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Five Metal-Organic Frameworks with Different Topologies Based on anthracene functionality tetracarboxylate acid: Syntheses, Structures, and Properties.

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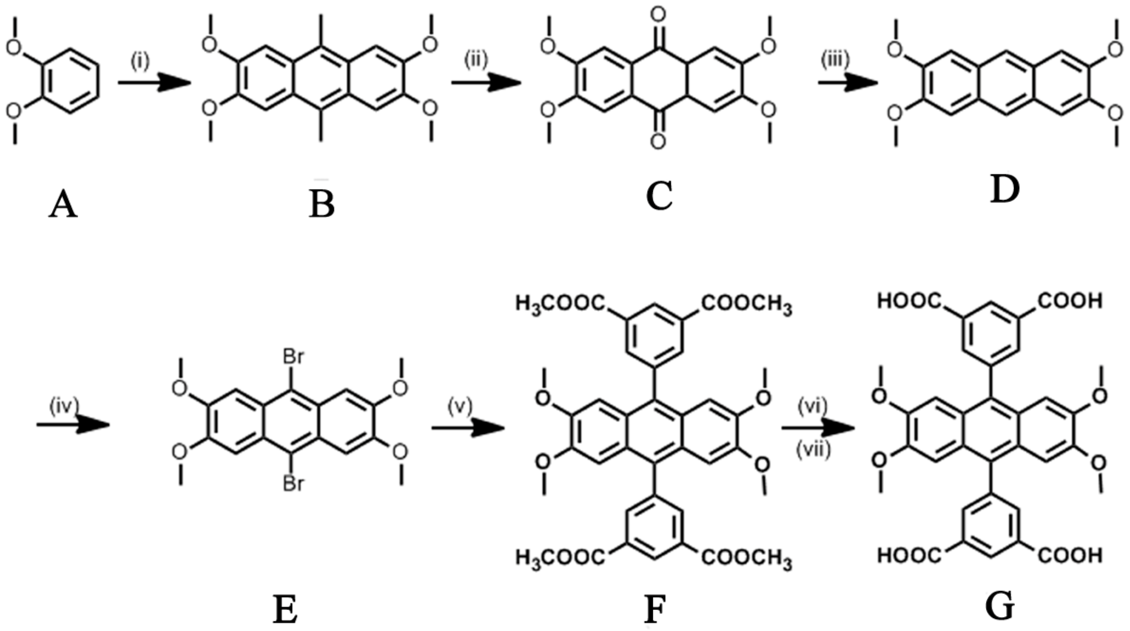
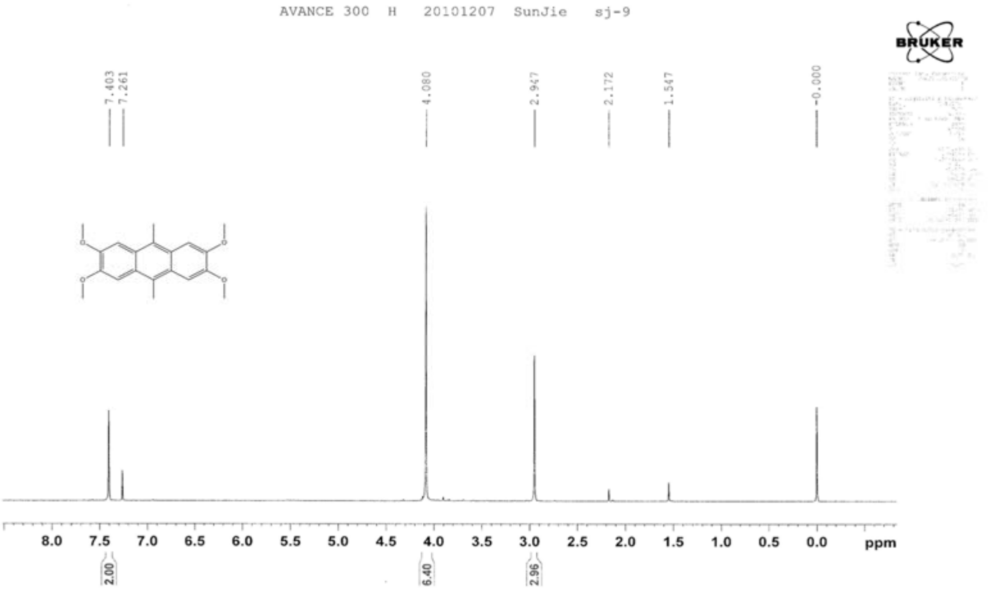
Content

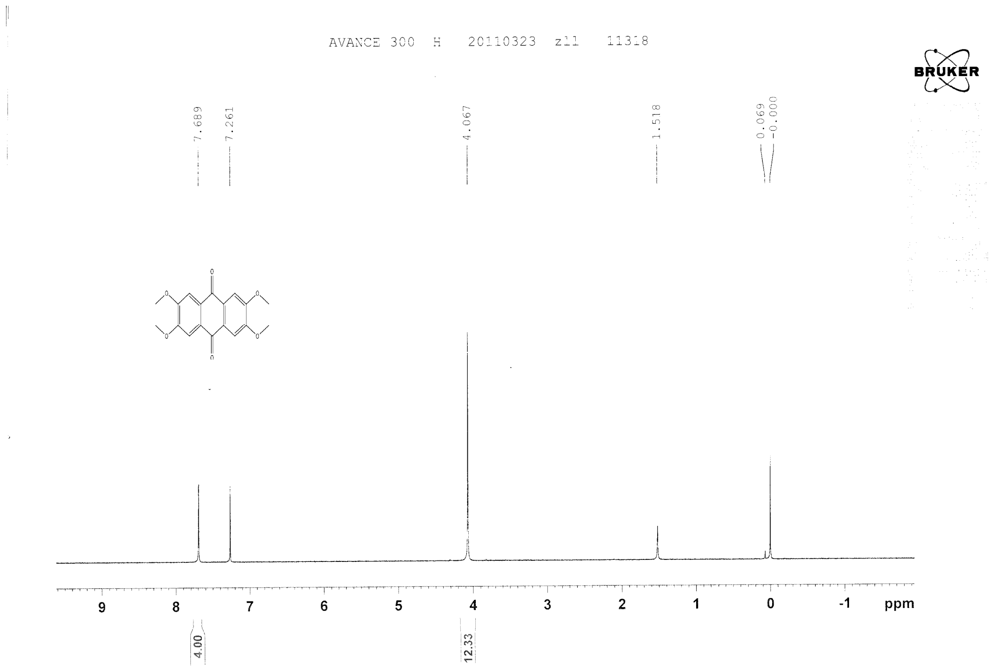
(1) Synthesis of H_4L^{OMe}



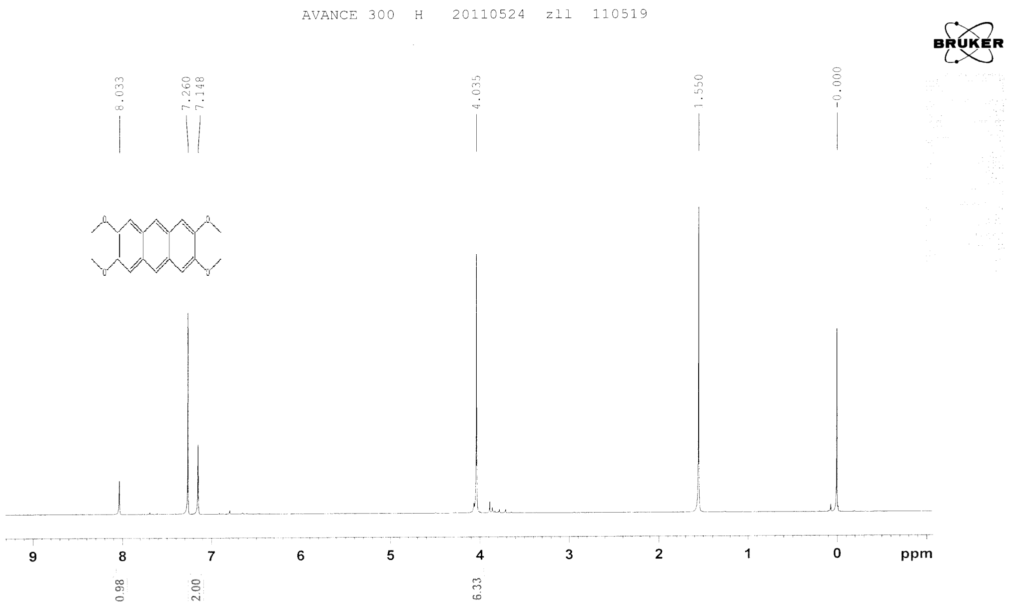
Synthesis of B: To a cooled solution (0 °C) of veratrole (**A**) (32 mL,250 mmol) in acetic acid (125 mL) was slowly added ice-cold solution of acetaldehyde (21 mL,375 mmol) in methanol (20 mL).The resulting mixture was then stirred for 1h and concentrated H_2SO_4 (95 %, 125 mL) was added dropwise over 2h. The reaction mixture was then stirred at 0 °C for 20h,and poured onto ice-water which precipitated the product out as beige solid and collected by vacuum filtration. The product washed with water and dried. It was further-purified by column chromatography (silica, $CHCl_3$) to afford the final product as a yellow solid (47.4 % yield). ^1H NMR ($CDCl_3$): $\delta = 7.40$ (s, 4H), 4.08 (s, 12H), 2.95 (s, 6H).



Synthesis of C: A mixture of finely powdered **B** (10.0 g, mmol), sodium dichromate (50 g, mmol) and 500 cm^3 acetic acid were refluxed for 60 min. After the solvent was cooled to room temperature, the precipitate filter washed with water and dried. 6.1 g of yellow precipate was obtained (60.3 % yield). ^{1}H NMR ($CDCl_3$): $\delta = 7.69$ (s, 4H), 4.07 (s, 12H). It is almost insoluble in benzene, acetic acid or ethanol, a bit in pyridine.

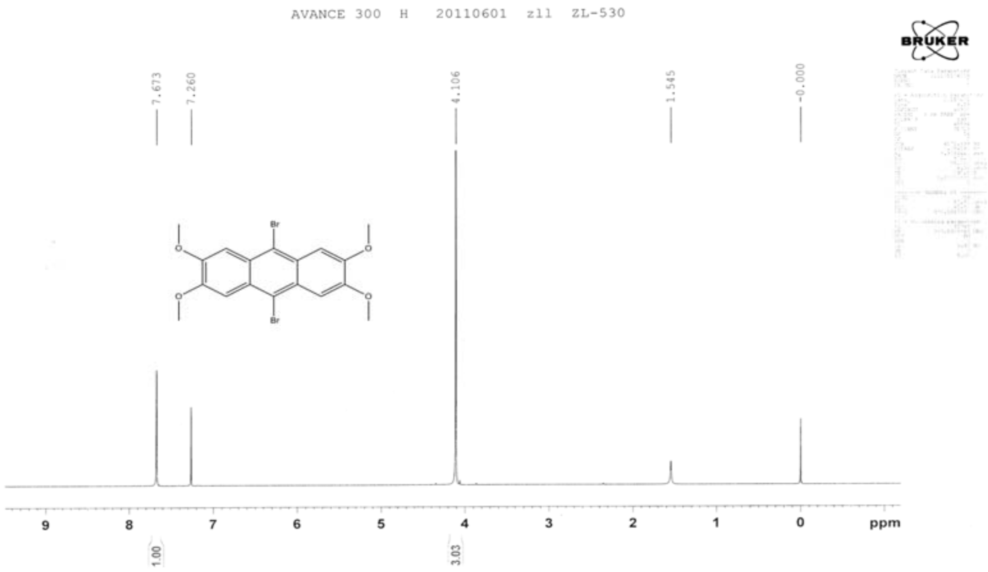


Synthesis of D: The active zinc powder (167 g, 2.6 mol) and **C** (10 g, 41.3 mmol) were added to a stirred aqueous solution (670 mL) of sodium hydroxide (50 g, 1.25 mol) under a N_2 atmosphere. The mixture was heated at 100 °C for 48 h, and then cooled to room temperature. Concentrated hydrochloric acid (570 mL) was added. The reaction mixture was stirred for 1 h, and then filtrated. The solid was dried to give the pale-white pure compound **D** 7.3 g, yield 82.6 %, ^{1}H NMR ($CDCl_3$): $\delta = 8.03$(s, 2H), 7.15(s, 4H), 4.04(s, 12H).

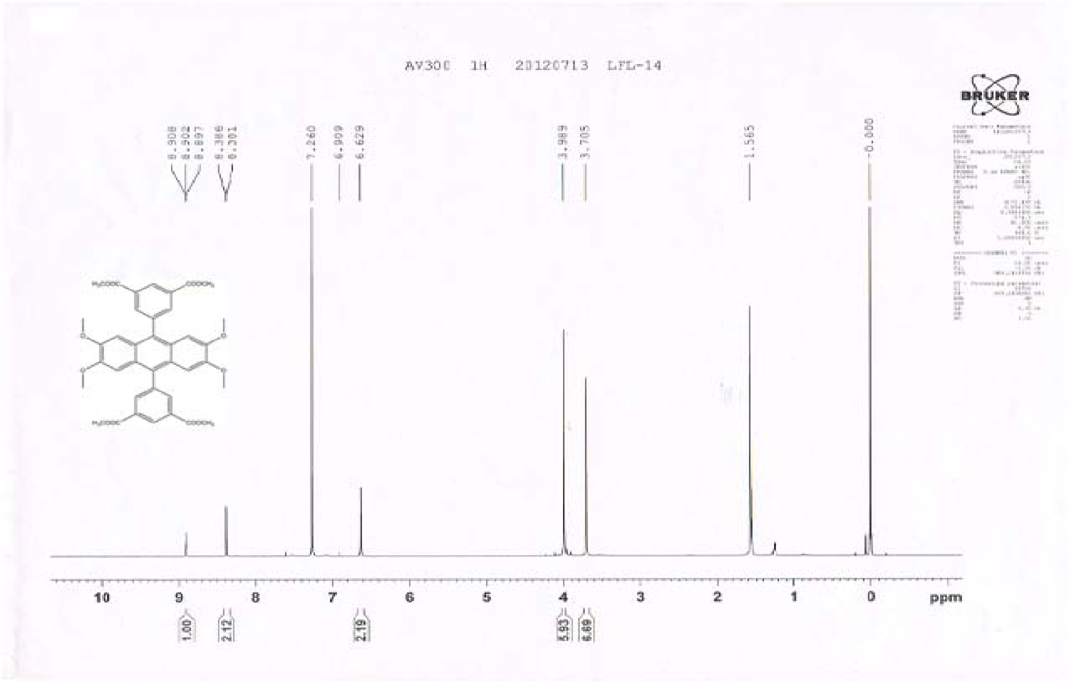


Synthesis of E: **D** was dissolved in boiling CCl_4 (100 mL). After cooling to room temperature ,Br_2 (1.2 g, 0.38

mL,7.5 mmol) was added via syringe .The mixture was heated (100 °C, bath temp) to a gentle boil when HBr start to evolve .The reaction was stopped after 35 min at reflux, the mixture cooled and the precipitate filter and dried. The solid was cooked in toluene for another 30 min, then filter to give the brown pure **E**. ^{1}H NMR ($CDCl_3$): δ = 7.67 (s, 4H), 4.11 (s, 12H).

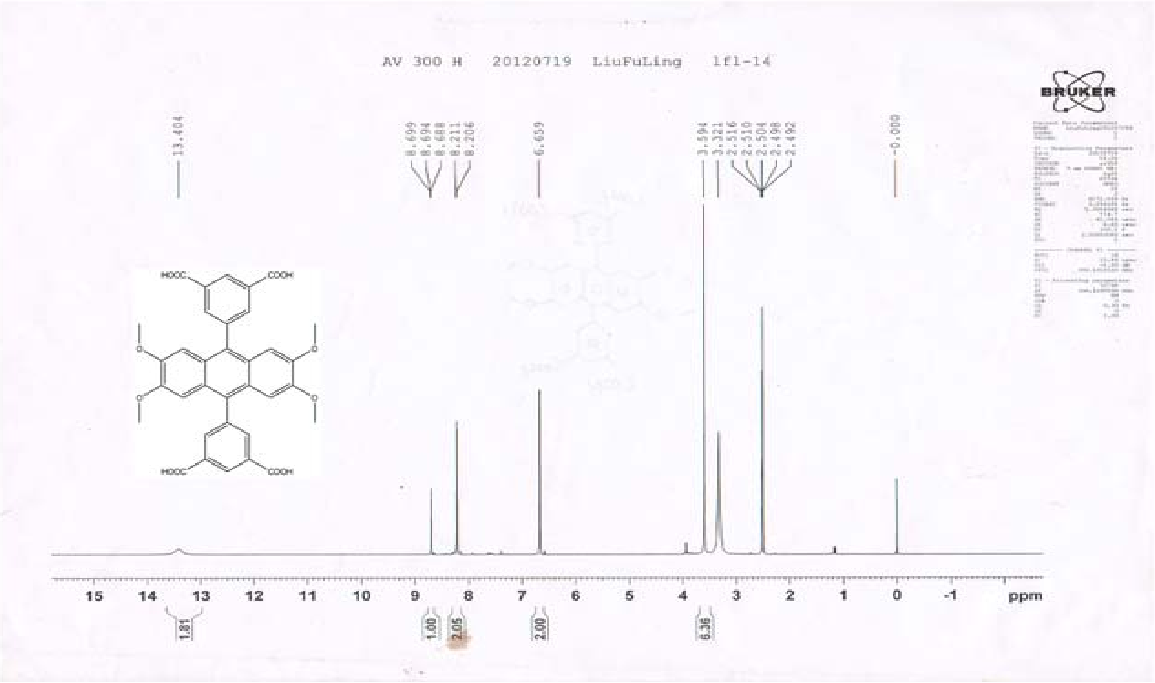


Synthesis of F: E and (3,5-bis(methoxycarbonyl)phenyl)boronic acid (mol/mol = 1:2.3), CsF and $Pd(PPh_3)_4$ were mixed in a two-necked shclenk flak and pumped for 30 minutes. 200 mL degassed $CH_3OCH_2CH_2OCH_3$ (DME) was added through a canula. The mixture was heated to reflux under N_2 for 48 hours. After the mixture was cooled to RT, water was added. The water phase was washed with $CHCl_3$. The mixed organic phases were dried with $MgSO_4$. After the solvent was removed, the crude product was purified by column chromatography (silica, $CHCl_3$) to give the pure product. ^{1}H NMR ($CDCl_3$): δ = 8.90 (t, 2H), 8.38 (d, 4H), 6.63 (s, 4H), 4.00 (s, 12H), 3.70 (s, 12H).

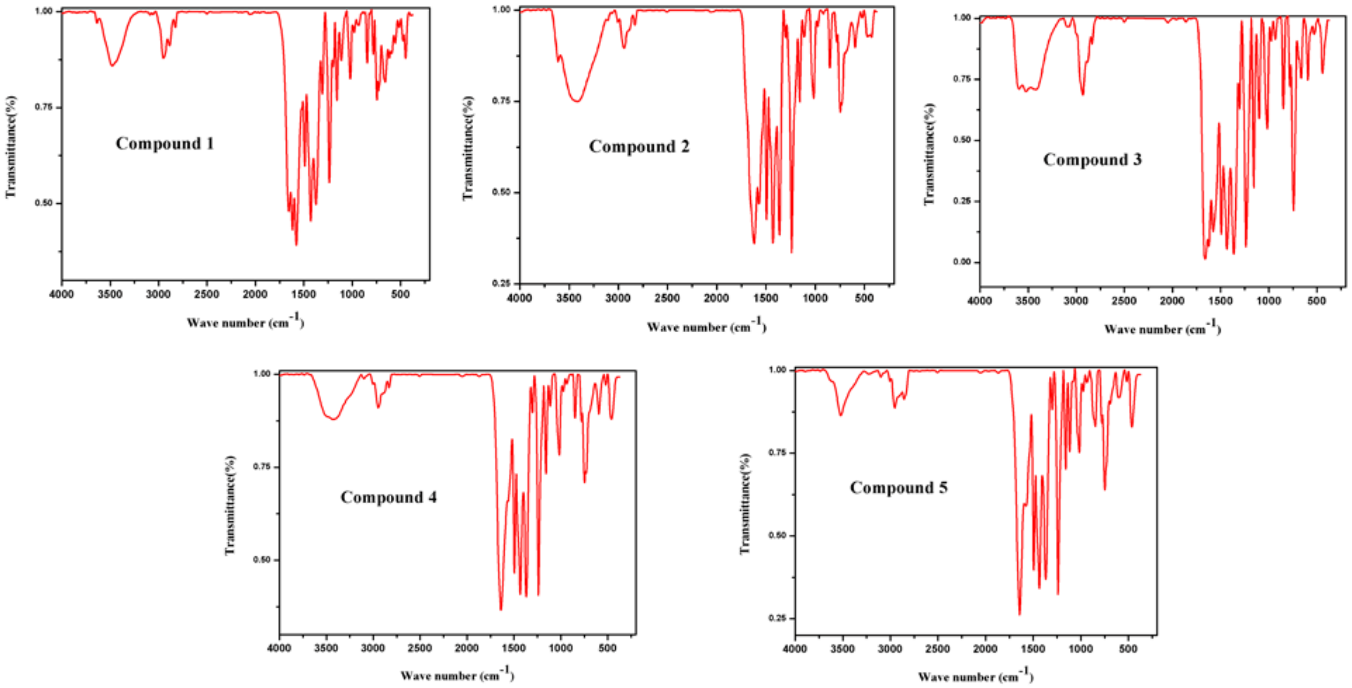


Synthesis of G: F(1.1 g, 1.58 mmol) was then suspended in a mixture of THF (20 mL) and MeOH (20 mL), to which

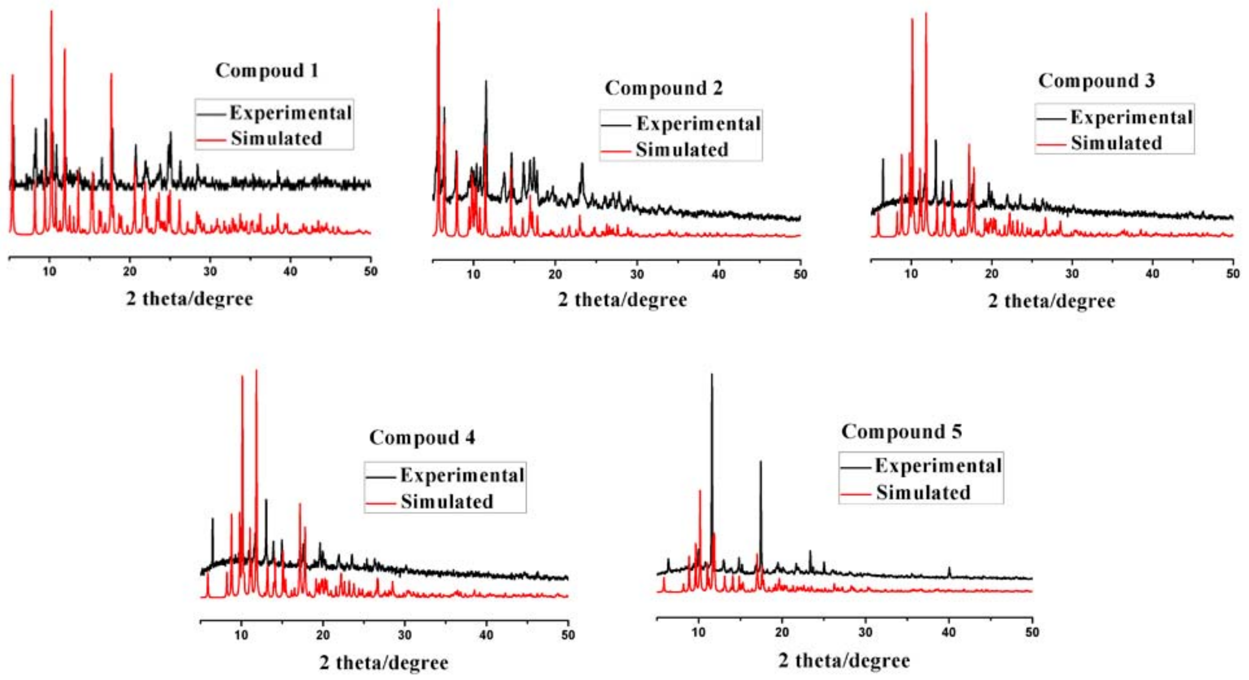
5 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF and MeOH were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at pH = 2. The solid was collected by filtration, washed with water and MeOH, and dried to give the yellow solid **7** (0.95 g, 96.3 % yield). ^{1}H-NMR (400 MHz, DMSO): δ = 13.4 (s, 4H), 8.69 (t, 2H), 8.2 (d, 4H), 6.65 (s, 4H), 3.59 (s, 12H)



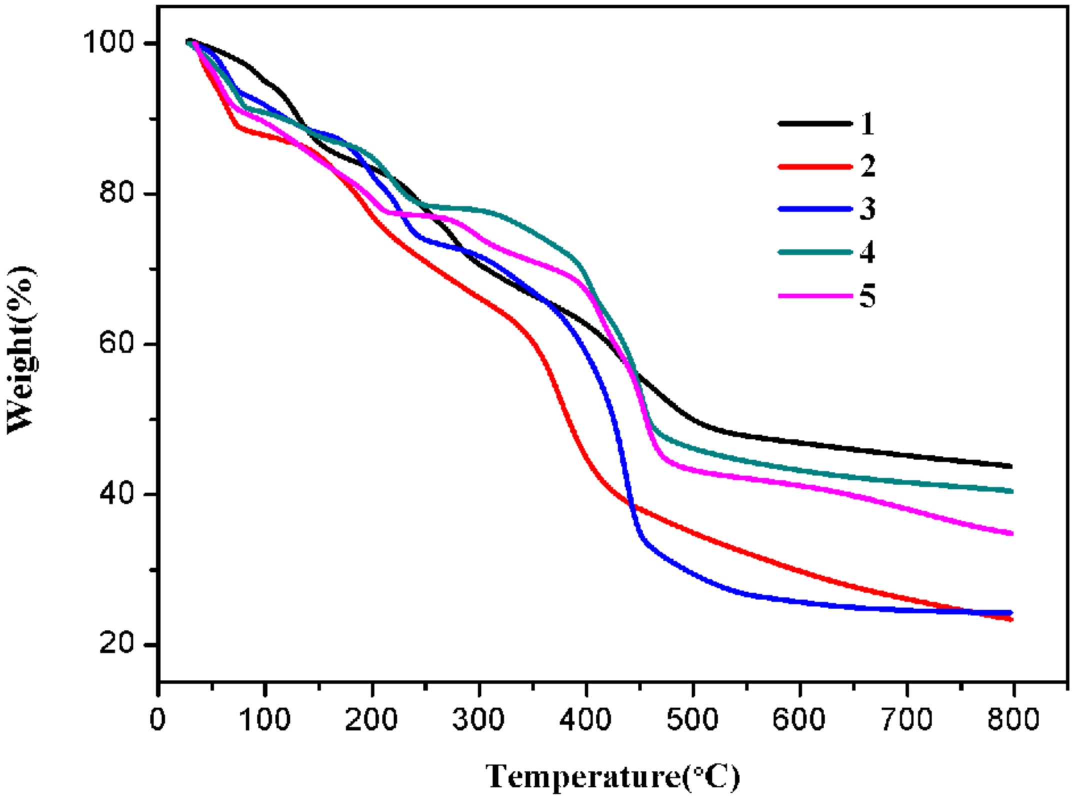
(2) Figure S1 IR of compounds 1-5



(3)Figure S2 The powder XRD patterns and the simulated one from the single-crystal diffraction data for compounds 1-5



(4)Figure S3 TGA of compounds 1-5



(5)Figure S4 Photoluminescences of H_4L^{OMe}