Electronic Supplementary Information for

A novel low density metal-organic framework with pcu topology by dendritic ligand

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Contents: The preparation and characterization of the ligand and single crystal, TGA, PXRD, IR, NMR and other measurements.

General Methods: All the chemical reagents used were bought from commercial supplier without further purification, unless otherwise noted. Powder X-ray diffractions (XRD) were carried out on Scintag X1 diffractometer with Cu-Kα (λ = 1.5418 Å) at 40 kV, 35 mA. The elemental analyses were carried out on a PerkinElmer 240C element analyzer. Fourier-Transform infrared spectras were got with a Nicolet Impact 410 FT-IR spectrometer where KBr disks dispersed with sample powders was used in the 4000–400 cm^{-1} range. Thermogravimetric analysis (TGA) curve were collected on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 ºC/min at air. ^{1}H NMR and ^{13}C NMR spectra were collected using a Bruker AV 400 or VARIAN 300 spectrometer at 298 K. Tetramethylsilane (TMS) of internal standard in 1H NMR experiments was used, and deuterated solvents as internal standard in ^{13}C NMR experiments ($CDCl_3$, δ = 77.00 ppm; D_6-DMSO, δ = 39.52 ppm). Nitrogen and hydrogen adsorption experiments were performed with Autosorb-iQ2-MP-AG. High resolution mass spectra (HRMS) were collected using a FT-ICR-MS instrument (model: IonSpec 7.0T).

Synthesis of the Ligand and JUC-100:

Dimethyl 5′-bromo-[1,1′:3′,1″-terphenyl]-4,4″-dicarboxylate (1):

1,3,5-Tribrombenzene (5.0 g, 16 mmol), *p*-methoxyl-carbonphenylboronic acid (7.2 g, 40 mmol), Na_2CO_3 (8.4 g, 79 mmol), $Pd(PPh_3)_4$ (1.3 g, 1.1 mmol) were added to a three-necked flask with degassed toluene-methanol-water (80 ml: 40 ml: 40 ml). The solution was stirred under nitrogen atmosphere for 50 h with reflux. The product was extracted using dichloromethane (80 ml × 3), washed with brine (80 ml), and dried with anhydrous $MgSO_4$. The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography of silica gel (dichloromethane/ petroleum = 1/ 2, v/ v) to obtain compound **1** of 2.5 g (yield: 37%). ^{1}H NMR ($CDCl_3$) 8.15 (d, 4 H, J = 8.0 Hz), 7.78 (s, 2 H), 7.75 (s, 1 H), 7.69 (d, 4 H, J = 8.0 Hz), 3.96 (s, 6 H).

Dimethyl 5′-pinacolatoborontel-[1,1′:3′,1″-terphenyl]- 4,4″-dicarboxylate (2):

Compound **1** (2.3 g, 5.3 mmol), bis(pinacolato)diboron (1.4 g, 5.7 mmol), KOAc (4.0 g, 40 mmol), and $Pd(dppf)Cl_2$ (0.12 g, 0.16 mmol) were added to a three-necked flask

with degassed 100ml 1,2-dimethoxyethane (DME). The solution was stirred for 3 h with reflux to get the product which was eliminated under reduced pressure. The residue was extracted using dichloromethane (80 ml× 3), washed with brine and dried with anhydrous $MgSO_4$. The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography of silica gel (dichloromethane/ petroleum = 1/ 1, v/ v) to obtain **2** of 2.0 g (yield: 78%). ^{1}H NMR ($CDCl_3$), 8.13 (d, 4 H J = 8.2 Hz), 8.09 (d, 2 H, J = 6.0 Hz), 7.94 (t, 1 H, J = 2.0Hz), 7.76 (d, 4 H, J = 8.2 Hz), 3.95 (s, 6 H), 1.39 (s,12 H); ^{13}C NMR ($CDCl_3$) 166.953, 145.225, 140.147, 133.320, 130.066, 129.077, 128.956, 127.253, 84.162, 52.125, 24.877

1,3,5-Tri(3,5-di(4-methoxylcarboxyphenyl-1-yl)phenyl-1-yl)benzene (3):

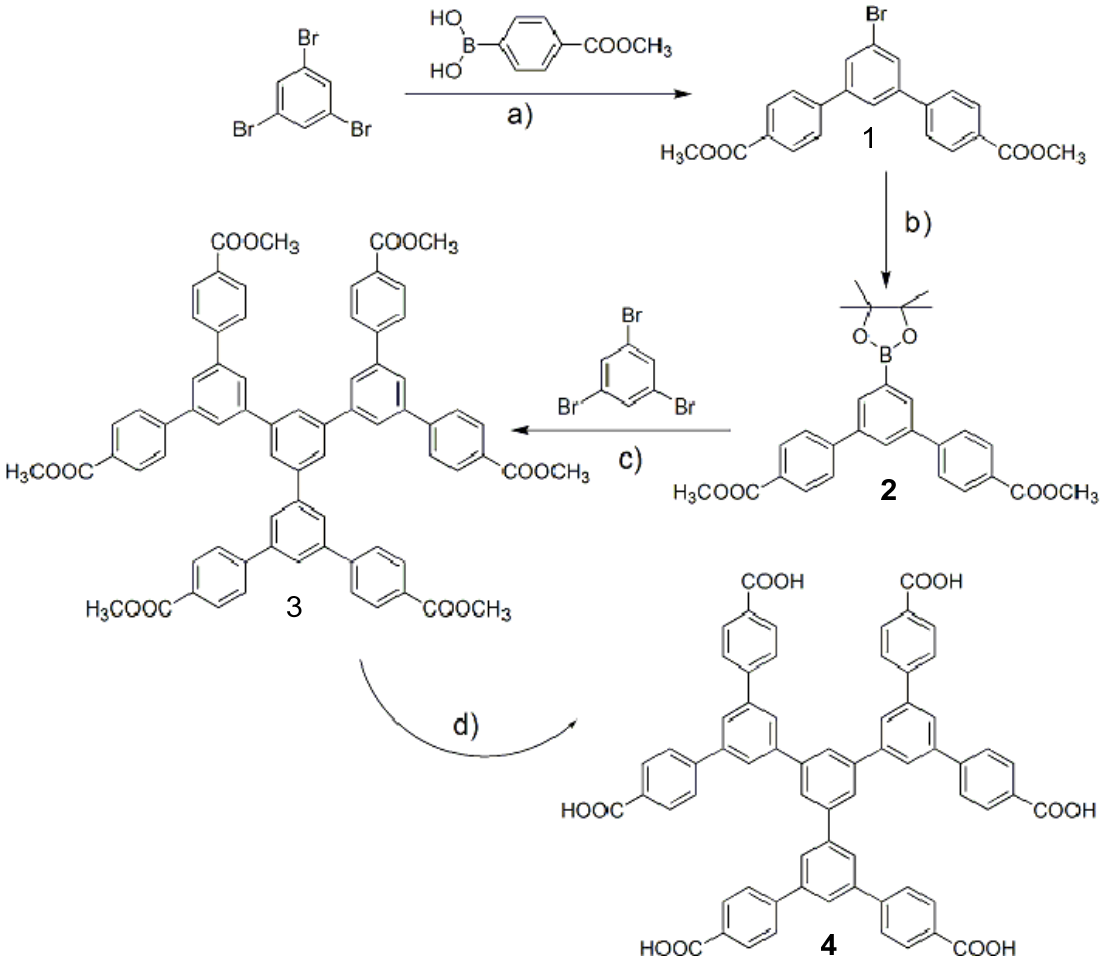
Compound **2** (2.0 g, 4.2 mmol), 1,3,5-tribromobenzene (0.31 g, 1.0 mmol), Na_2CO_3 (0.53 g, 5.0 mmol) and $Pd(PPh_3)_4$ (0.090 g, 0.076 mmol) were added to a three necked flask with degassed toluene-methanol-water (30 ml, 15 ml, 15 ml). The solution was stirred under nitrogen atmosphere for 50 h with reflux. The product was extracted using $CHCl_3$ (80 ml × 3), washed with brine (80 ml), and dried with anhydrous $MgSO_4$.The filtered solution was eliminated under reduced pressure. The residue was purified using column chromatography with silica gel ($CHCl_3$/ petroleleum/ CH_3OH = 50/ 10/ 1, v/ v/ v) to obtain **3** of 0.70 g (yield: 63%). ^{1}H NMR ($CDCl_3$) 8.162 (d, 12 H, J = 8 Hz), 7.980 (s,3 H), 7.945 (s,6 H), 7.888 (s, 3 H), 7.794 (d, 4 H, J = 12 Hz), 3.953 (s, 18 H) ^{13}C NMR (D_6-DMSO) 166.832, 145.012, 142.488, 141.713, 132.298, 130.263, 129.488, 127.329, 126.264, 126.128, 125.839, 52.216.

1,3,5-Tri(3,5-di(4-carboxyphenyl-1-yl)phenyl-1-yl)benzene (4, TDCPB) :

Compound **3** (0.70 g, 0.63 mmol) and NaOH (2.0 g, 50 mmol) were added to a flask with THF-methanol-water (40ml:40ml:40ml). The solution was stirred for 24 h with reflux. After the solution was cool down, 1M HCl was added to it to get a solution with pH= 2.0. White precipitation was filtered to obtain **4** of 0.60 g (yield: 92%). ^{1}H NMR (D_6-DMSO) 8.3513 (s, 3 H), 8.236 (s, 6 H), 8.107-8.057 (q, 18 H). ^{13}C NMR (D_6-DMSO) 167.014, 14.165, 142.202, 141.784, 140.628, 129.892, 127.539, 126.266, 125.065. HRMS (ESI) (m/z) calcd for $C_{66}H_{42}O_{12}$+Na: 1049.25685, found:

1049.26219.

Zn_4O(TDCPB) (JUC-100): **4** (10 mg, 0.0097 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (20 mg, 0.067 mmol) were added to a solvent of DMF (3.0 ml), enthanol (0.20ml) and then 0.10 ml concentrated HNO_3 was added. After ultrasonic diffusion, the solution was heated at 85 ^oC for 24 h to obtain the product of 70% (yield based on Zn) with colorless crystal. Anal. Calcd (Found) for $Zn_4C_{96}H_{116}N_{10}O_{28}$: C, 54.41 (54.88); H, 5.47(5.91); N, 6.61 (6.71) %. According to element analysis and TGA measurements , the crystal formula is $Zn_4O(TDCPB){\cdot}10DMF{\cdot}5H_2O$.



Scheme 1： The synthetic route of TDCPB

Crystallography data: Colorless, block-shaped crystal of JUC-100 was picked for X-ray structural analysis on a Bruker SMART CCD diffractometer at 296(2) K. The complex crystallized in the space group *R*-3*c*, trigonal, $a = 20.4586(8)$, $b = 20.4586(8)$, $c =$

80.370(3) Å, V = 29132(2) Å^3, λ = 0.71073 Å, ρ_{calc} = 0.888 g/cm^3. A total of 51924 reflections were collected, of which 6430 were unique (R_{int} = 0.0490). Final *GooF* = 1.061, R_1 = 0.0743, wR_2 = 0.2258. The structure was solved and refined by full matrix least-squares on F^2 values (SHELXL-97).[1] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined using a riding mode. The routine SQUEEZE was applied to the structures in order to remove diffuse electron density associated with badly disordered DMF molecules.[2]

Low-pressure gas and vapor sorption measurements: The JUC-100 sample after activation is used to N_2 adsorption measurement. The as-synthesized sample is soaked in CH_2Cl_2 for 3 days and then heated at 135 °C and vacuum for 12 h. The N_2 and H_2 sorption-desorption experiments were performed on an Autosorb-iQ2-MP-AG machine. N_2 and H_2 used were of 99.999% purity. The sample was treated at 130 ºC under vacuum for 12 h before the measurement. The H_2 sorption-desorption isotherms were collected at 77 K and 87 K. Surface area was determined by the N_2 gas isotherm measured at 77 K.

Reference:

[1]. SHELX-97, Program for Structure Refinement, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), 1997.

[2]. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

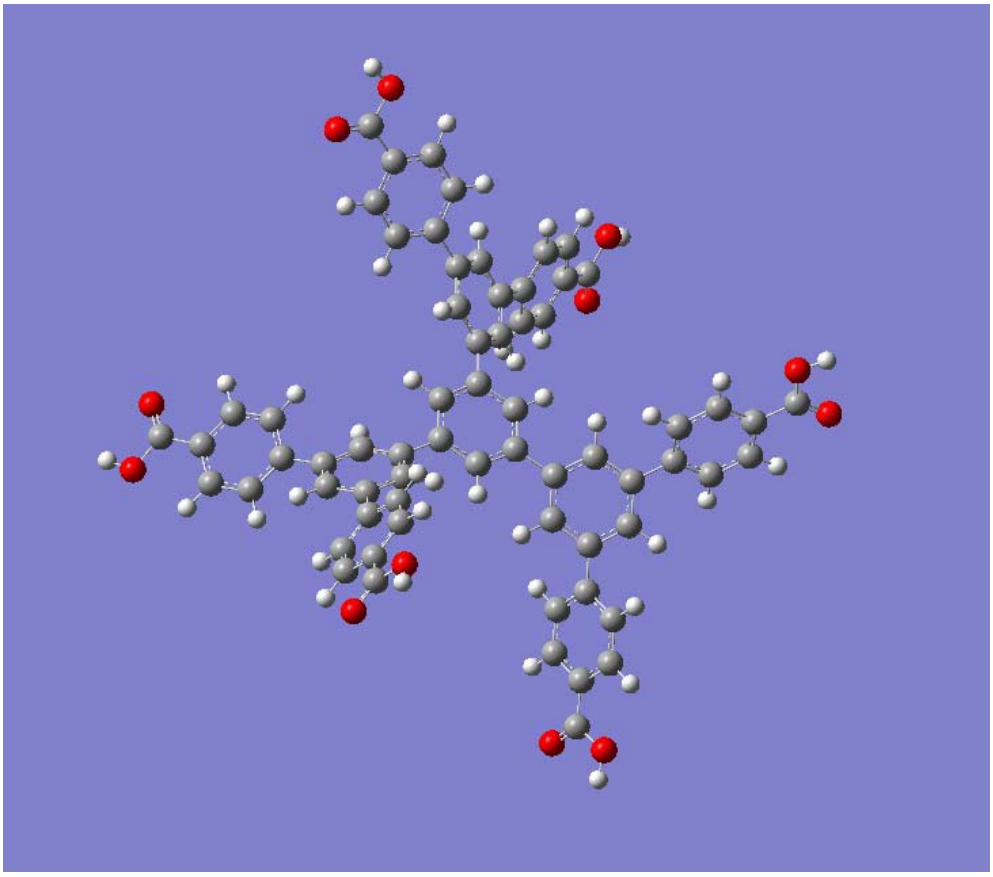


Fig. S1 The optimized configuration of TDCPB: The configuration of TDCPB was optimized by DFT method with the software of Gaussian09. The density functional B3LYP level using the 6-31G(d) basis set was utilized for the geometry optimizations. After the calculation, we got the most optimized configuration as shown above and it just took a distorted octahedral configuration.

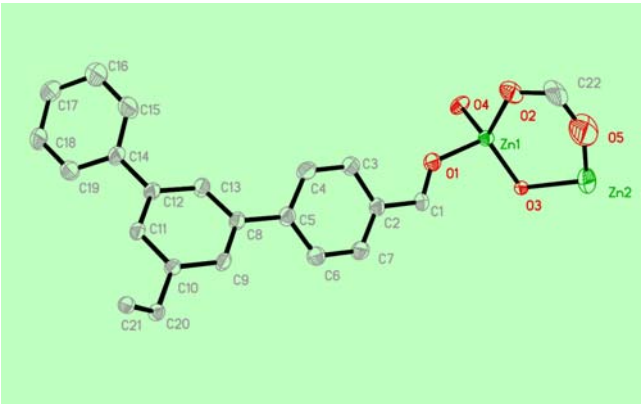


Fig. S2 The asymmetric unit of JUC-100

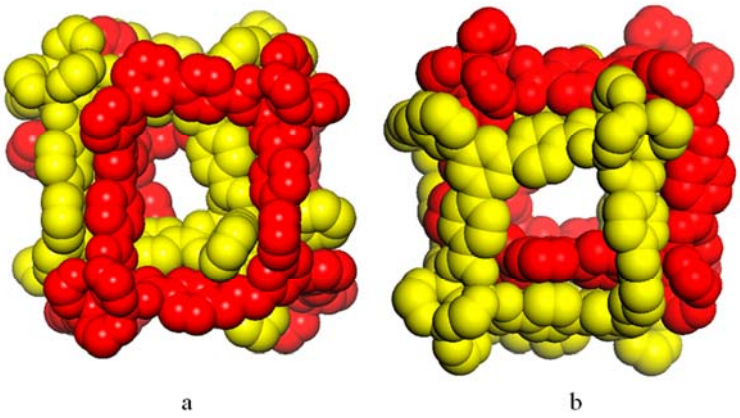


Fig. S3 View outside (a) and inside (b) of the nanocage

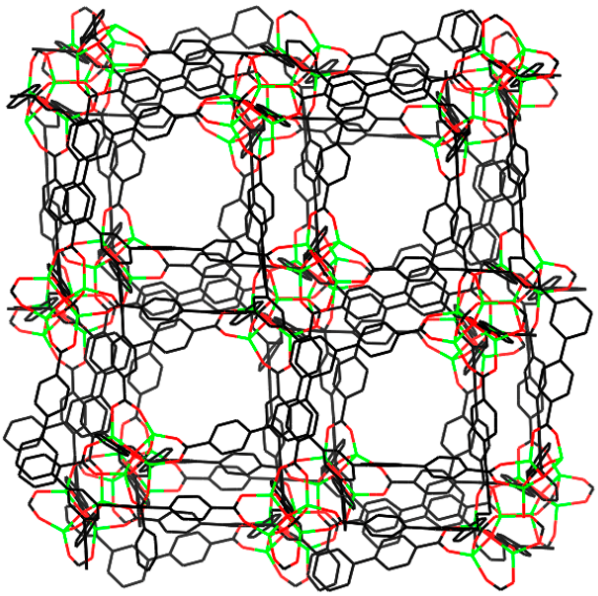


Fig. S4 3D space packing of JUC-100 view along (111)

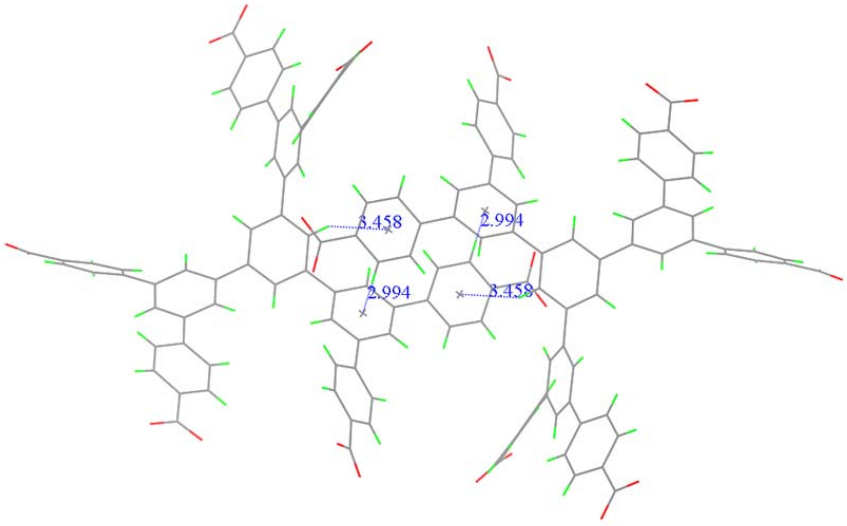


Fig. S5 C-H···π effect between ligands (C atom-black, O atom-red, H atom-green, distance (Å)-blue).

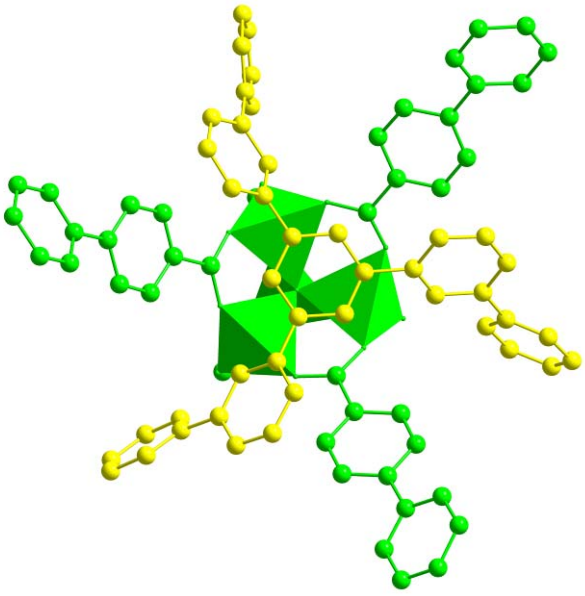


Fig. S6 Staggered conformation between the ligand TDCPB and SBU Zn_4O

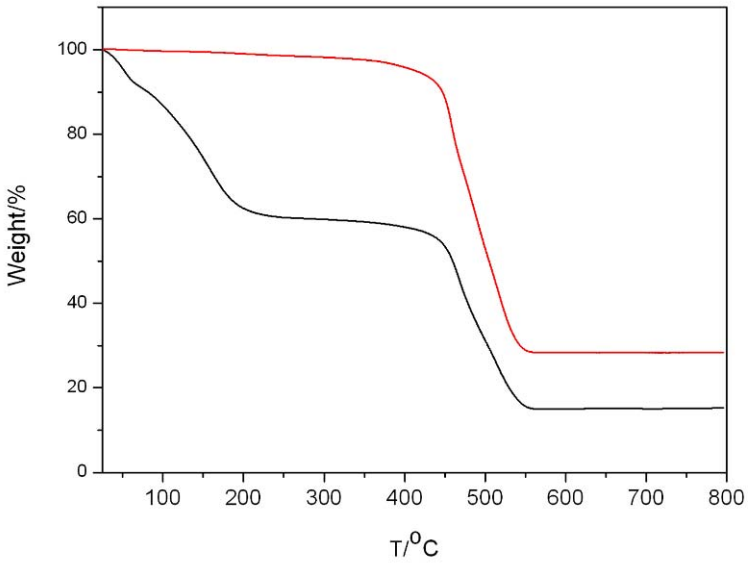


Fig. S7 TGA curves of desolvated (red) and solvated (black) form of JUC-100. The desolvated sample starts to decompose at about 420 °C, and up to 550 °C, the decomposition finishes, and there is 70.44 % weight loss attributed to the destruction of organic part. The solvated sample starts to lose guests at the beginning of heat-up, and there is 41.14 % weight loss attributed to the departure of guests before 200 °C. Furthermore, this sample starts to decompose at about 420 °C, and the decomposition finishes up to 550 °C, and there is 43.66 % weight loss attributed to the loss of organic framework part.

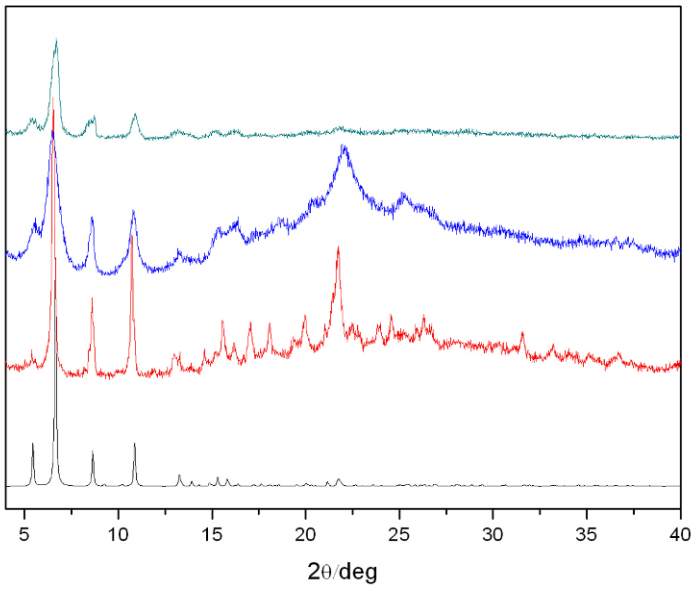


Fig. S8 PXRD patterns of JUC-100 (calculated, black; as-synthesized, red; activated at 130 °C for 12 h, blue; heated at 300 °C for 2 h, green)

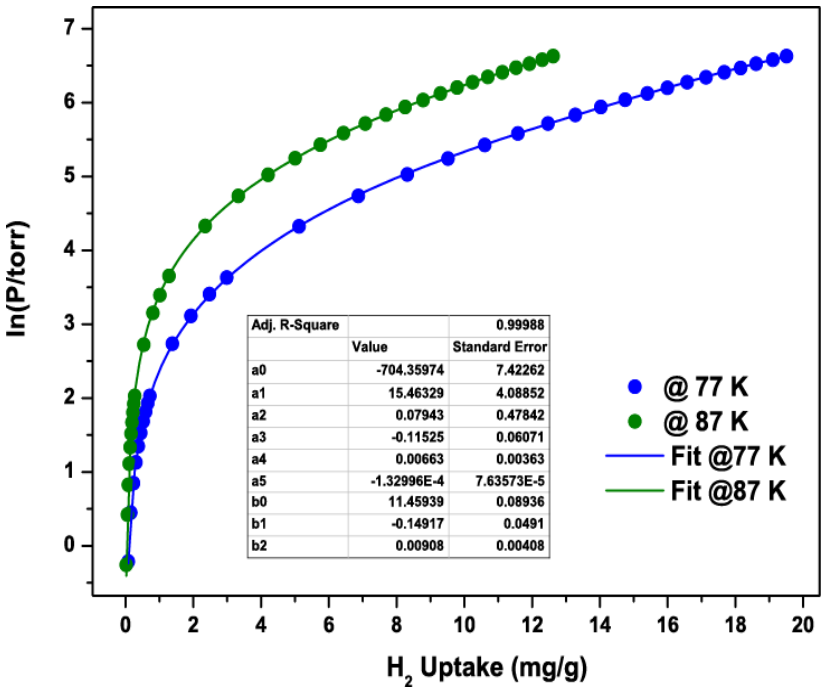


Fig. S9 H_2 uptake data recorded at 77 K (blue) and 87 K (green) in JUC-100, and the corresponding virial curves fitted to the data. Inset: virial coefficients obtained from the fit of the data.

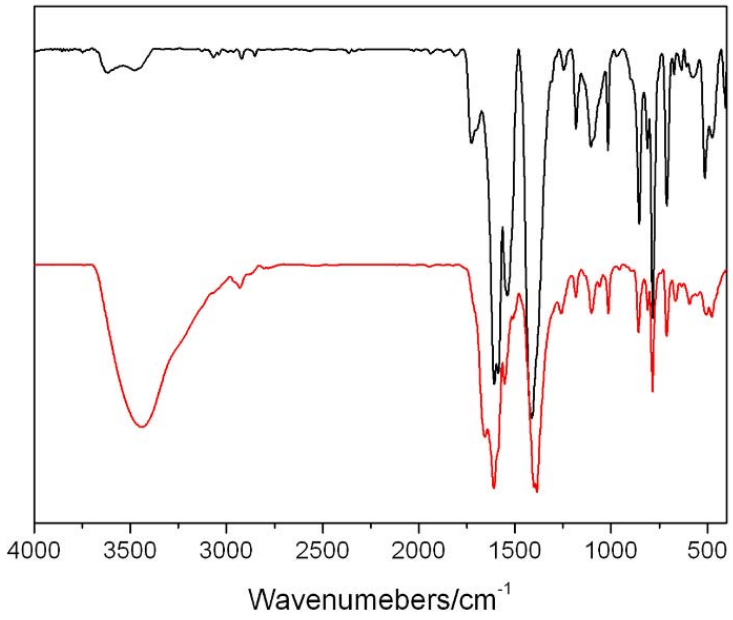


Fig. S10 FT-IR spectra of desolvated (black) and solvated (red) form of JUC-100. The characteristic peak of C=O of DMF at 1664 cm^{-1} was only found in the red curve, implying that the guest was removed completely.

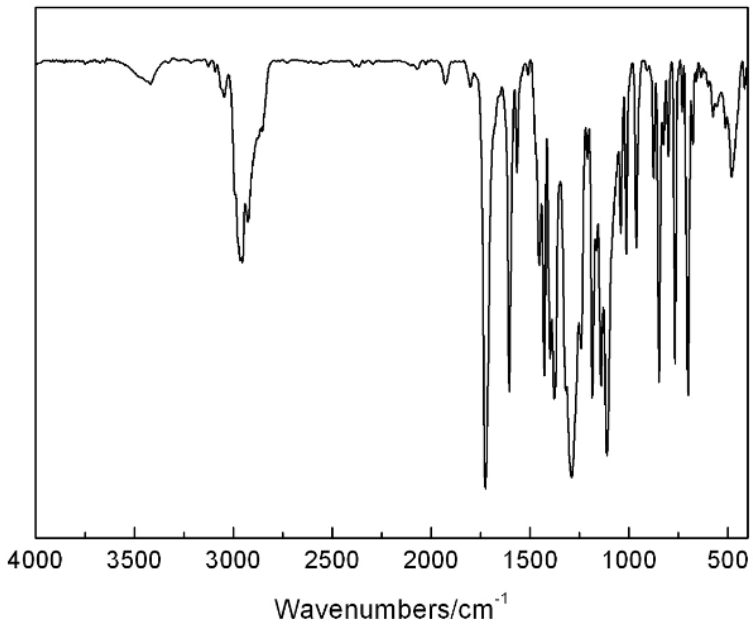


Fig. S11 FT-IR spectra of compound **2**

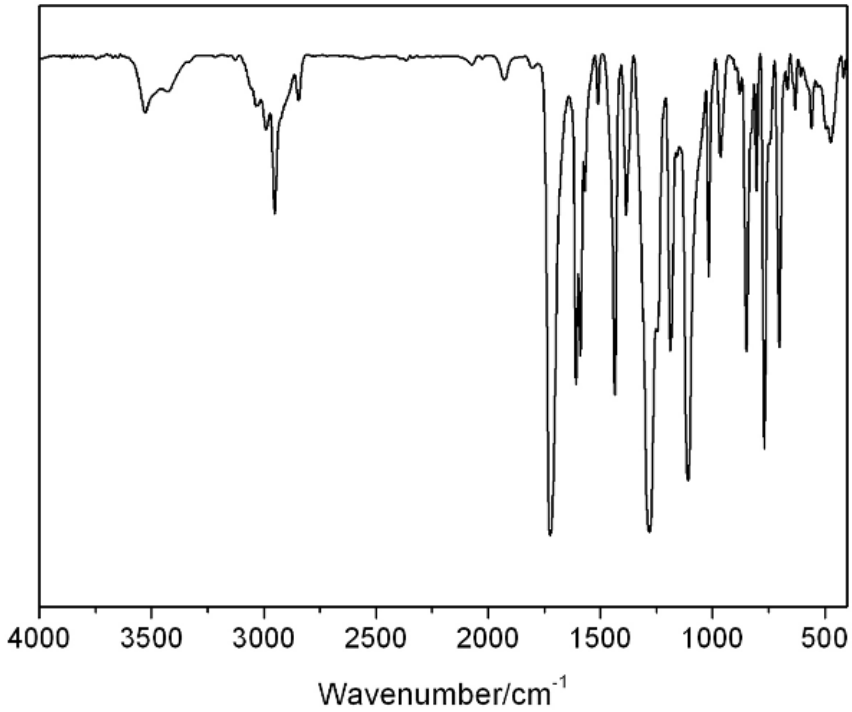


Fig. S12 FT-IR spectra of compound **3**

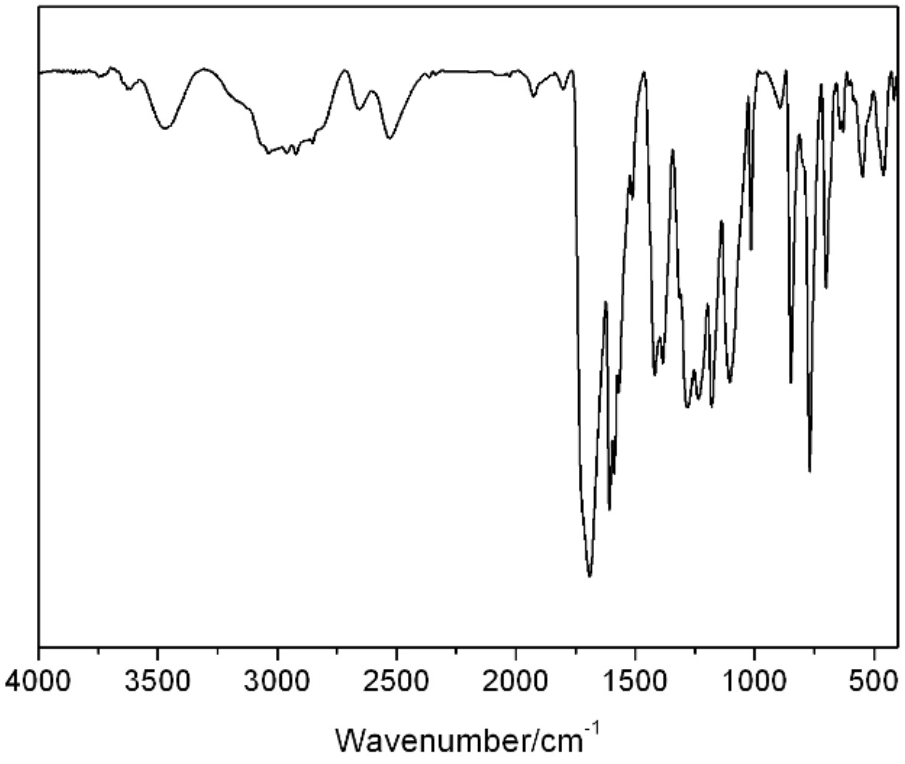
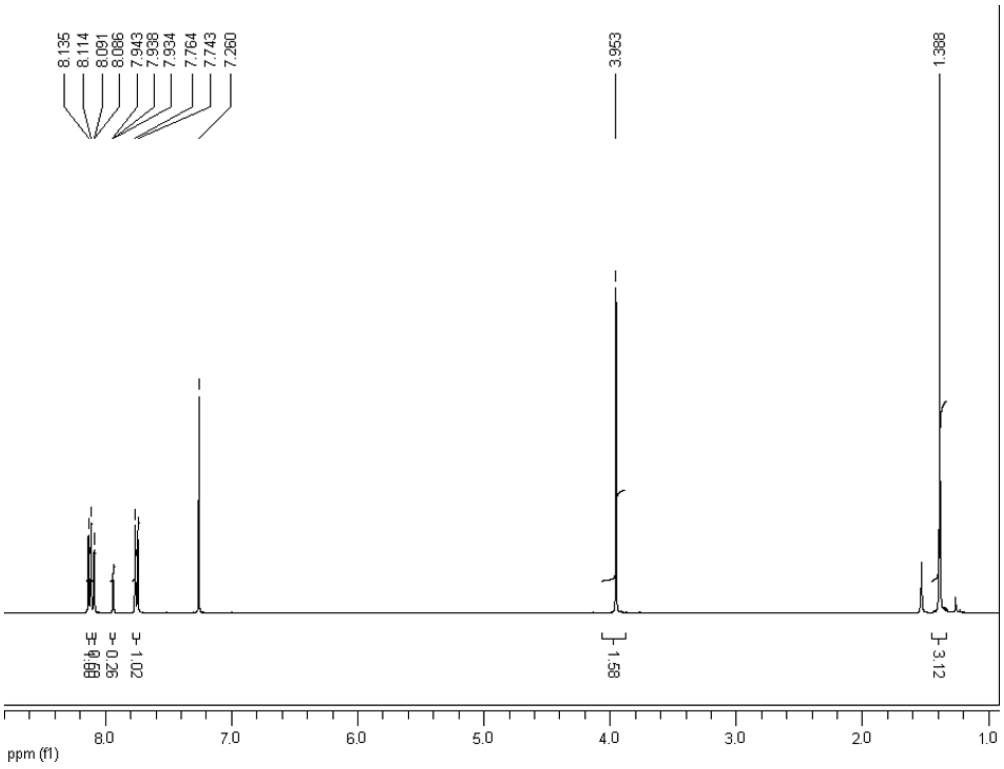


Fig. S13 FT-IR spectra of compound **4**



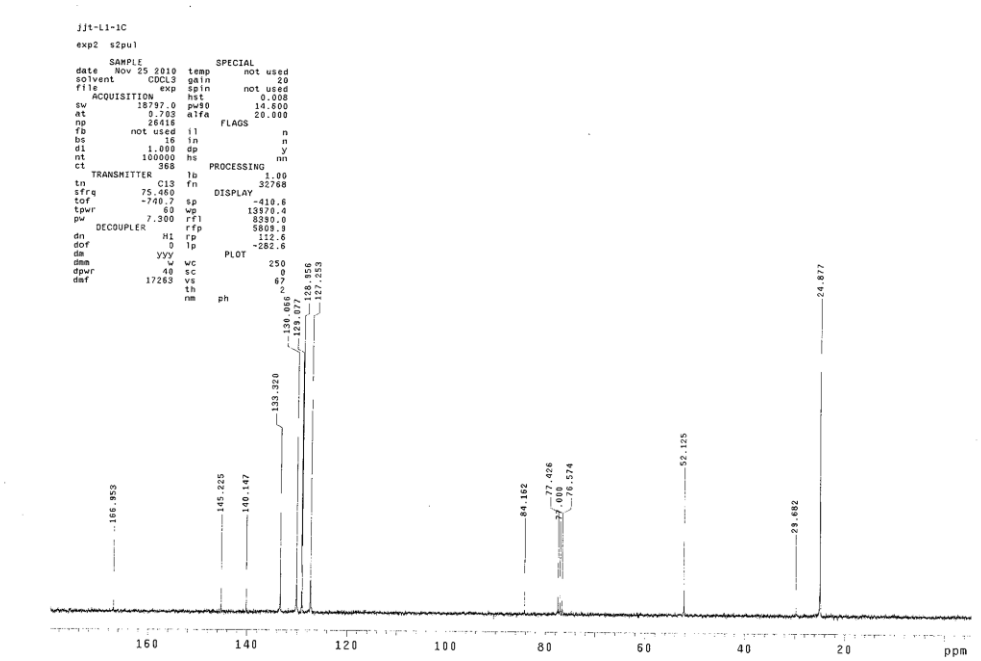


Fig. S14 ^{1}H and ^{13}C NMR spectra of compound **2** recorded in neat $CDCl_3$.

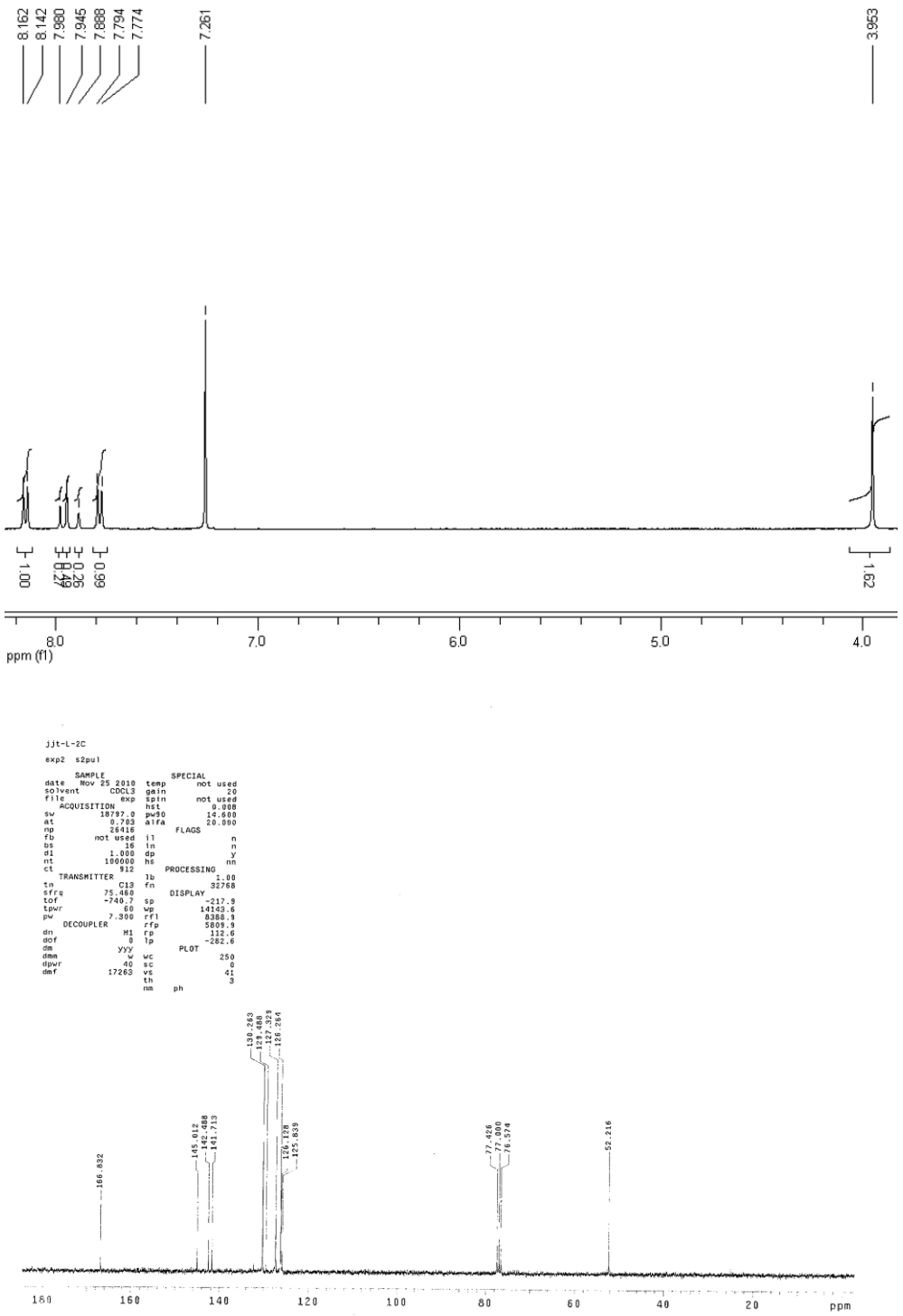


Fig. S15 ^{1}H and ^{13}C NMR spectra of compound **3** recorded in neat $CDCl_3$.

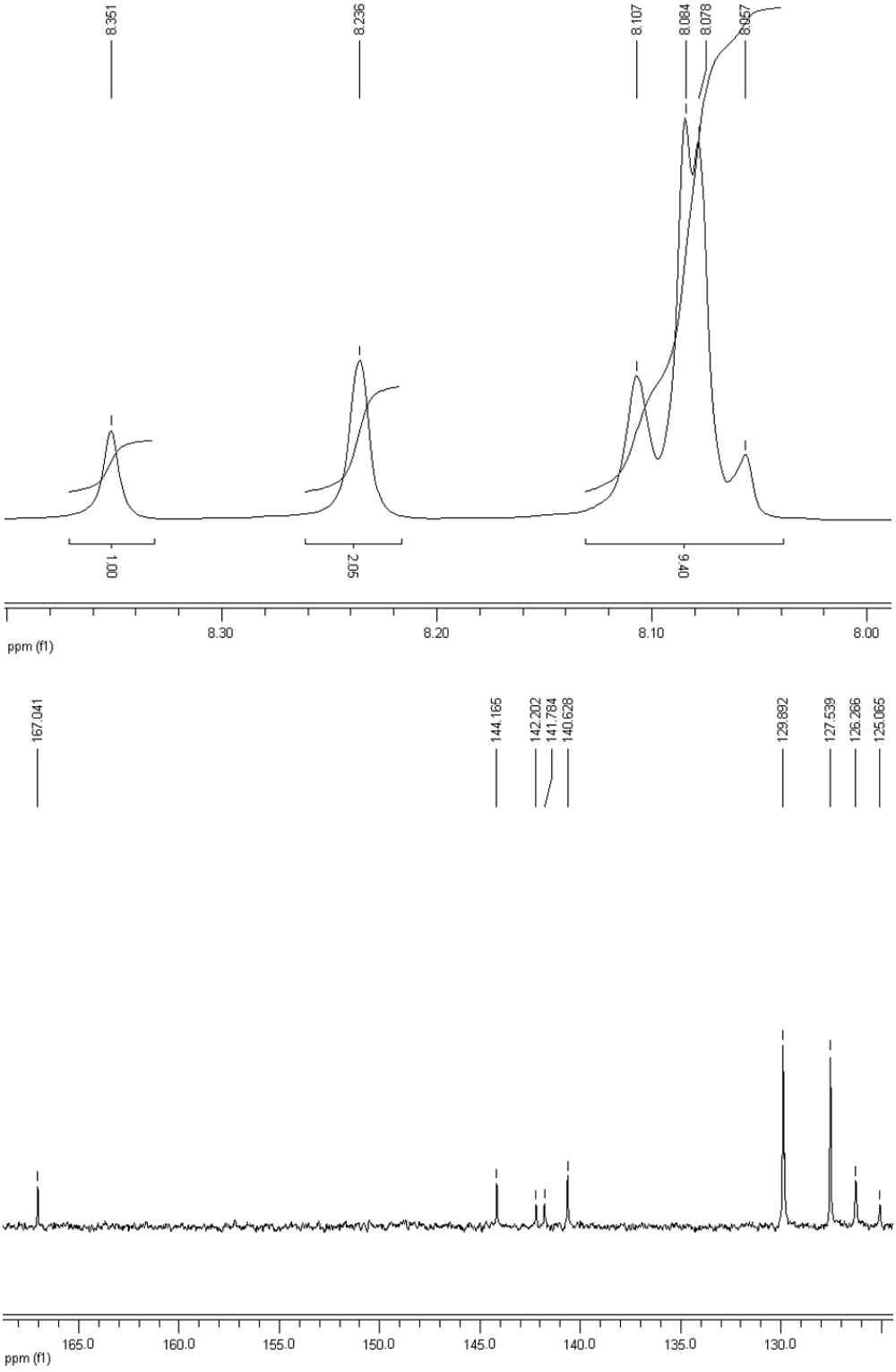


Fig. S16 ^{1}H and ^{13}C NMR spectra of compound **4** recorded in neat D_6-DMSO.

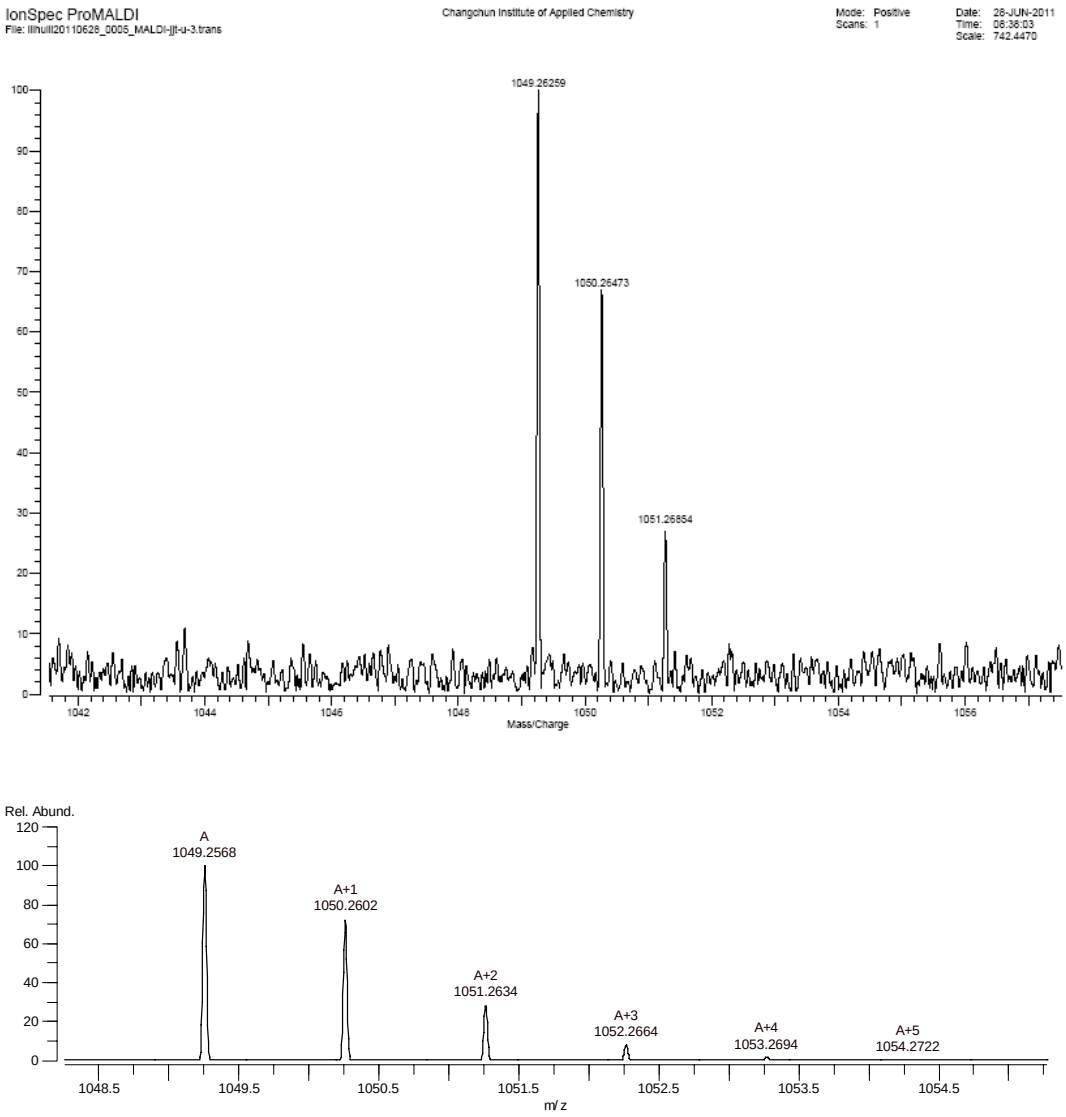


Fig. S17 The HRMS spectra of ligand TDCPB (top: measured; bottom: calculated).