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A pore-expanded supramolecular organic framework and its en-richment of photosensitizers and catalysts for visible-induced hydrogen production

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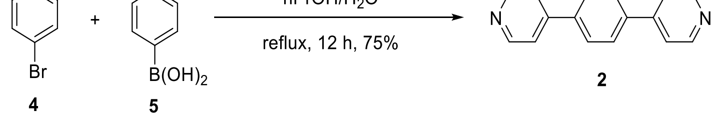
Contents

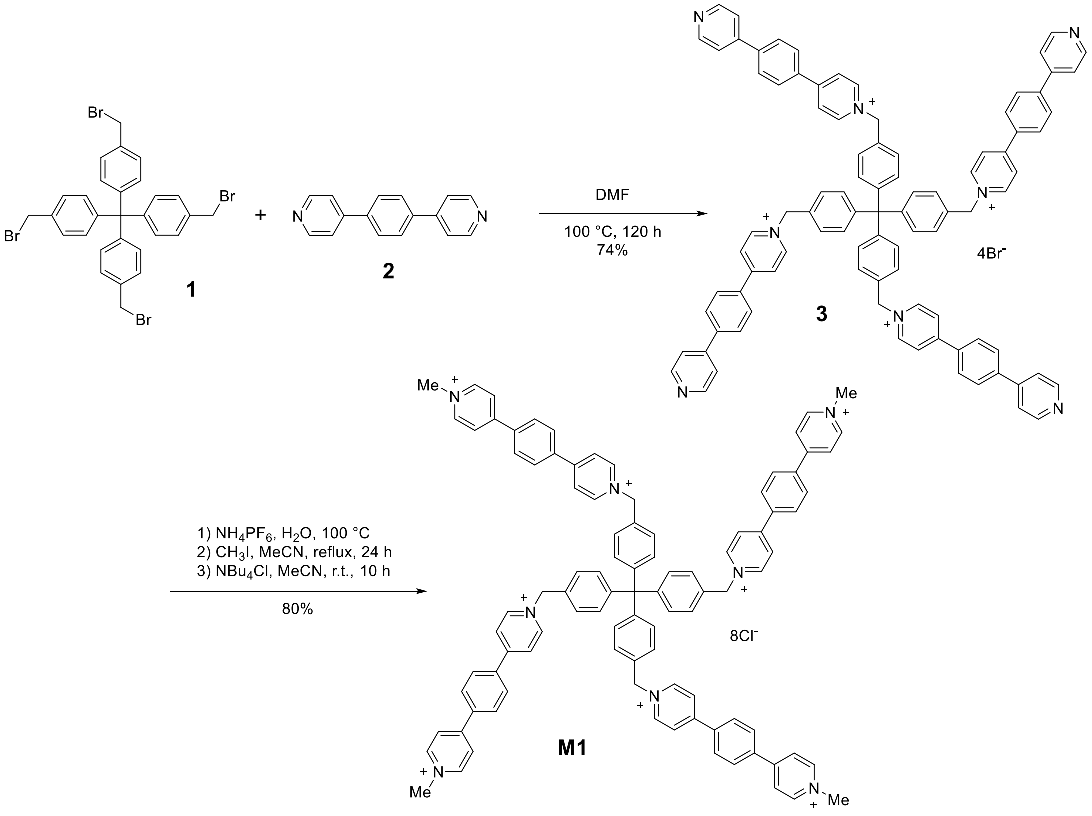
Materials and general methods: All reagents were obtained from commercial suppliers and used without further purification unless otherwise noted. All reactions were carried out under a dry nitrogen atmosphere. All solvents were dried before use following standard procedures. ^{1}H NMR spectra were recorded with a 400 MHz spectrometer. ^{1}H NMR diffusion-ordered spectroscopic experiments were carried out with a 400 NMR spectrometer. Solid-phase or solution-phase synchrotron X-rayscattering experiments were performed on the BL16B beamline of Shanghai Synchrotron Radiation Facility. Scanning electron micrographs of the samples were obtained on a Nova nano SEM 450 Field Emission Scanning Electron Microscope at 3.00 kV with the material adhered to the SEM sample holder directly or on a Phenom China Scanning Electron Microscope at 15.00 kV after the material that adhered to the sample holder was been gilded to 10-1-10-2 vacuum degree. TGA experiments were performed on a Model TGA/SDTA 851 instrument. Samples were placed in alumina pans and heated at a rate of 10 °C per minute from 100 to 800 °C under a nitrogen atmosphere. UV-Vis spectra were performed on a Perkin-Elmer 750s instrument from 200-700 nm at the scan rate of 3 nm/ internal. DLS experiments were performed on a Malvern Zetasizer Nano ZS90 light scattering Instrument. Fluorescence measurements were performed on PerkinElmer LS 55 Luminescence spectrometer. H_2 was characterized by GC-2010 using helium as the carrier gas with a BDI plasma detector. Dialysis experiments were conducted according to the reported method.[1] The Ru^{2+} complexes were detected using absorption spectroscopy which did not afford the absorption of the complexes in the outside solution, whereas WD-POM was detected using EDX experiment which did not show the existence of W and P elements in the outside solution. Compound **1** was prepared according to reported method.[2]

Photocatalytic H_2 production: The photocatalytic water reduction was carried out in an external illumination type reaction vessel with a magnetic stirrer. Samples for photocatalytic hydrogen production were prepared in 10 mL septum-sealed glass vials. Each sample was made up to a volume of 2 mL 20% methanol (v/v) aqueous solution with the pH value of 1.8 (adjusted by 2 M HCl). Samples typically contained 0.001 to 0.2 mM of **SOF-bpb**, 0.002 to 0.02 mM of Ru Sensitizer and 0.0002 to 0.002 mM. Sample vials were capped and deoxygenated by bubbling nitrogen through them for 15 min to ensure complete air removal. The solution was irradiated by a 300 W solid state light source with a 500 nm filter. After the hydrogen evolution reaction, the gas in the headspace of the vial was analyzed by GC-2010 to determine the amount of hydrogen generated. TON is defined as n(1/2H_2)/n(POM).



4 **5** **2**

Synthesis of compound 2. The procedure has been modified for a reported method.[3] 4-Bromopyridine **4** hydrochloride (1.94 g, 10 mmol) and benzene-1,4-diboronic acid **5** (0.82 g, 5 mmol) were added to a 150 mL of three-necked flask containing *n*-propanol (20 ml) and water (15 ml). Potassium carbonate (5.5 g, 40 mmol) and tetrakis(triphenylphosphine)palladium (0.86 g, 0.75 mmol) were then added under stirring. The mixture was heated at reflu (100 °C) for 2 days and then cooled to room temperature and divided into two layers. The water layer was extracted with ethyl acetate (20 mL × 2) and the solution was combined with the n-propanol layer and concentrated with a rotavapor. The resulting black paste was sonicated in water (100 mL) and the brownish solid was filtrated and washed with water and dried in vacuum. The solid was then sonicated in n-hexane (50 mL) and subjected to filtration. The resulting solid was dissolved in dichloromethane (20 mL) and decolorized with charcoal and filtrated through celite. Hydrochloric acid (1 mL, 37%) was then added dropwise and the precipitate formed thereout was filtrated and washed with dichloromethane and then dissolved in water (100 mL). Dilute sodium hydroxide solution (1N) was added to pH >10. The white solid formed thereout was filtrated and washed with water and dried in vacuum to give compound **2** as a white solid (1.74 g, 7.5 mmol) in 75% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.67 (d, *J* = 4.0 Hz, 4H), 7.97 (s, 4H), 7.78 (d, *J* = 4.0 Hz, 4H). These ^{1}H NMR peaks are consistent with those reported in the literature [2].



Compound 3. To a solution of compound **1** (0.35 g, 0.50 mmol) in DMF (10 mL) was added compound **2** (1.16 g, 5.0 mmol). The mixture was stirred at 100 ℃ for 5 days and then cooled to room temperature. The solid formed thereout was filtrated and washed with DMF (10 mL × 2) and dichloromethane (10 mL) and dried in vacuum to give compound **3** as a yellowish solid (0.60 g, 0.37 mmol) in 74% yield. ^1H NMR (400 MHz, DMSO-d_6): δ 9.26 (d, *J* = 4.0 Hz, 8H), 8.71 (d, *J* = 4.0 Hz, 8H), 8.63 (d, *J* = 8.0 Hz, 8H), 8.23 (d, *J* = 8.0 Hz, 8H), 8.09 (d, *J* = 8.0 Hz, 8H), 7.83 (d, *J* = 8.0 Hz, 8H), 7.46 (d, *J* = 4.0 Hz, 8H), 7.24 (d, *J* = 4.0 Hz, 8H), 5.79 (d, *J* = 8.0 Hz, 8H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 154.7, 150.9, 147.2, 145.8, 145.4, 141.0, 134.4, 132.9, 131.3, 129.5, 128.8, 128.4, 125.4, 121.8, 64.5, 62.2. HRMS (ESI): Calcd for $C_{93}H_{72}N_8$: 325.0872 $[M-4Br]^{4+}$. Found: 325.0881.

Compound M1. To a saturated solution of compound **3** (0.20 g, 0.12 mmol) in water was added dropwise saturated aqueous solution of potassium hexafluorophosphate until no precipitate was formed. The precipitate was filtrated and washed with H_2O (20 mL × 2) and dried at 50 ℃ in vacuum to give a paleyellow solid. This solid was added to a 50 mL of pressure flask and the content of the flask and then acetonitrile (10 mL) and methyl iodide (0.27 g, 1.85 mmol) were added. The mixture in the sealed flask was stirred at 80 ℃ for 24 hours and then cooled to room temperature. To the solution was added dropwise a saturated tetrabutylammonium chloride in acetonitrile until no precipitate was formed. The precipitate was filtrated and washed with acetonitrile (10 mL × 2) and dichloromethane (10 mL) and dried at 50 ℃ in vacuum to give compound **M1** as a paleyellow solid (0.16 g, 0.098 mmol) in 80 % yield. ^1H NMR (400 MHz, DMSO-d_6): δ 9.35 (d, *J* = 4.0 Hz, 8H), 9.10 (d, *J* = 8.0 Hz, 8H), 8.70 (d, *J* = 8.0 Hz, 8H), 8.64 (d, *J* = 8.0 Hz, 8H), 8.34 (s, 16H), 7.52 (d, *J* = 8.0 Hz, 8H), 7.23 (d, *J* = 8.0 Hz, 8H), 5.85 (s, 8H), 4.38 (s, 12H). ^{13}C NMR (400 MHz, D_2O): δ 154.9, 154.8, 154.2, 147.9, 145.2, 145.1, 144.1, 136.9 (d), 136.0, 131.5, 123.0, 128.8, 125.3, 125.1, 124.9, 114.8, 64.3, 63.1, 47.4.

References:

(1) J. Tiana, C. Yao, W.-L. Yang, L. Zhang, D.-W. Zhang, H. Wang, F. Zhang, Y. Liu and Z.-T. Li, *Chin. Chem. Lett*., 2017, **28**, 798-806.
(2) J. Tian, Y.-D. Ding, T.-Y. Zhou, K.-D. Zhang, X. Zhao, H. Wang, D.-W. Zhang, Y. Liu and Z.-T. Li, *Chem. Eur. J*., 2014, **20**, 575-584.
(3) Y.-S. Su and C.-F. Chen, *Org. Lett.,* 2010, **12**, 1888-1891.

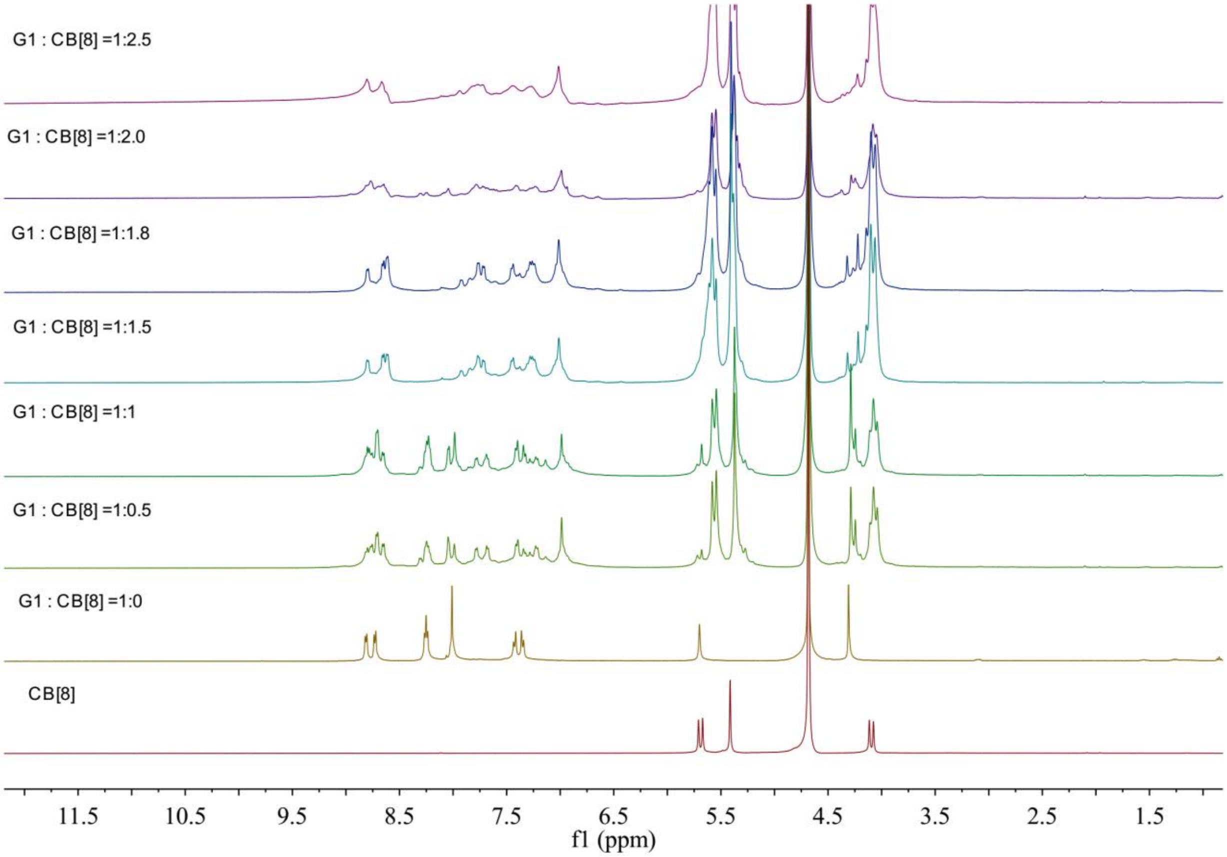


Fig. S1 ^{1}H NMR spectra (400 MHz) of **M1** (2 mM) and CB[8] of increasing amounts in D_2O at 25 °C.

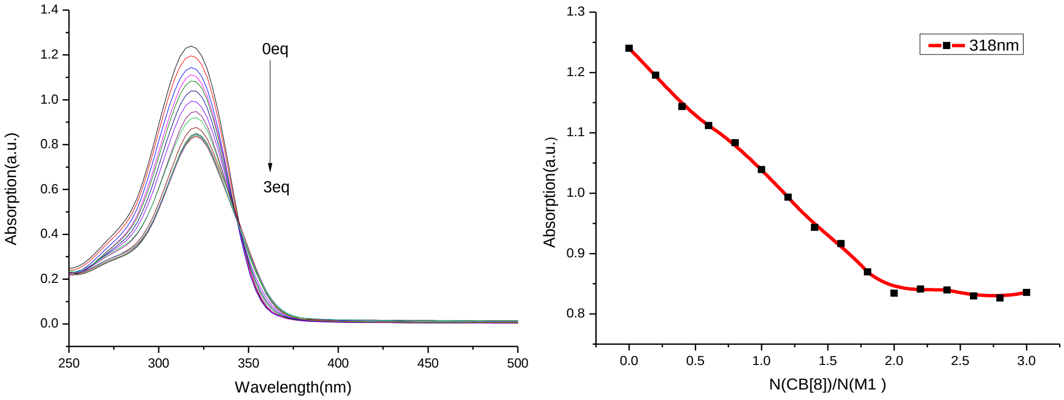


Fig. S2 UV-visible spectra of **M1** (1 mM) in the presence of CB[8] (0-3 equiv), highlight an inflection point at [CB[8]]/[**M1**] = 2.

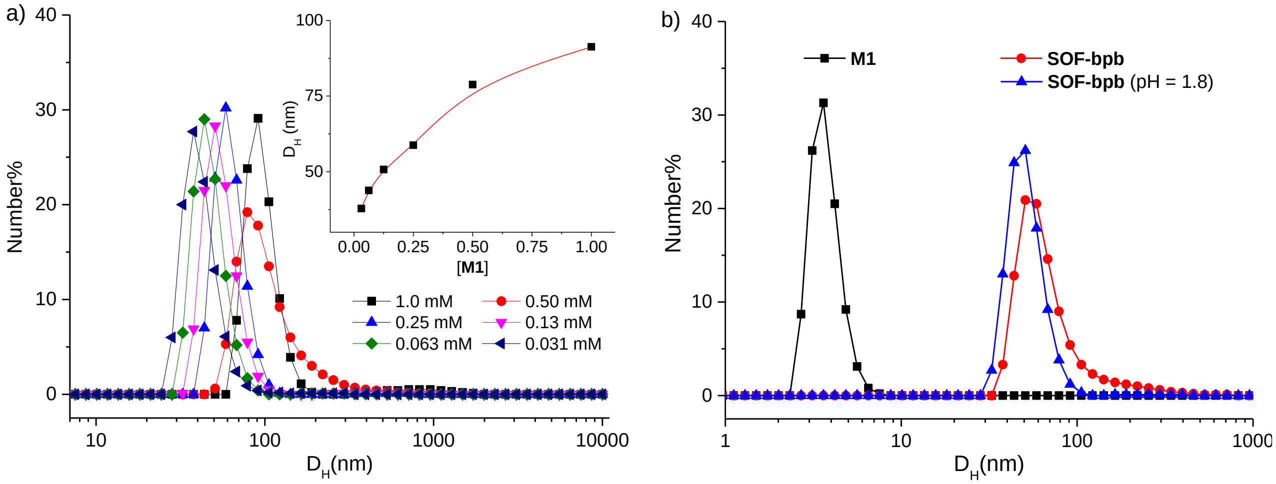


Fig. S3 a) DLS profiles of the 1:2 solution of **M1** and CB[8] (1:2) of varying concentration in water at 25 °C. Inset: D_H vs [**M1**]. b) DLS profiles of the aqueous solutions of **SOF-bpb** ([**M1**] = 0.1 mM, red, pH = 7, blue, pH = 1.8) and **M1** (0.1 mM) with CB[8] in water at 25 °C. The measurements were conducted after the solutions were left to stand for 36 hours.

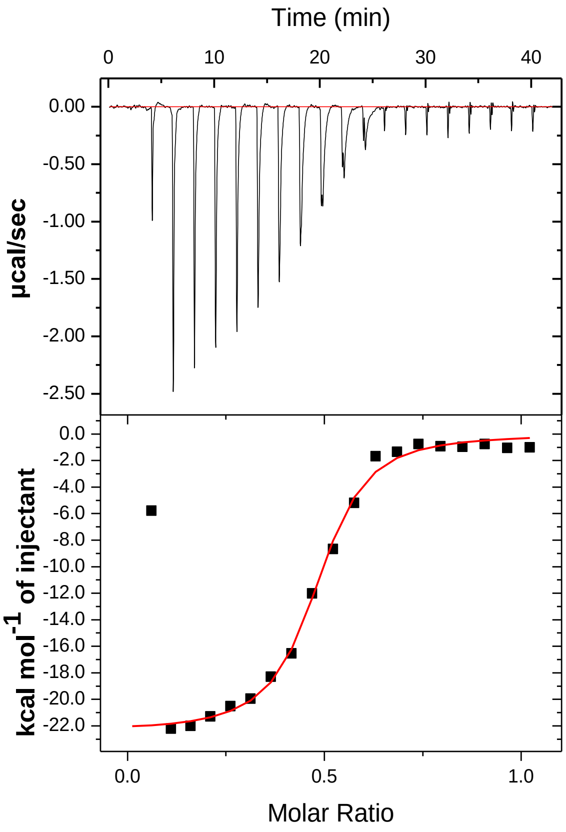


Fig. S4 Isothermal titration thermogram for the titration of CB[8] (0.1 mM) by **M1** in water.

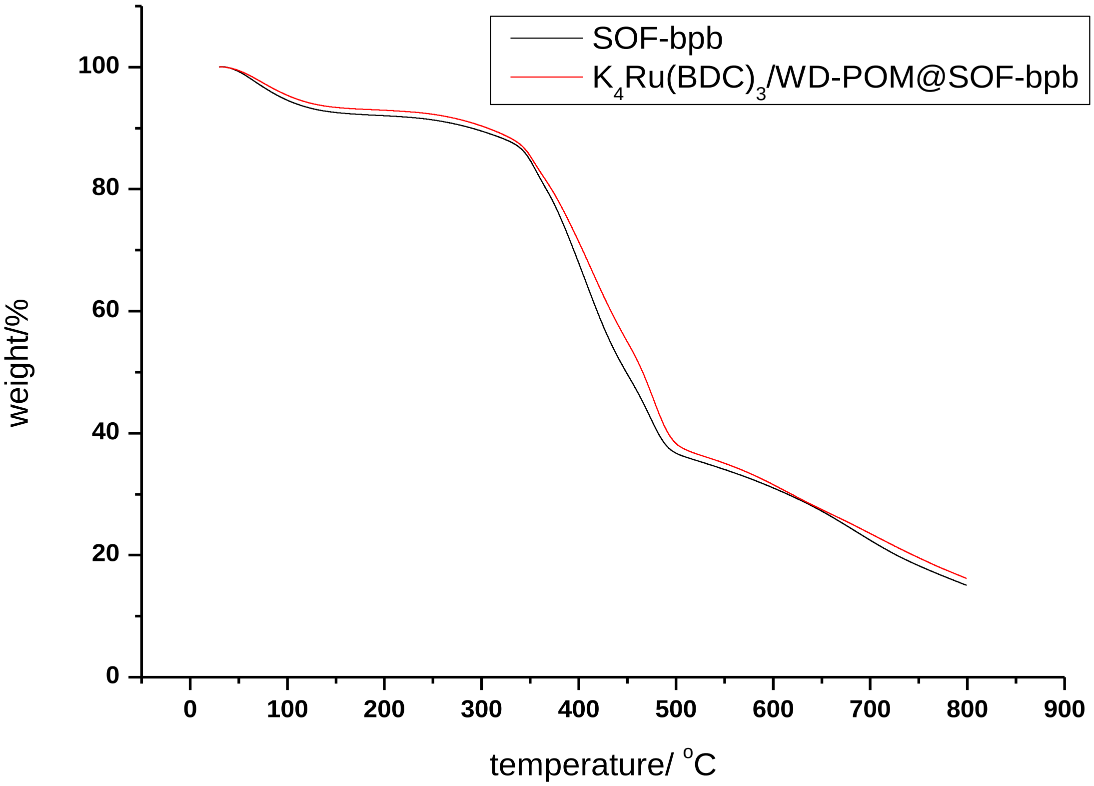


Fig. S5 Thermogravimetric analysis of **SOF-bpb** (black) and $K_4Ru(bdc)_3$/WD-POM@**SOF-bpb** (red). The examples were obtained by slow evaporation of their aqueous solution.

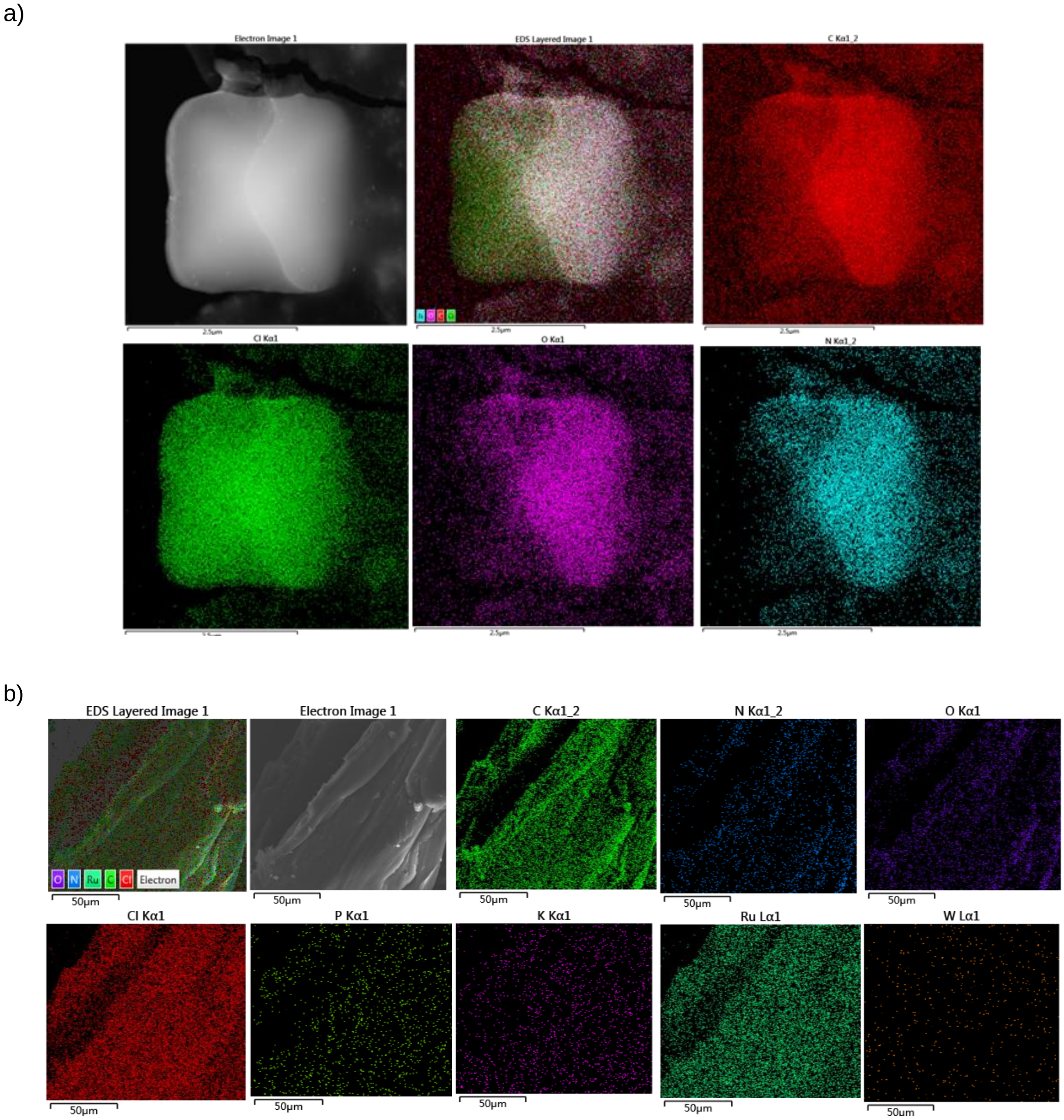


Fig. S6 a) TEM images of **SOF-bpb** exhibiting uniform bulk morphology and EDX results. b) Element distribution mapping images of the microcrystals of $K_4Ru(bdc)_3$/WD-POM$\subset$**SOF-bpb**, showing the respective distribution of the C, N, O, Ru, Cl, W and P elements.

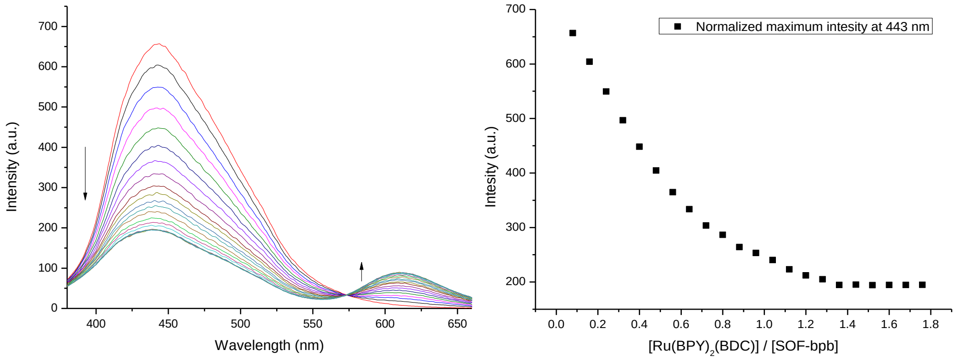


Fig. S7 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 μM) in **SOF-bpb** in water with the addion of Ru(bpy)$_2$(bdc) (0-15.2 μM).

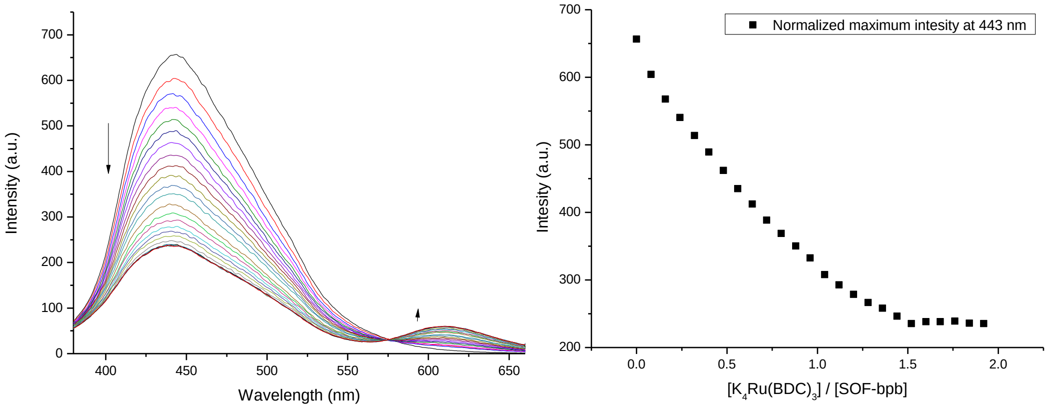


Fig. S8 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 μM) in **SOF-bpb** in water with the addion of K$_4$Ru(bdc)$_3$ (0-16 μM).

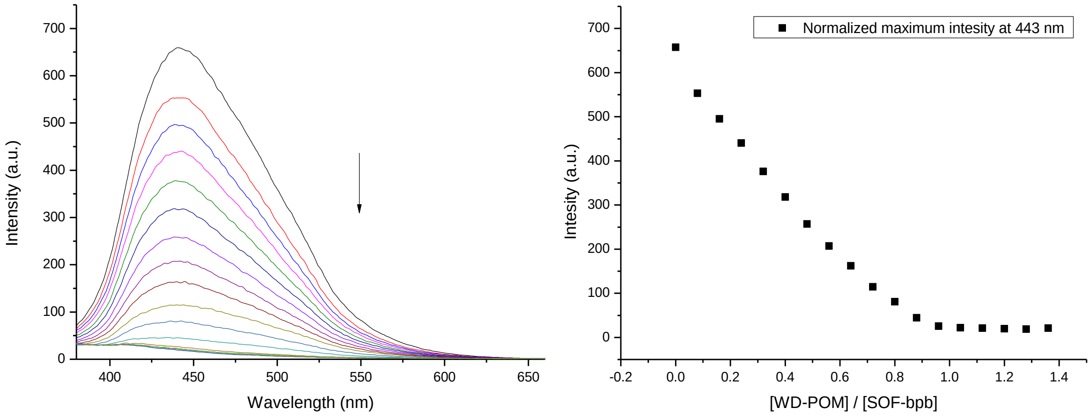


Fig. S9 Fluorescence quenching (λ_{ex} = 370 nm) of **M1** (10 μM) in **SOF-bpb** in water with the addion of WD-POM (0-13.6 μM).

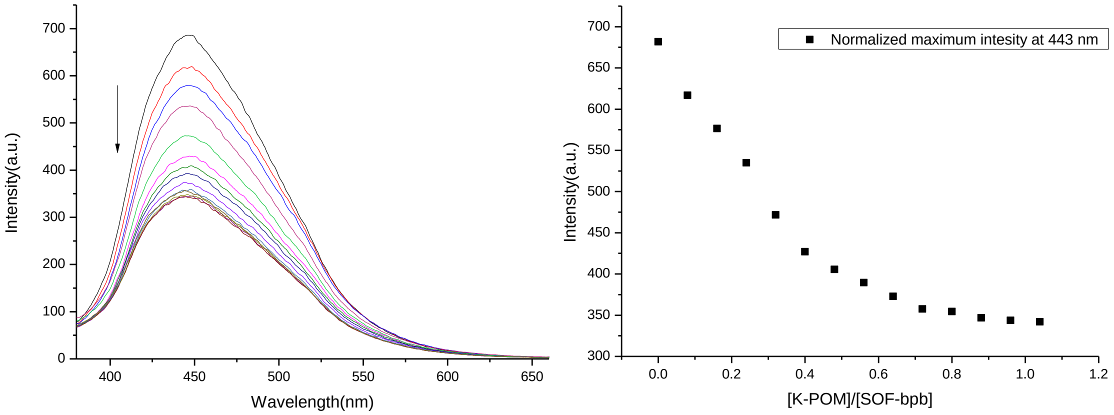


Fig. S10 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 μM) in **SOF-bpb** in water with the addion of K-POM (0-18 μM).

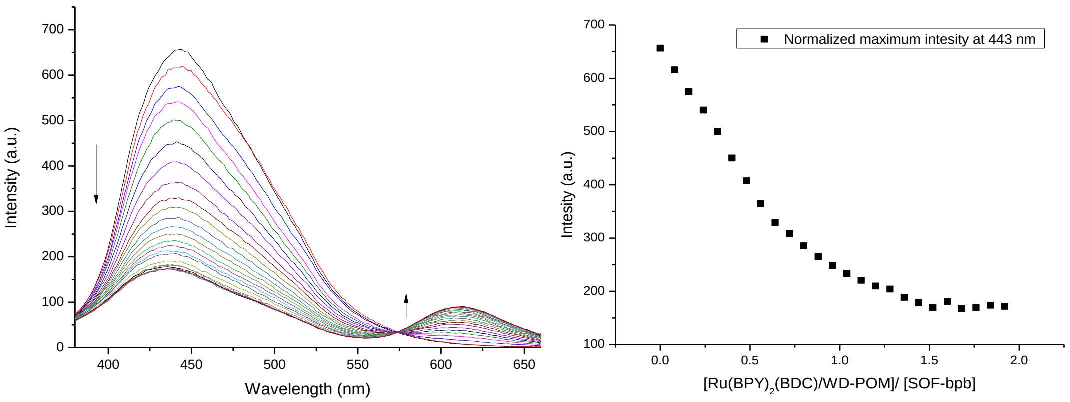


Fig. S11 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 μM) in **SOF-bpb** in water with the simultaneous addition of $Ru(bpy)_2(bdc)$ and WD-POM (10:1) ([Ru^{2+}] = 0-16.8 μM).

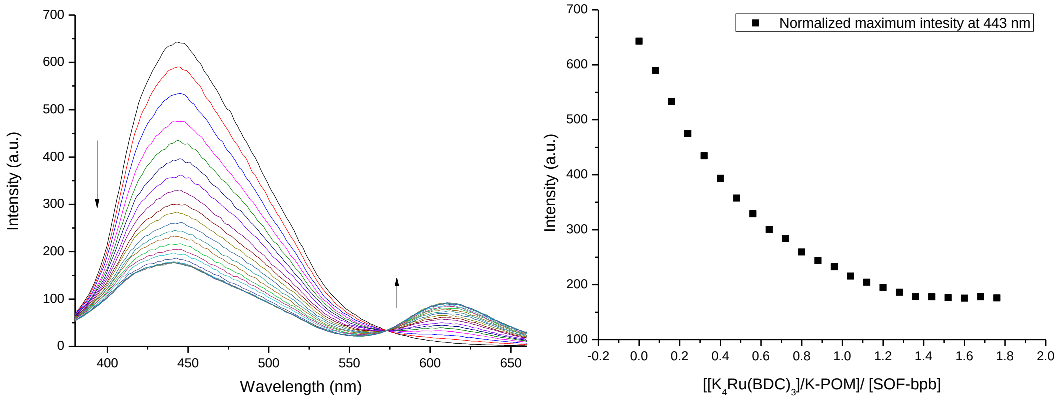


Fig. S12 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 μM) in **SOF-bpb** in water with the simultaneous addition of $K_4Ru(bdc)_3$ and K-POM (10:1) ([Ru^{2+}] = 0-17.6 μM).

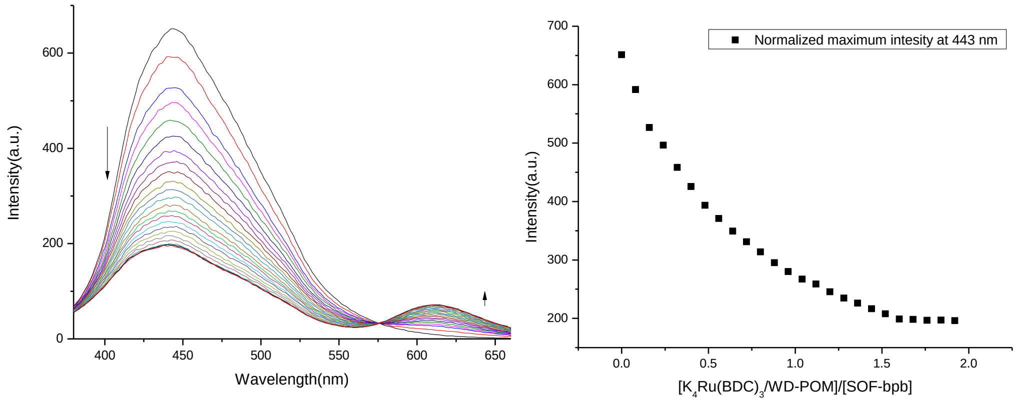


Fig. S13 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 µM) in **SOF-bpb** in water with the simultaneous addition of $K_4Ru(BDC)_3$ and WD-POM (10:1) ([Ru^{2+}] = 0-16.8 µM).

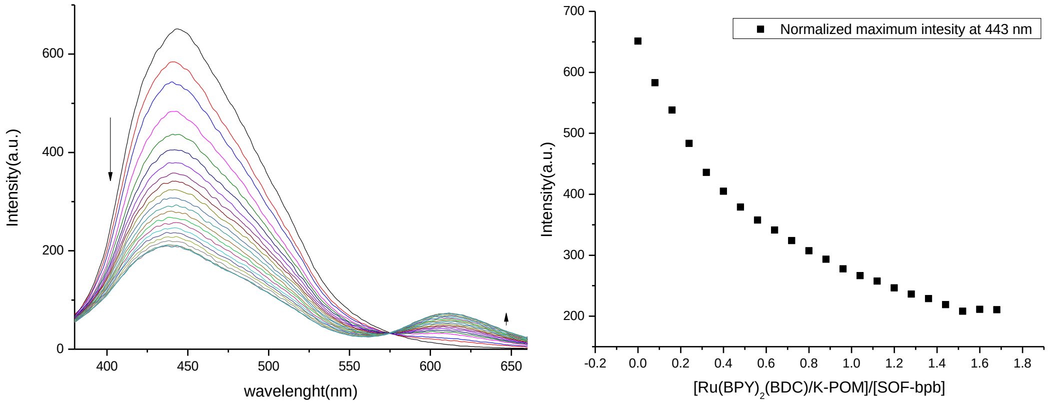


Fig. S14 Fluorescence quenching (λ_{ex} = 360 nm) of **M1** (10 µM) in **SOF-bpb** in water with the simultaneous addition of $Ru(bpy)_2(bdc)$ and K-POM (10:1) ([Ru^{2+}] = 0-16.8 µM).

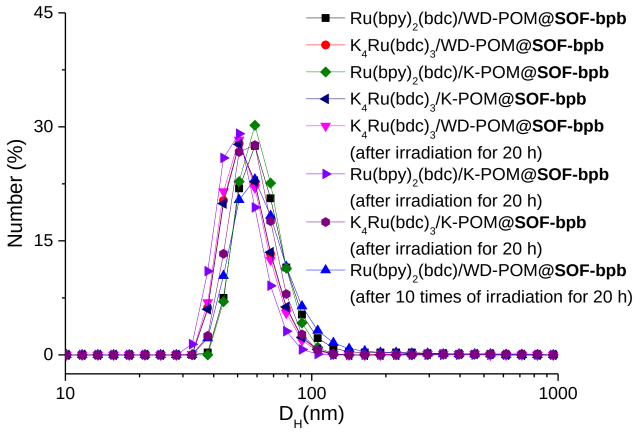


Fig. S15 DLS profiles of the solution of **SOF-bpb** (0.1 mM), the ruthenium complexes (20 µM) and POMs (2 µM) before and after irradiation for 20 h in dilute hydrochloride solution (pH = 1.8).

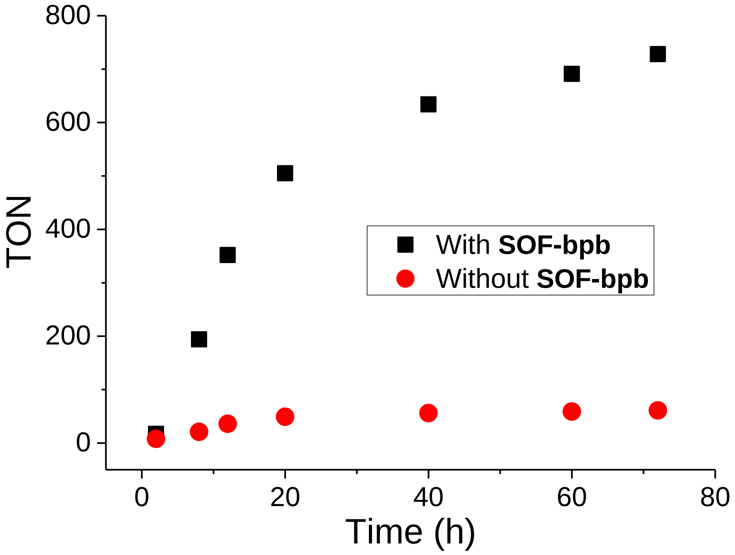


Fig. S16 TON values of the H_2 generation systems in water and methanol (4:1, v/v, pH = 1.8 with HCl) versus irradiation time in the presence and absence of **SOF-bpb** ([**M1**] = 0.1 mM). The reaction system contained $K_4[Ru(BDC)_3]$ (20 μM), WD-POM (2 μM).

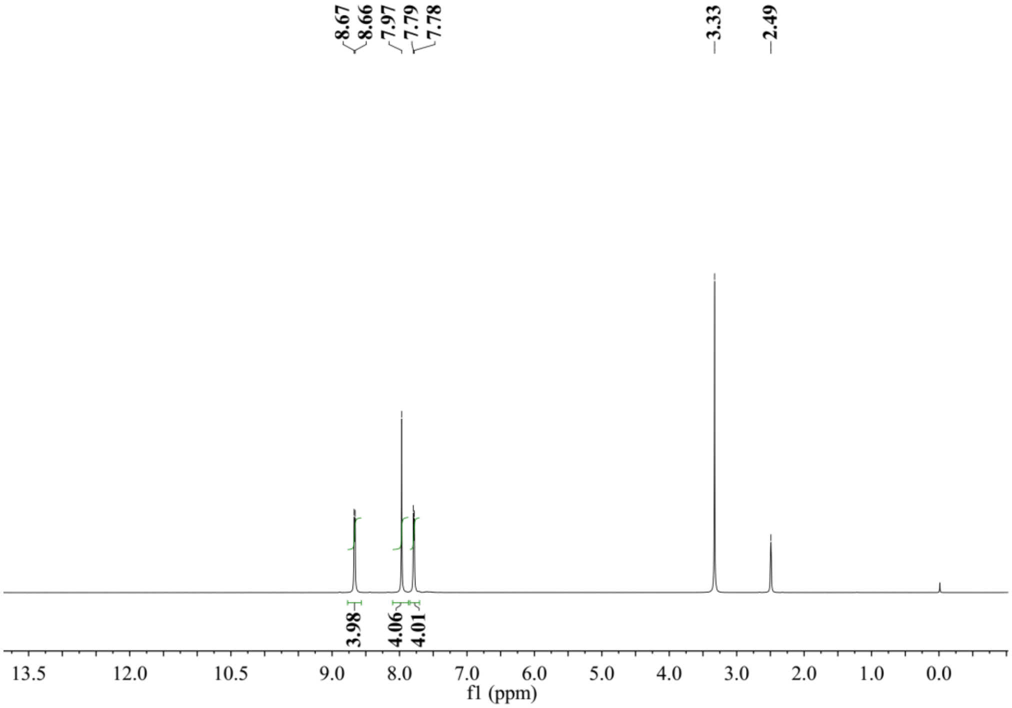


Fig. S17 ^1H NMR spectrum (400 MHz) of compound **2** in DMSO-d_6.

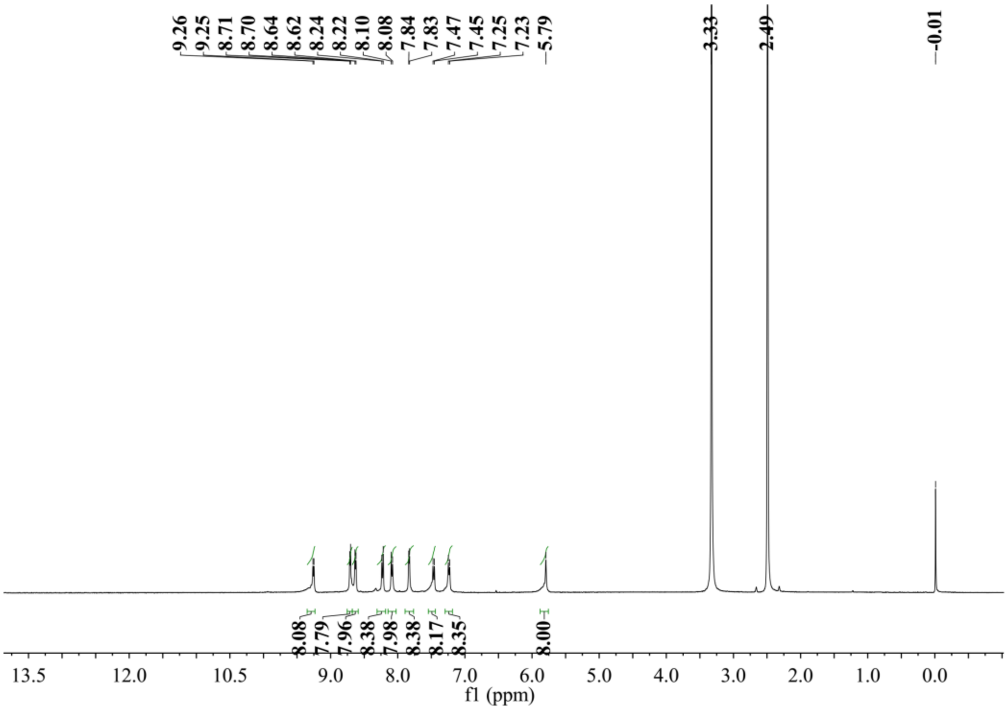


Fig. S18 ^{1}H NMR spectrum (400 MHz) of compound **3** in DMSO-d_6.

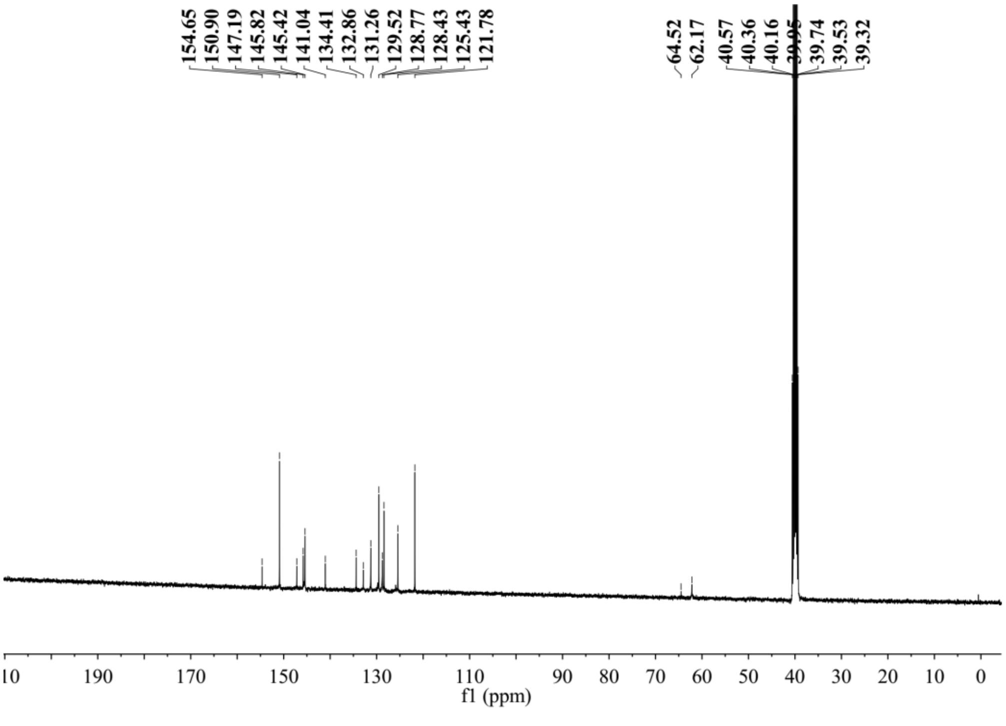


Fig. S19 ^{13}C NMR spectrum (100 MHz) of compound **3** in D_2O.

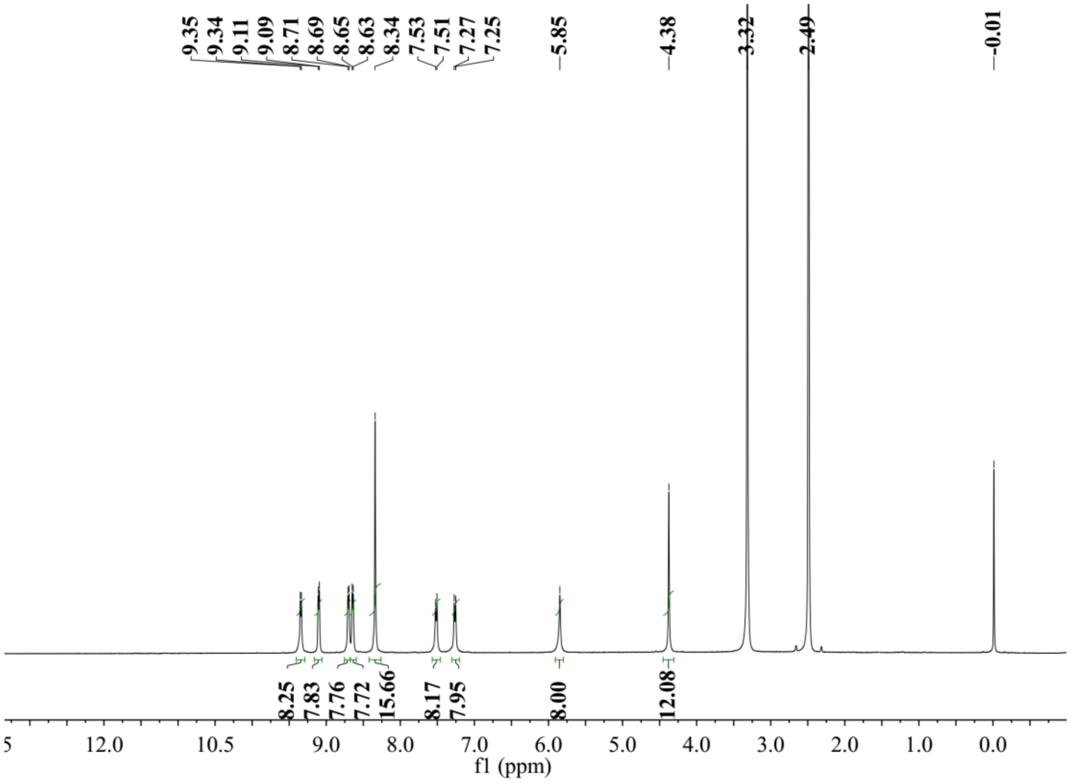


Fig. S20 ^{1}H NMR spectrum (400 MHz) of compound **M1** in DMSO-d_6.

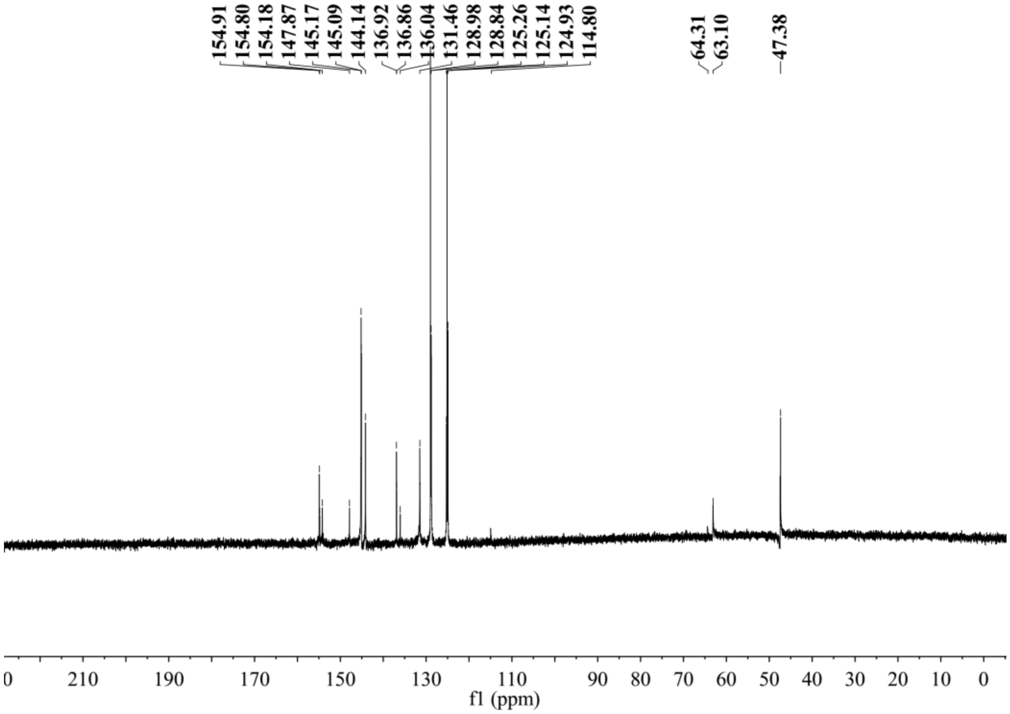


Fig. S21 ^{13}C NMR spectrum (100 MHz) of compound **M1** in D_2O.