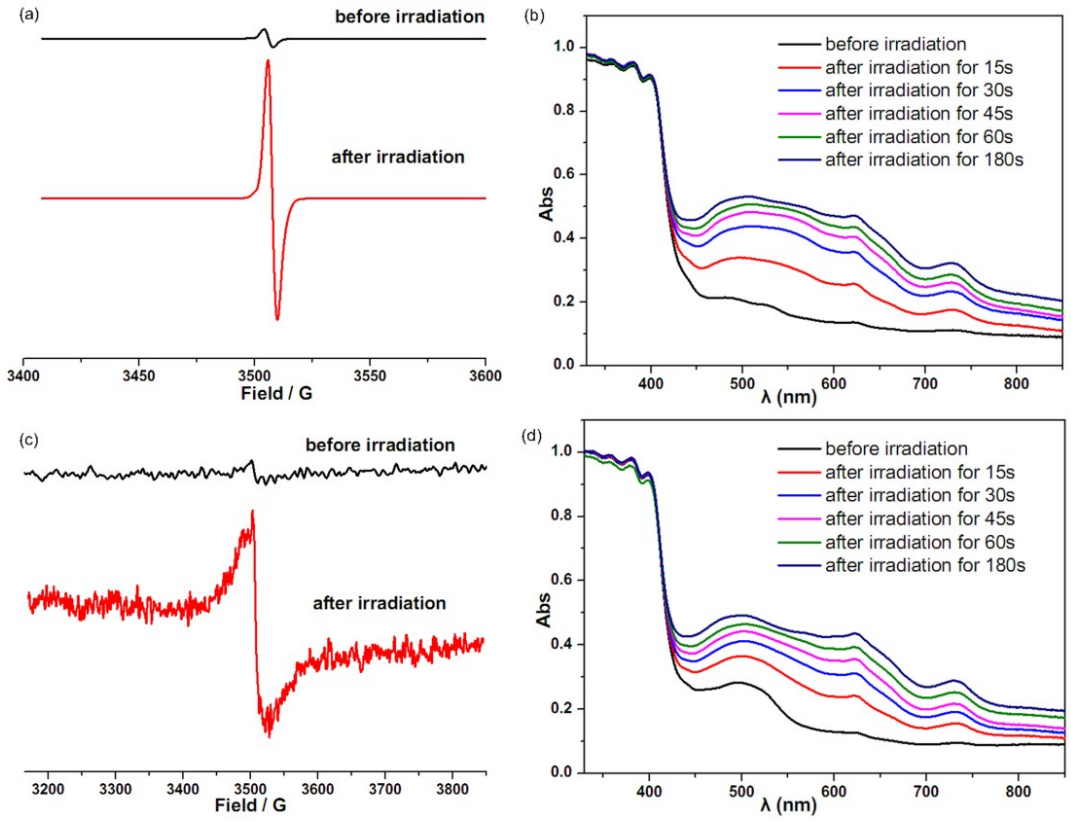

Figure S6. (a) ESR spectrum with g=2.0042 of **cryst-Mg** at room temperture (before irradiation and after irradiation by LED light (460-465 nm) for 3 min); (b) The *in-site* UV-Vis spectra of **cryst-Mg** irradiated by LED light with different times (0s, 15s, 30s, 45s, 60s and 180s, respectively); (c) ESR spectrum with g=2.0046 of **cryst-Co** at room temperture (before irradiation and after irradiation by LED light for 3 min); (d) The *in-site* UV-Vis spectra of **cryst-Co** irradiated by LED light with different times (0s, 15s, 30s, 45s, 60s and 180s, respectively).

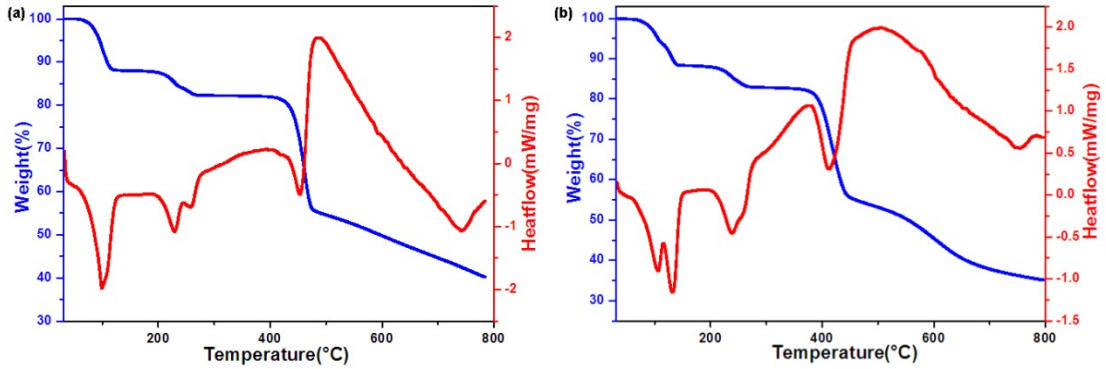

Figure S7. TGA curve of **cryst-Mg** (a) and **cryst-Co** (b).

For **cryst-Mg**, in the temperature range of 65-120°C, the amount of weight loss was ascribed to the loss of four coordinated water molecules (experiment value: 11.78%, calculated value: 11.75%). The following weight losses occurred in the temperature range of 200°C-268°C, which were attributed to the loss of two coordinated water molecules (experiment value: 5.84%, calculated value: 5.87%). The last weight losses were assigned to the decomposition of TauNDI molecules. **Cryst-Co** has similar thermal decompositions, in the temperature range of 70-128°C,

the amount of weight loss was ascribed to the loss of four coordinated water molecules (experiment value: 11.17%, calculated value: 11.13%). The following weight losses occurred in the temperature range of 200°C-250°C, which were attributed to the loss of two coordinated water molecules (experiment value: 5.54%, calculated value: 5.55%). The last weight losses were assigned to the decomposition of TauNDI molecules.

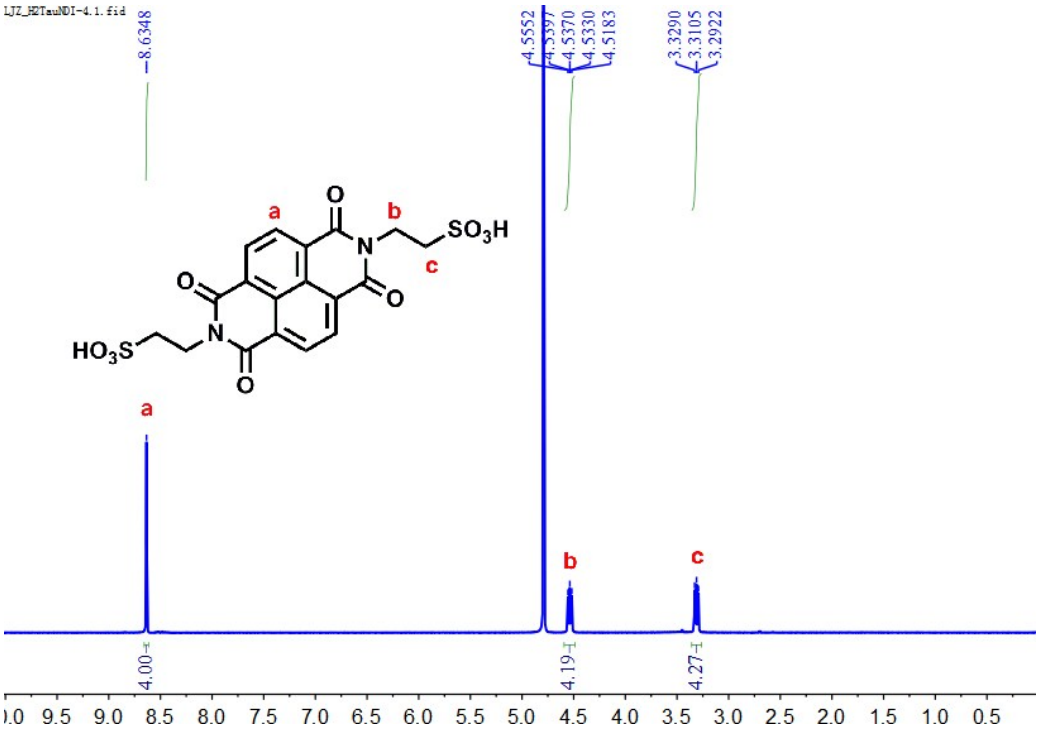

Figure S8. ^{1}H NMR of the H_2TauNDI

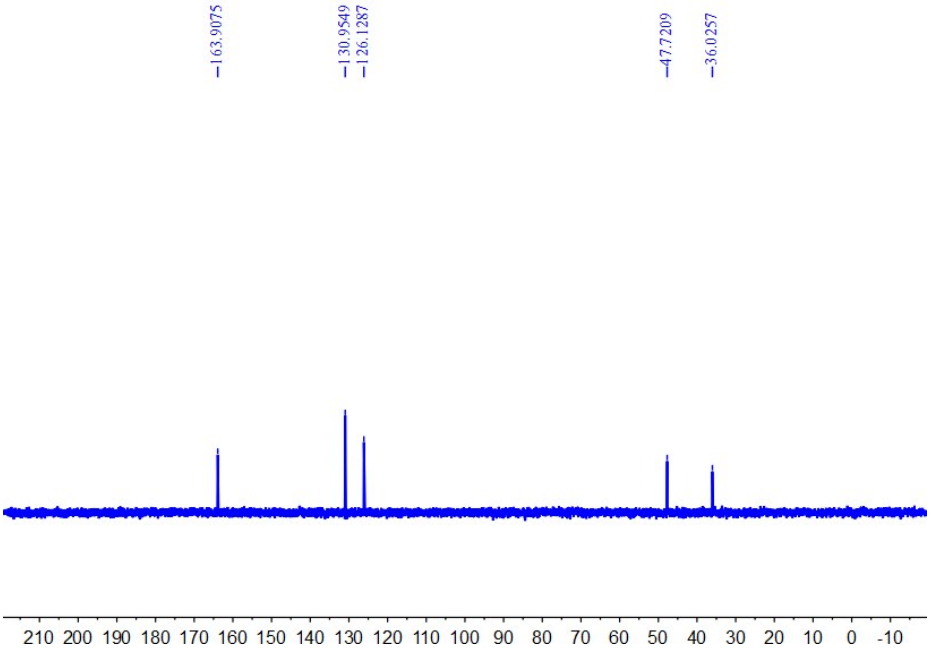

Figure S9. ^{13}C NMR of the H_2TauNDI.

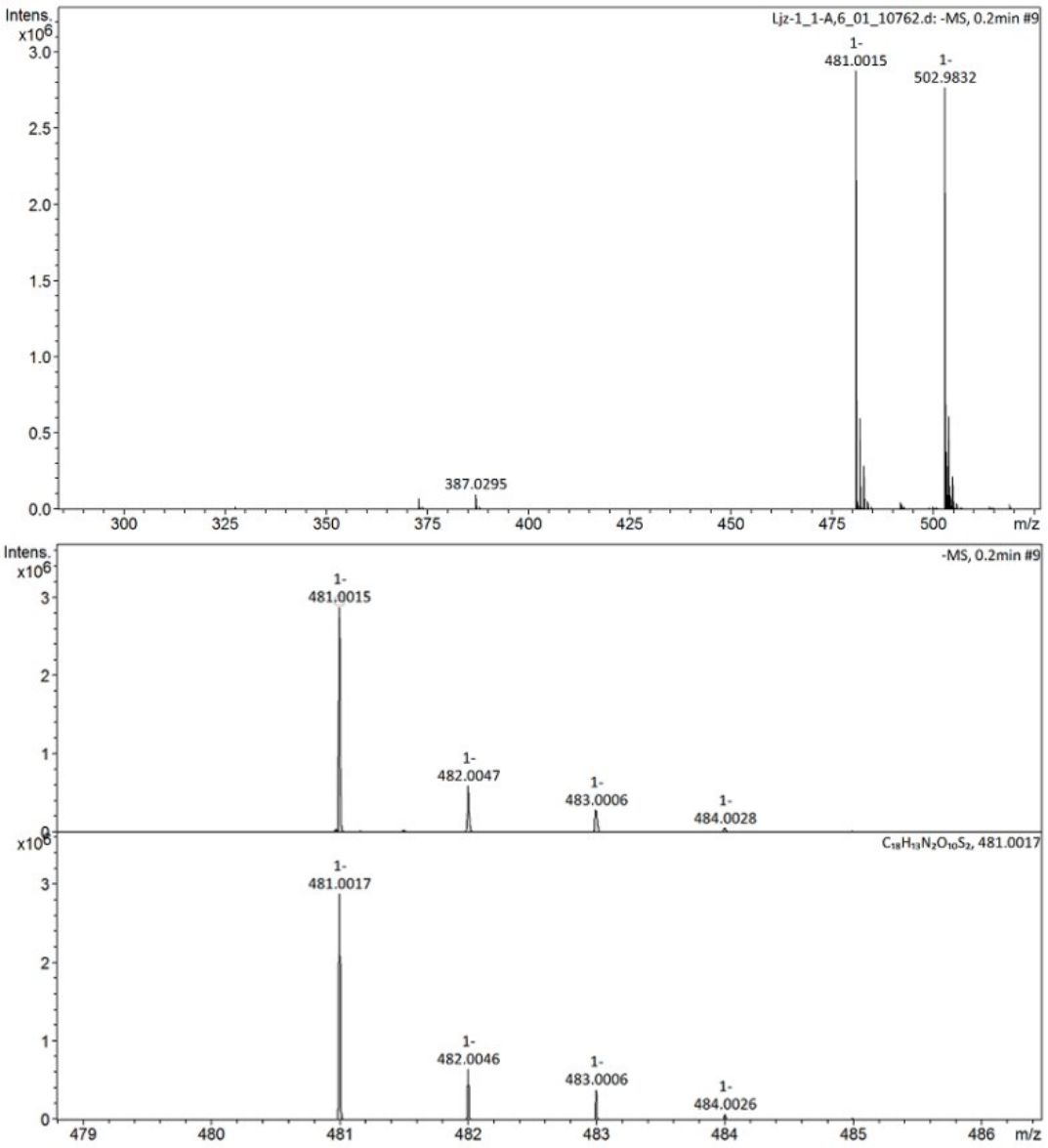

Figure S10. The HRMS of the H_2TauNDI.

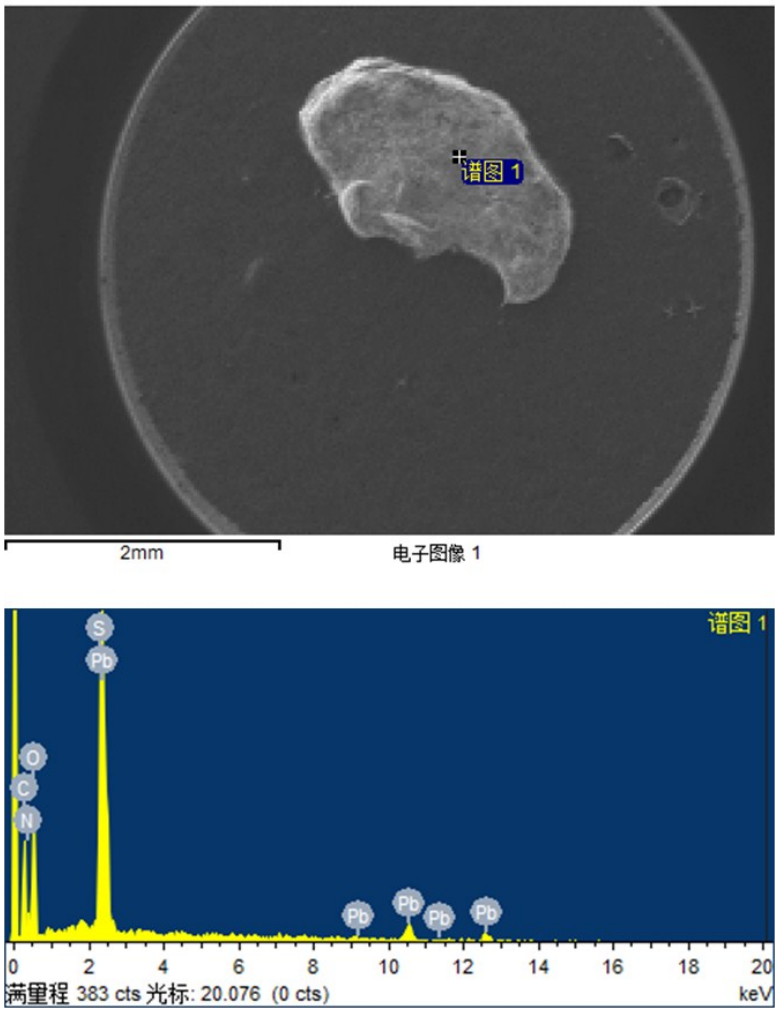

Figure S11. Image and EDS of **gel-Pb** hydrogel.

6. Reference

[1] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.

[2] Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.

[3] Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.