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Room-Temperature Acetylene Hydration by a Hg(II)-laced Metal-Organic Framework

Ka-Kit Yee,[a] Yan-Lung Wong,[a] Meiqin Zha,[a] Ramesh Y. Adhikari,[b] Mark T. Tuominen,[b] Jun He,[c] and Zhengtao Xu*[,a]

[a] Department of Biology and Chemistry, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China.

[b] Department of Physics, University of Massachusetts, Amherst, Massachusetts 01003, USA.

[c] School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, Guangdong, China.

* Corresponding author.

Supporting Information

Experimental section

General Procedures. Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich, Merck and Acros) and used without further purification. Elemental analysis was performed with a Vario Micro CUBE CHN elemental analyzer. FT-IR spectra were obtained using a Nicolet Avatar 360 FT-IR spectrophotometer. Solution ^1H and ^{13}C NMR spectra were recorded on a 400 MHz

Bruker superconducting magnet high-field NMR spectrometer at room temperature, with tetramethylsilane (TMS) as the internal standard. Thermogravimetric analyses (TG) were carried out in a nitrogen stream using PerkinElmer Thermal analysis equipment (STA 6000) with a heating rate of 2°C/min. FT-Raman spectra were obtained using a FT-IR, NIR-FT-Raman Perkin–Elmer Spectrum 2000 instrument equipped with a diode pumped Nd:YAG laser PSU and using the standard Spectrum v2.0 software.

The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. Each sample was outgassed at 0.03 torr with a 2 °C/min ramp to 90 °C and held at 90 °C for 36 hours. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using N_2 at 77 K (P/P_0 range of 1×10^{-5} to 0.995).

Powder X-ray diffraction data for the Zr-based MOF samples were collected in the reflection mode at room temperature on an Inel Equinox 1000 X-ray diffractometer (Inel, France) equipped with CPS 180 detector using monochromated Cu-Kα (λ = 1.5406 Å) radiation. The X-ray tube operated at a voltage of 30 kV and a current of 30 mA.

Anaerobic synthesis of ZrDMBD. A 25-mL Schlenk tube loaded with H_2DMBD (95 mg, 0.41 mmol) was evacuated and refilled by N_2 (3 times). A DMF (dimethylformamide, 16 mL) solution of $ZrCl_4$ (96 mg, 0.41 mmol) and acetic acid (3936 mg, 65.6 mmol, 160 equivalents to $ZrCl_4$), degassed beforehand by a bubbling flow of N_2, was then transferred into the Schlenk tube via cannula under N_2 protection. The tube was capped tightly and placed in a pre-heated oven at 120 °C for 24 hours. After the solution was cooled to rt, the resultant precipitate was collected by centrifugation, washed in sequence by DMF (10 mL x 3) and dichloromethane (10 mL x 2), and dried in air. The as-made product thus obtained is a slightly yellow solid powder (160 mg, 81.5 % yield based on H_2DMBD), and is used immediately for the ensuing steps without prolonged exposure in air. Elemental CHN analysis found [C (28.59%), H (3.66%), N (3.67%)], calcd for $Zr_6O_4(OH)_4{\cdot}(C_8H_6O_4S_2)_6{\cdot}(DMF)_7{\cdot}(H_2O)_{18}$ calcd [C (28.73%), H (3.95%), N (3.40%)].

Oxidation of ZrDMBD to ZrBDSO$_3$H. A 100-mL round bottom flask was loaded with a magnetic stirring bar and an as-made ZrDMBD sample (160.0 mg, 0.056 mmol). While the flask was being cooled by an ice bath, a H_2O_2 aqueous solution (10 %; 80 mL; cooled by an ice bath beforehand) was added. After the reaction mixture was stirred at rt for 16 hours, the solid was isolated by centrifugation, washed by H_2O (e.g., 10 mL x 2) until no H_2O_2 was indicated by the KI starch paper in the water phase. The obtained solid was then further washed by ethanol (10 mL x 2), and air-dried overnight to give the $ZrBDSO_3H$ product as a white solid powder (143.4 mg, 0.041 mmol, yield: about 73 % based on the as-made ZrDMBD sample). Elemental CHN analysis found [C (17.20%), H (3.90%), N (0.13%)], calcd for $Zr_6O_4(OH)_4{\cdot}(C_8H_2O_4(SO_3H)_2)_6{\cdot}(DMF)_{0.7}{\cdot}(H_2O)_{47}$ (mw 3523): [C (17.08%), H (3.63%), N (0.28%)]. For solution ^1H NMR (400 MHz) measurement, the $ZrBDSO_3H$ solid was dissolved in a mixture of HF (37% in H_2O, 0.05 mL) and DMSO-d_6 (0.7 mL): δ 7.96 (s, 2H, ArH). ^{13}C NMR (80 MHz, DMSO-d_6): δ 129.10, 132.84, 145.14, 167.74 (consistent with data reported in *Polym. Mater. Sci. Eng.*, 2001, **84**, 601-602). The percentage of solvent content (water and DMF) from the formula $Zr_6O_4(OH)_4{\cdot}(C_8H_4O_4(SO_3H)_2)_6{\cdot}(DMF)_{0.7}{\cdot}(H_2O)_{47}$ was calculated to be 898/3523×100=25.5%, which is, by comparison, closely corresponding with the weight loss in second stage in the TGA plot (~25%; shown in Fig. S10). On the other hand, ZrO_2 content was equal to 739/3523×100 = 21.0% from $Zr_6O_4(OH)_4{\cdot}(C_8H_4O_4(SO_3H)_2)_6{\cdot}(DMF)_{0.7}{\cdot}(H_2O)_{47}$. The value match the percentage of residual weight in TGA (ZrO_2 content = 21%). From calculation, the elemental analysis and the TGA data, the ratio between $Zr_6O_4(OH)_4$ and organic linkers was found to be 1:6. For mass spectrometry analysis, the $ZrBDSO_3H$ solid was dissolved in a mixture of HF (37% in H_2O, 0.05 mL) and methanol (1.5 mL). Negative-ion ESI-MS ion cluster at m/z: 325.1 (calcd for $[C_8H_5O_4(SO_3H)_2]^-$, m/z: 324.9).

Gas sorption of $ZrBDSO_3H$ sample. The porosity and surface area analysis was performed using a Quantachrome AutosorbiQ gas sorption analyzer. The sample was activated by Soxhlet extraction in methanol, outgassed at 0.03 torr with a 2 °C/min ramp to 90 °C and held at 90 °C for 11 hours. The sample was then held at vacuum until the analysis was run. Pore analysis was performed using N_2 at 77 K (P/P_0 range of 1×10^{-5} to 0.995) on the $ZrBDSO_3H$ sample revealed highly reproducible typical type-I gas adsorption isotherms (N_2 gas, 77 K, Fig. S11) with a Brunauer–Emmett–Teller (BET) surface area of 285.05 m^2/g.

Pore analysis of the activated $ZrBDSO_3H$ sample was performed both using CO_2 at 273 K (P range of 8×10^{-3} to 780 mmHg). Initial data analysis was done using the AS1Win and QuadraWin 5.05 software (both of Quantachrome instruments). DFT analysis on pore size distribution and pore volume (Fig. S12) of the CO_2 adsorption isotherms (273 K) indicated an average pore width of 0.524 nm and a modest micropore volume of 0.196 cm^3/g.

Preparation of ZrDMBD-Hg from ZrDMBD and $HgCl_2$. An as-made powder sample (light yellow) of ZrDMBD (160.0 mg, 0.056 mmol) and an aqueous solution (80.0 mL) of $HgCl_2$ (2.455 g, 9.06 mmol) were stirred at rt for 48 hours. The solid was then isolated by centrifugation and further washed with methanol (until no Hg^{2+} was indicated by NaSH in the methanol phase) to give the product of ZrDMBD-Hg as a solid powder with a darker yellow color (205 mg, 0.055 mmol, yield: about 98 % based on the as-made ZrDMBD sample). The weight percentage of Hg in the solid sample was found to be 21.40% using diphenylthiocarbazone extraction method (e.g., see Fig. S13 below)[1] while EDX indicated the ratio between Hg and Cl was 1:1.6. Elemental CHN analysis found [C (18.29%), H (2.25%), N (1.25%)], calcd for $Zr_6O_4(OH)_4{\cdot}(C_8H_2O_4(S^-)_{0.66}(SH)_{1.33})_6{\cdot}Hg_4{\cdot}Cl_{6.4}{\cdot}(DMF)_3{\cdot}(H_2O)_{26}$ (mw 3708): [C (18.46%), H (2.47%), N (1.13%), Hg (21.64%)].

Oxidation of ZrDMBD-Hg to $ZrBDSO_3$-Hg. A 100-mL round bottom flask was loaded with a magnetic stirring bar and a ZrDMBD-Hg sample (204.5 mg, 0.055 mmol). While the flask was being cooled by an ice bath, a H_2O_2 aqueous solution (10 %; 118 mL; cooled by an ice bath beforehand) was added. After the reaction mixture was stirred at rt for 16 hours, the solid was isolated by centrifugation, washed by H_2O (e.g., 10 mL x 2) until no H_2O_2 was indicated by the KI starch paper in the water phase. The obtained solid was then further washed by ethanol (10 mL x 2), and air-dried overnight to give the ZrBDSO$_3$-Hg as a white solid powder (210.7 mg). The weight percentage of Hg in the solid sample was found to be 11.8% using diphenylthiocarbazone extraction method. Elemental CHN analysis found [C (14.61%), H (3.03%), N (0.06%)], calcd for $Zr_6O_4(OH)_4\cdot(C_8H_2O_4(SO_3^-)_{0.8}(SO_3H)_{1.2})_6\cdot Hg_{2.4}\cdot(H_2O)_{50}$ (mw 4007): [C (14.39%), H (3.22%), Hg (12.01%)]. For solution NMR measurements, the ZrBDSO$_3$-Hg solid was dissolved in a mixture of HF (37% in H$_2$O, 0.05 mL) and DMSO-*d$_6$* (0.7 mL). ^{1}H NMR (400 MHz): δ 7.99 (s, 2H, ArH). ^{13}C NMR (80 MHz): δ 128.71, 133.03, 144.89, and 168.07.

Oxidation of ZrDMBD-Hg with a H_2O_2 solution containing saturated $Hg(NO_3)_2\cdot H_2O$ to suppress the Hg leaching during the oxidation process. In a 7.5 mL glass, 0.1% HNO$_3$ (2.5 mL, 0.040 mmol), $Hg(NO_3)_2\cdot H_2O$ (30 mg, 0.086 mmol) and 30% H_2O_2 aqueous solution (2 mL, 17.6 mmol) were added. Upon addition of 30% H_2O_2 solution, white solid was formed and this solution was passed through a syringe filter to obtain a clear solution. A ZrDMBD-Hg sample (10.0 mg, 0.0027 mmol) was added to this solution. After the reaction mixture was stirred at rt for 16 hours, the solid was isolated by centrifugation, washed by 0.1% HNO$_3$ (1.5 mL x 3) and H_2O (e.g., 1.5 mL x 2) until no H_2O_2 was indicated by the KI starch paper in the water phase. The obtained solid was then further washed by ethanol (1.5 mL x 3), dichloromethane (1.5 mL x 3), and air-dried overnight to give the light yellow solid. The weight percentage of Hg in the solid sample was found to be 20.4% using diphenylthiocarbazone extraction method.

Ion exchange tests of $ZrBDSO_3H$ with saturated $Hg(NO_3)_2 \cdot H_2O$ in 0.1% HNO_3 water solution. A $ZrBDSO_3H$ sample (5 mg) was stirred with 0.1% HNO_3 aqueous solution (0.079 mmol HNO_3, 5 mL) of $Hg(NO_3)_2 \cdot H_2O$ (60 mg, 0.175 mmol, 1.2 % w/w) at 70°C for 18 hrs. The resultant white solid was collected by centrifugation and washed with 0.1% HNO_3 aqueous solution (1.5 mL x 3), ethanol (1.5 mL x 3) and dichloromethane (1.5 mL x 3). The solid sample was dried in air and the weight percentage of Hg in the solid sample was found to be 2.8% using diphenylthiocarbazone extraction method.

Ion exchange tests of $ZrBDSO_3H$ with saturated $HgCl_2$ water solution. A $ZrBDSO_3H$ sample (5 mg) was stirred with aqueous solution (5 mL) of $HgCl_2$ (50 mg, 0.184 mmol, 1.0 % w/w) at 70°C for 18 hours. The resultant white solid was collected by centrifugation and washed with water (1.5 mL x 3), ethanol (1.5 mL x 3) and dichloromethane (1.5 mL x 3). The solid sample was dried in air and the weight percentage of Hg in the solid sample was found to be 3.0% using diphenylthiocarbazone extraction method.

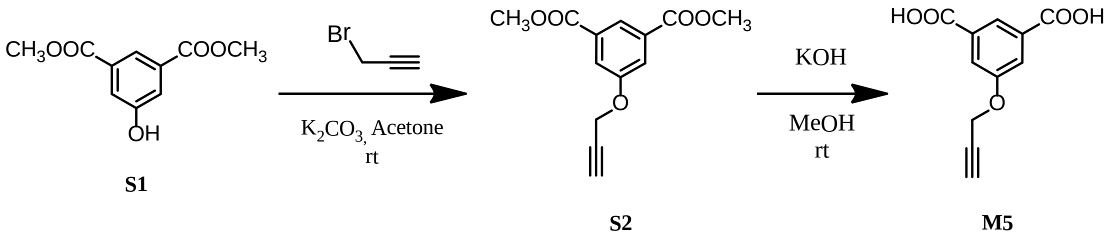
Size selective thiol seperation using ZrBDSO$_3$-Hg. Ethane-1,2-dithiol (**M1**, 0.75 mg, 0.008 mmol), 4-methoxybenzenethiol (**M2**, 1.12 mg, 0.008 mmol), naphthalene-2-thiol (**M3**, 1.28 mg, 0.008 mmol) and phenylmethanethiol (**M4**, 1.00 mg, 0.008 mmol) were dissolved in dichloromethane-*d₂* (CD_2Cl_2, 0.6 mL) in a Schlenk tube and tetramethylsilane was added as an internal standard. ZrBDSO$_3$-Hg (105 mg, 11.8 wt% of Hg, 0.062 mmol of Hg) was added to the tube. The tube was sealed then placed at rt for 12 hours. ^{1}H NMR spectra were measured at 0 hour, 3 hours and 12 hours. The region containing signals contributed from **M1** was absent after 12 hours suggesting the complete removal of that **M1** in the solution while the larger, **M2**, **M3** and **M4** remained unchanged in concentrations.

2-Mercaptoethanol removal using ZrBDSO$_3$-Hg. 2-Mercaptoethanol ($HOCH_2CH_2SH$; 0.62 mg, 0.008 mmol) was added in dichloromethane-d_2 (CD_2Cl_2, 0.6 mL) in a Schlenk tube and tetramethylsilane was added as an internal standard. ZrBDSO$_3$-Hg (27 mg, 11.8 wt% of Hg, 0.016 mmol of Hg) was added to the tube. The tube was sealed then placed at rt for 6 hours. ^{1}H NMR spectra were measured at 0 hour and 6 hours. The region containing signals contributed from 2-mercaptoethanol was absent after 6 hours suggesting the complete removal of 2-mercaptoethanol from the solution (see Figure S7).

Catalytic hydration of acetylene using ZrBDSO$_3$-Hg solid. A 1000-mL Schlenk flask was first filled with acetylene gas, and then the ZrBDSO$_3$-Hg solid (100 mg, 11.8 wt % of Hg, 0.059 mmol of Hg), H_2O (2.7 mL) and a stirring bar were loaded into the tube under acetylene gas flow protection. The flask was sealed and the mixture was stirred at rt for 7.5 hours; afterwards, the solid catalyst of ZrBDSO$_3$-Hg was removed by centrifugation. To determine the concentrations of the hydration products (i.e., acetaldehyde and ethane-1,1-diol) in the supernatant, an aliquot (the weight measured) was added to D_2O (0.5 mL) for quantification by solution ^{1}H NMR measurement, using potassium acetate (e.g., 2.93 mg, 0.0299 mmol) as the internal standard (see Fig. 3 for a representative NMR spectrum).

Catalytic hydration of acetylene using a $HgSO_4$/H_2SO_4 solution. A similar procedure was applied as above, with a solution of $HgSO_4$ (18.2 mg, 0.061 mmol) in 18 % H_2SO_4 (2.7 mL) being stirred at rt for 7.5 hours in a 1000-mL Schlenk flask filled with acetylene gas. The hydration products were quantified by solution ^{1}H NMR as described above.

General procedure of reactivation of ZrBDSO$_3$-Hg solid. For the subsequent cycles of catalysis tests, the recovered ZrBDSO$_3$-Hg solid was activated (i.e., to convert the reduced Hg specie--formed in the previous cycle--into Hg^{2+}) by immersion in a mixture of a 30% H_2O_2 (0.1 mL, 0.88 mmol) solution and a HNO_3 (0.1%, 2.5 mL, 0.040 mmol) solution containing $Hg(NO_3)_2 \cdot H_2O$ (30 mg, 0.088 mmol) at rt for 15 minutes. The solid catalysts were collected by centrifugation and washed with 0.1% HNO_3 aqueous solution (1.5 mL x 3), ethanol (1.5 mL x 3) and dichloromethane (1.5 mL x 3) before being reused in the next catalytic cycle. Prior to each catalytic cycle, the mercury content in the solid catalyst thus recovered was also determined by diphenylthiocarbazone extraction method.



Scheme S1. Synthetic procedures of 5-Prop-2-ynyloxy-isophthalic acid (**M5**)

Synthesis of 5-prop-2-ynyloxy-isophthalic acid dimethyl ester (S2). 5-Hydroxy-isophthalic acid dimethyl ester (**S1**, 200.0 mg, 0.952 mmol) and 15 mL anhydrous acetone were loaded into a 50 mL two-necked round-bottom flask charged with a magnetic stirring bar. The mixture was bubbled by N_2 for 10 minutes, and then K_2CO_3 (287.9 mg, 2.086 mmol), KI (16.6 mg, 0.100 mmol) were added into the reaction mixture which was bubbled by N_2 for another 10 minutes. The acetone solution of 3-bromo-propyne (163.5 mg, 1.374 mmol, diluted in 5mL acetone) was degassed and injected via cannula under N_2 protection. The flask was then sealed and stirred at rt for 6 hours. The solvents were removed in vacuo after the reaction was completed, and the white residue was purified by a silica gel plug (silica gel, with 1:2 hexane/dichloromethane as the eluent) to provide a white crystalline solid (215.0 mg, yield 91.0% based on 5-hydroxy-isophthalic acid dimethyl ester). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (t, 1H, CHAr), 7.83 (d, 2H, CHAr), 4.78 (d, 2H, OCH_2), 3.94 (s, 6H, $COOCH_3$), 2.55 (s, 1H, CCH).

Synthesis of 5-prop-2-ynyloxy-isophthalic acid (M5). A suspension of dimethyl 5-prop-2-ynyloxy-isophthalic acid dimethyl ester (**S2**, 215.0 mg, 0.866 mmol) in KOH CH_3OH solution (3 M, 3 mL) was stirred at rt overnight in a 10-mL round-bottom flask charged with a magnetic stirring bar. After that, the reaction mixture was poured into 20 mL of water, and 10% HCl(aq) was then added slowly upon vigorous stirring. After the pH value of the mixture became lower than 2, the precipitate was collected by suction filtration and washed with water extensively (185.6 mg, yield 97.3% based dimethyl 5-prop-2-ynyloxy-isophthalic acid dimethyl ester). ^{1}H NMR (400 MHz, DMSO-d_6): δ8.11 (t, 1H, CHAr), 7.71 (s, 2H, CHAr), 4.95 (d, 2H, OCH_2), 3.64 (t, 1H, CCH). ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.35, 157.35, 132.68, 122.94, 119.63, 79.00, 78.71, 55.98.

Hydration of 5-prop-2-ynyloxy-isophthalic acid (M5) using ZrBDSO$_3$-Hg solid. ZrBDSO$_3$-Hg (17.2 mg, 11.8 wt % of Hg, 0.010 mmol of Hg), **M5** (18.0 mg, 0.082 mmol) and THF/H_2O (1 mL, 2:1, v/v) were loaded to a 7.5-mL glass vial. The vial was sealed by a cap and the mixture was stirred at rt for 7.5 hours. TLC monitoring showed no reaction after 7.5 hours (see also NMR spectrum B of S8). The solid catalyst of ZrBDSO$_3$-Hg was removed by centrifugation. A drop of supernatant was added to 0.5 mL DMSO-d_6 for solution ^1H NMR measurement.

Hydration of 5-prop-2-ynyloxy-isophthalic acid (M5) using $HgSO_4/H_2SO_4$ solution. $HgSO_4$ (3.1 mg, 0.010 mmol of Hg), **M5** (18.0 mg, 0.082 mmol) and THF/18% H_2SO_4 (1 mL, 2:1, v/v) were loaded to a 7.5-mL glass vial. The vial was sealed by a cap and the mixture was stirred at rt for 7.5 hours. TLC monitoring showed the reaction was completed after 7.5 hours. A drop of supernatant was added to 0.5 mL DMSO-d_6 for solution ^1H NMR measurement. Solution ^1H NMR spectrum indicated all the starting material was converted to 5-(2-oxo-propoxy)-isophthalic acid (spectrum C in Fig. S8). The solvents in the crude reaction mixture were removed in vacuo. The obtained white solid was washed by H_2O (1.5 mL x 3) and dried in air to provide a white solid product as 5-(2-oxo-propoxy)-isophthalic acid (18.5 mg, yield 94.7% based on 5-prop-2-ynyloxy-isophthalic acid). ^{1}H NMR (400 MHz, DMSO-d_6; spectrum D in Fig. S8): δ 8.08 (s, 1H, CHAr), 7.60 (s, 2H, CHAr), 5.00 (s, 2H, OCH_2), 2.17 (s, 3H, $COCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 203.68, 166.39, 158.07, 132.66, 122.67, 119.25, 72.444, 26.28.

Hydration of acetylene using ZrBDSO$_3$H solid. A 250-mL two neck flask was first filled with acetylene gas, and then the ZrBDSO$_3$H solid (25 mg), H_2O (0.675 mL) and a stirring bar were loaded into the flask under acetylene gas flow protection. The flask was sealed and the mixture was stirred at rt for 7.5 hours; afterwards, the solid catalyst of ZrBDSO$_3$H was removed by centrifugation. No hydration product can be detected in the supernatant as indicated from solution ^{1}H NMR measurement (Figure S14).

Hydration of acetylene using ZrDMBD-Hg solid. A 250-mL two neck flask was first filled with acetylene gas, and then the ZrDMBD-Hg solid (25 mg), H_2O (0.675 mL) and a stirring bar were loaded into the flask under acetylene gas flow protection. The flask was sealed and the mixture was stirred at rt for 7.5 hours; afterwards, the solid catalyst of ZrDMBD-Hg was removed by centrifugation. No hydration product can be detected in the supernatant as indicated from solution ^{1}H NMR measurement (Figure S14).

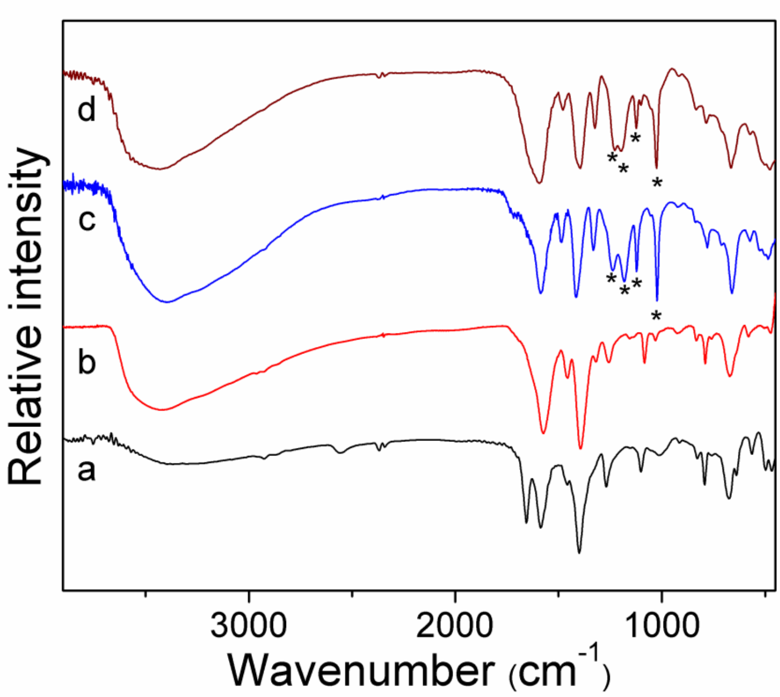


Fig. S1 IR spectra of (a) an as-made sample of ZrDMBD; (b) a sample of ZrDMBD-Hg; (c) a sample of ZrBDSO$_3$H; and (d) a sample of ZrBDSO$_3$-Hg. The asterisked peaks are ascribed to the sulfonate group.

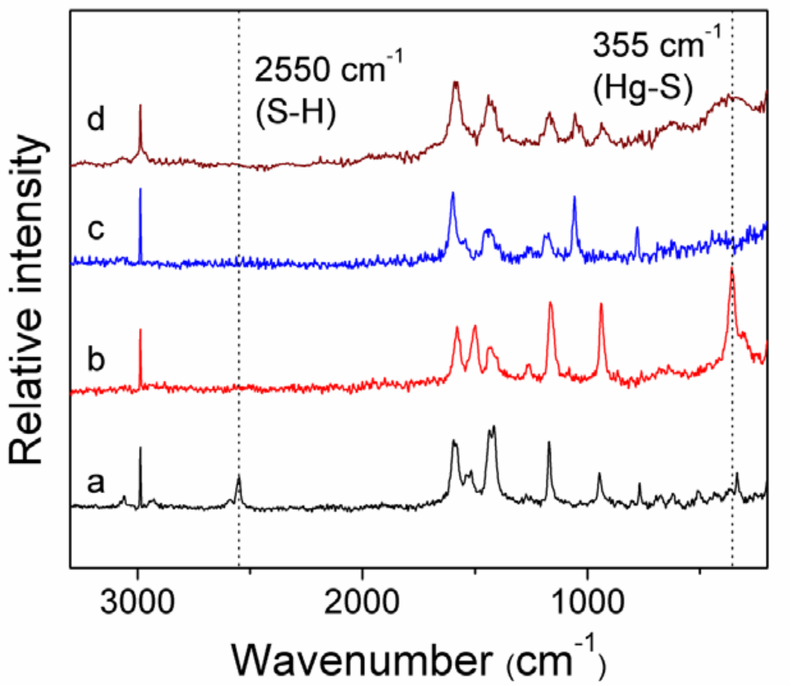


Fig. S2 Raman spectra of (a) an as-made sample of ZrDMBD; (b) a sample of ZrDMBD-Hg; (c) a sample of $ZrBDSO_3H$; and (d) a sample of $ZrBDSO_3$-Hg.

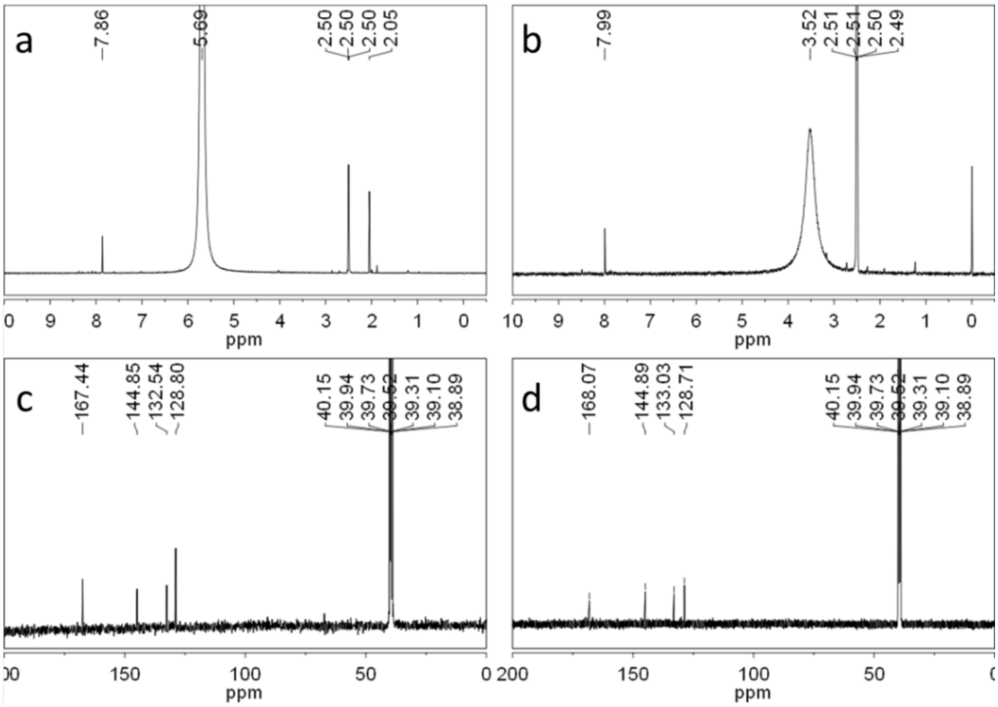


Fig. S3 ^1H NMR spectra of (a) a sample of $ZrBDSO_3H$; and (b) a sample of $ZrBDSO_3$-Hg; ^{13}C NMR spectra of (c) a sample of $ZrBDSO_3H$; and (d) a sample of $ZrBDSO_3$-Hg. Both samples were dissolved in a mixture of HF (37% in H_2O, 0.05 mL) and DMSO-d_6 (0.7 mL) for solution ^1H NMR measurement.

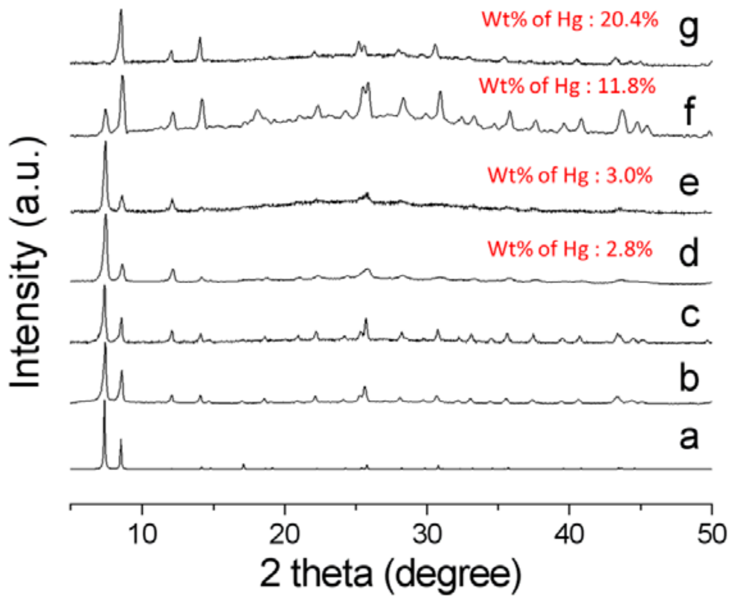


Fig. S4 Powder X-ray patterns of (a) a simulation from a structure model of Zr-DMBD; (b) an as-made sample of Zr-DMBD; (c) a sample of $ZBDSO_3H$; (d) a sample of $ZBDSO_3H$ after ion exchange with $Hg(NO_3)_2 \cdot H_2O$ in 0.1% $HNO_3(aq)$ and (e) a sample of $ZBDSO_3H$ after ion exchange with $HgCl_2$ in water; (f) $ZBDSO_3$-Hg and (g) ZrDMBD-Hg after oxidation with $Hg(NO_3)_2.H_2O/HNO_3/H_2O_2$ solution.

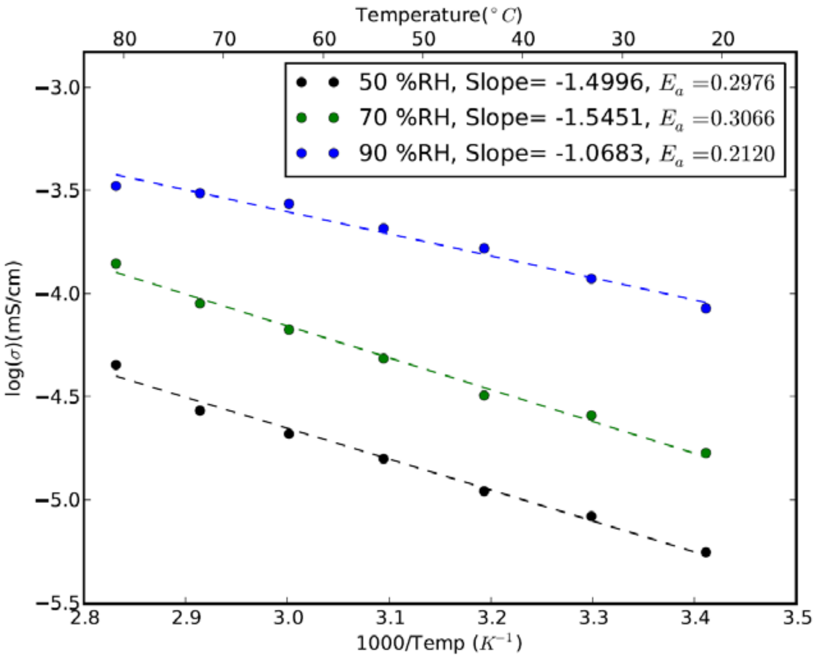


Fig. S5 Arrhenius plot of (temperature dependence of) the proton conductivity of a powder sample of $ZrBDSO_3H$ at various relative humidities (RH).

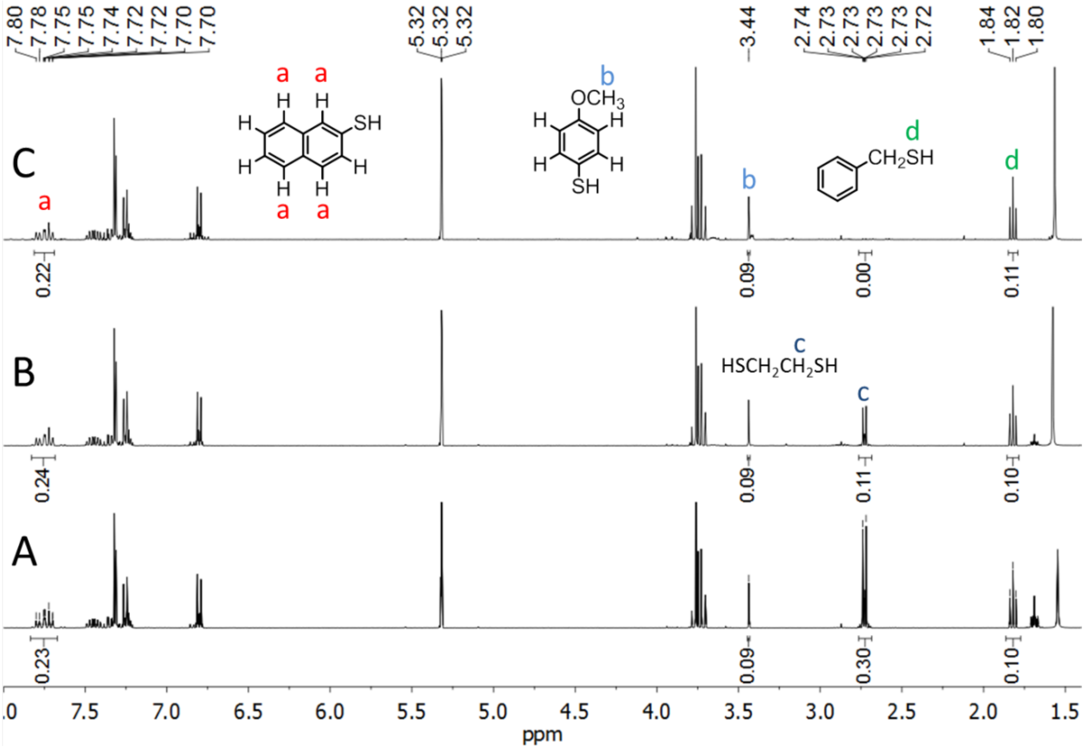


Fig. S6 ^{1}H NMR spectra recorded in situ for the thiol solution after ZrBDSO$_3$-Hg was added for (A) 0 hour, (B) 3 hours, and (C) 12 hours.

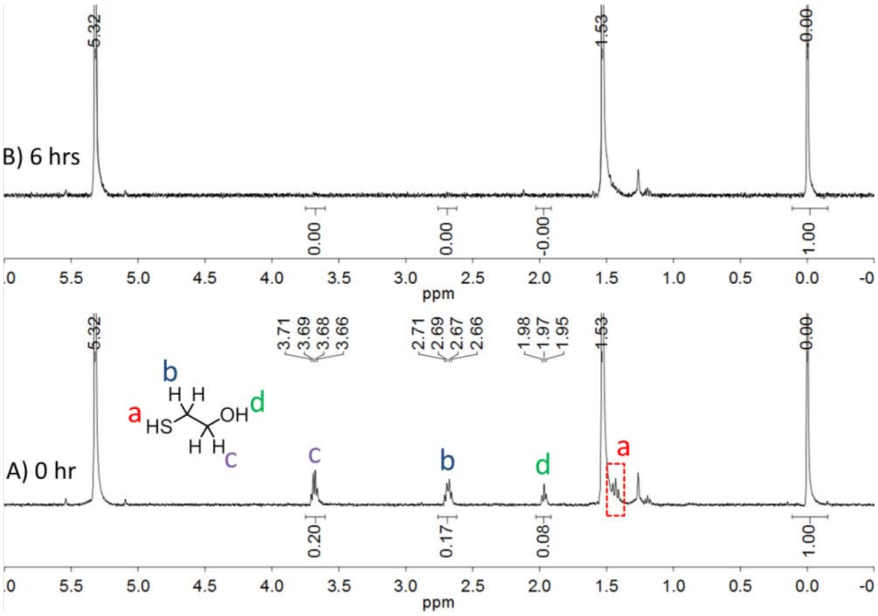


Fig. S7 ^{1}H NMR spectra recorded in situ for a CD_2Cl_2 solution of 2-mercaptoethanol after ZrBDSO$_3$-Hg was added for (A) 0 hour and (B) 6 hours.

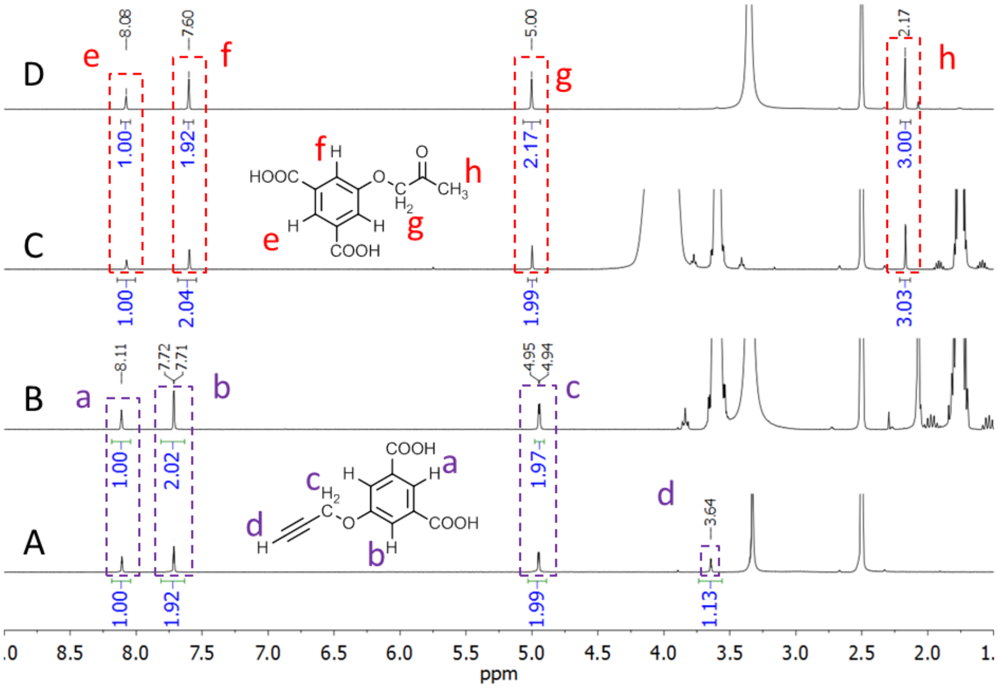


Fig. S8 Solution ^{1}H NMR spectra of (A) **M5**; the reaction supernatant of hydration of **M5** by using (B) ZrBDSO$_3$-Hg and (C) HgSO$_4$/H$_2$SO$_4$ at rt for 7.5 hours; and (D) the hydration product of **M5**. Both of the samples were dissolved in DMSO-d_6.

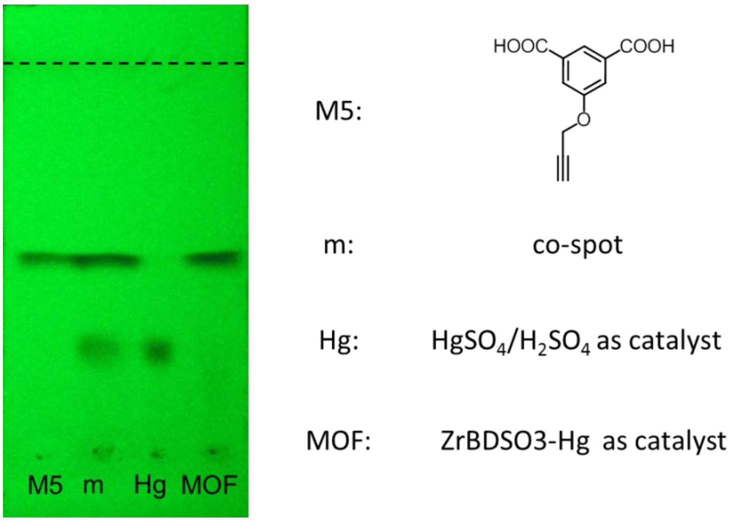


Fig. S9 A photograph (taken under a UV lamp) of the TLC plate for monitoring the hydration reaction of **M5** using two different catalysts: heterogeneous catalyst of ZrBDSO$_3$-Hg (marked as MOF in this TLC test) and homogeneous catalyst of HgSO$_4$/H$_2$SO$_4$ solutions (marked as Hg). The TLC plate was developed by 2:1 THF/*n*-hexane.

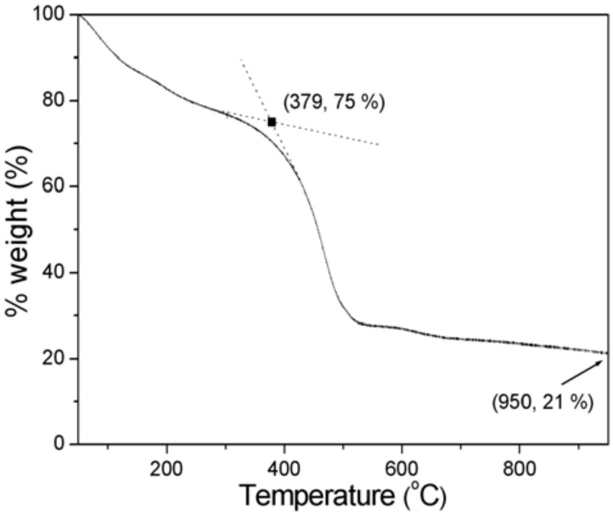


Fig. S10 Thermogravimetric analysis (TGA) of a sample of $ZrBDSO_3H$.

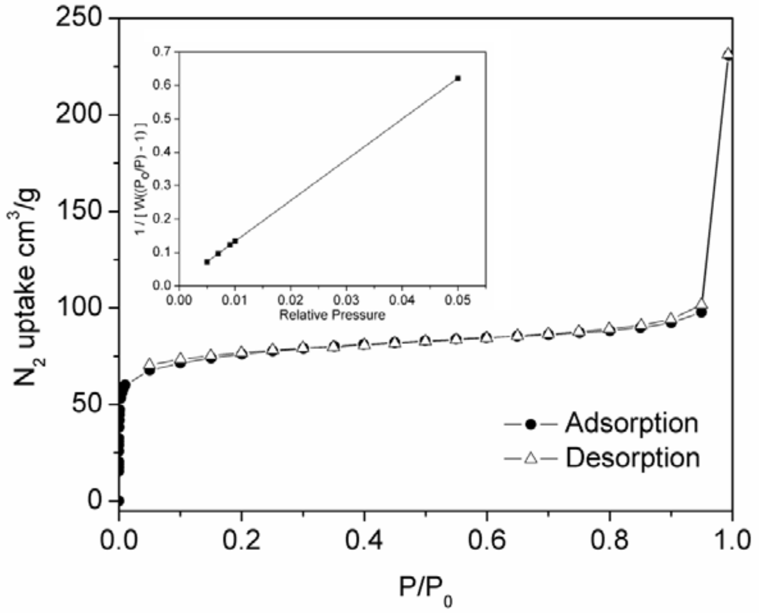


Fig. S11 $\mathbf{N_2}$ sorption isotherm at 77 K for an activated smaple of $ZrBDSO_3H$ (67.2 mg, activated by evacuating at 90 °C for 11 hours). Inset: the BET isotherm.

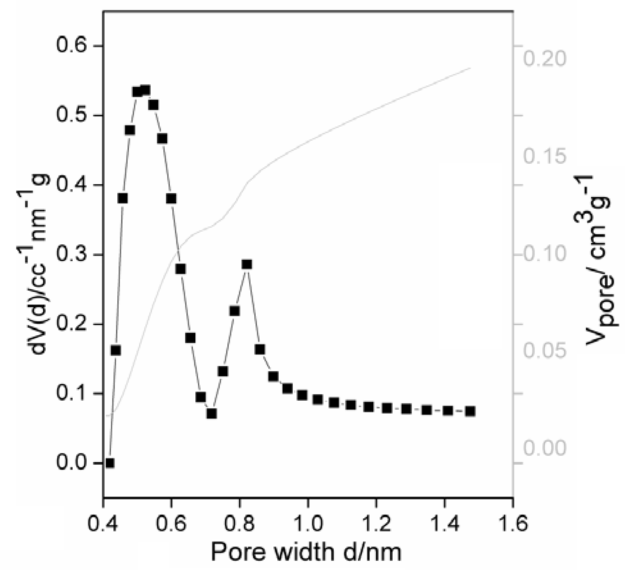


Fig. S12 Pore size distribution and Pore volume of an activated sample of $ZrBDSO_3H$ (CO_2 gas at 273 K; DFT model).

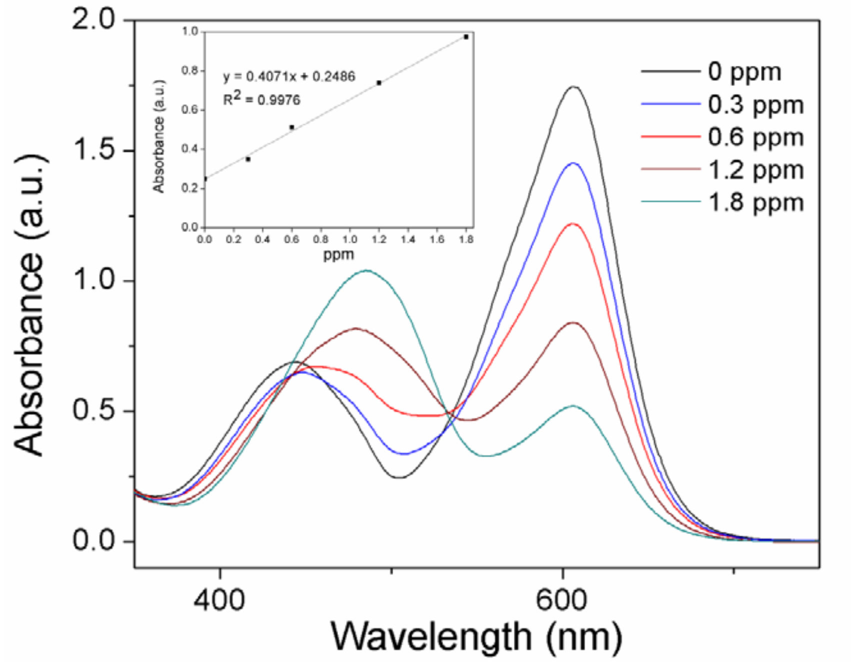


Fig. S13 UV-Visible absorption spectra of Hg(II)-diphenylthiocarbazone complex in $CHCl_3$ at different concentrations. The related Hg(II) concentration was shown at the top right hand corner. Inset: the dynamic range of Hg(II) concentration which produced linear response at 490 nm (R= 0.998).

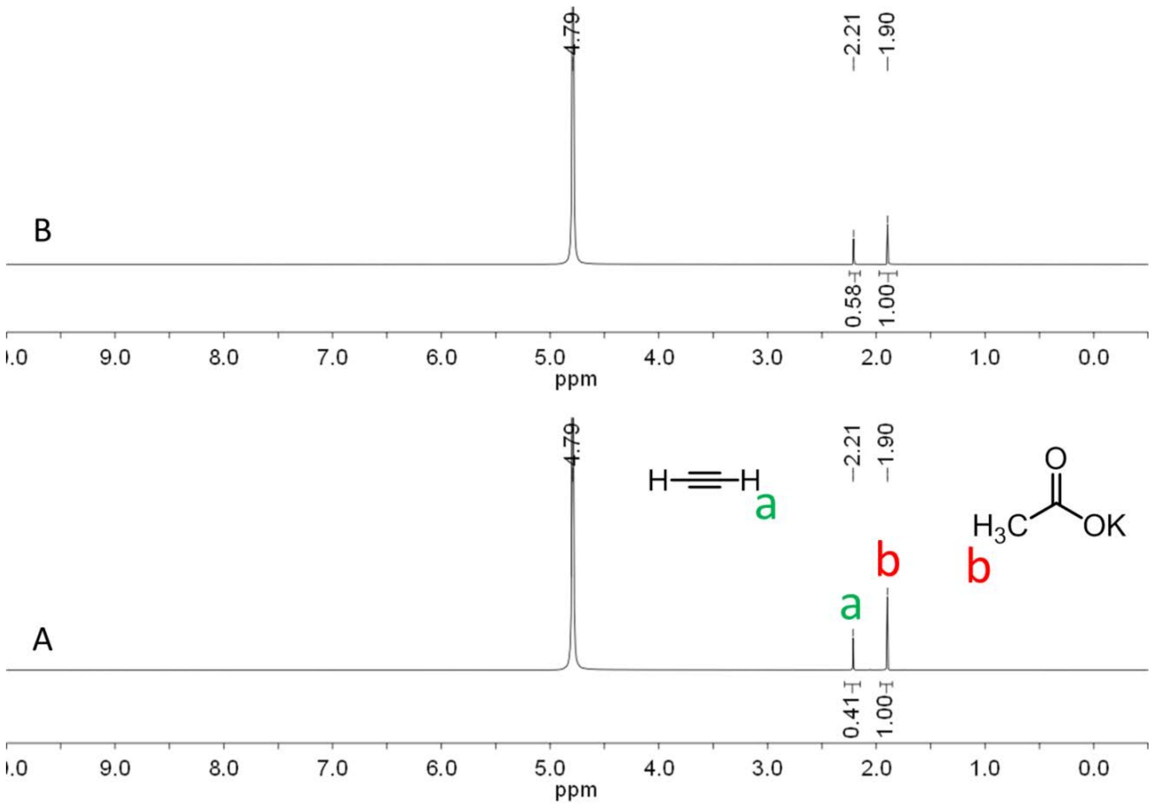


Fig. S14 ^{1}H NMR spectra of the supernatants of acetylene hydration reactions (dissolved in D_2O with CH_3COOK added as an internal standard) catalyzed by (A) $ZrBDSO_3H$ and (B) ZrDMBD-Hg. Neither spectra show any hydration products in the supernatants.

Reference

1. C. T. Elly, *Dithizone Procedure for Mercury Analysis*, Water Pollution Control Federation, 1973.