Selective Binding and Removal of Organic Molecules in a Flexible Polymeric Material with Stretchable Metallosalen Chains

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1. **Materials and General Procedures**.

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400 - 4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ºC min^{-1} on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. Gas chromatography was conducted on Lunan Ruihong SP-6890 equipped with a flame ionization detector. The N_2 adsorption isotherms were measured at 77 K by using a Micromeritics ASAP 2010 M+C system. Before the adsorption measurement, the sample was outgassed at 398 K in the port of the adsorption analyzer for 12 h. The sorption isotherms for benzene, toluene and cyclohexane vapors were measured at 298 K by using an automatic gravimetric adsorption apparatus (IGA-003 series, Hiden Isochema Ltd.). The as-synthesized samples (150-200 mg) were placed in a quartz tube and dried under high vacuum at 393 K for 12 h to remove the solvated molecules prior to measurements.

X-ray Crystallography. Single-crystal XRD data for the compounds was collected on a Bruker Smart 1000 CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at room temperature. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on *F*2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997).

Although PLATON suggests C2/c space group for all five crystals, the mode of cyclohexane group is not correct if C2/c is used. The aromatic rings in all five structures are refined using geometric restrains for a reasonable bond distance and ring geometried. For all five complexes, the *tert*-butyl groups of the **L** ligands involving C14, C32, C56 and C74 were all treated as having rotational disorder with three methyl groups each occupying two half-weighted sites. IN addition, the benzene molecules in **1a** are disordered over two positions.

Crystal data and details of the data collection are given in Table S1. The selected bond distances and angles are presented in Tables S2-S6.

CCDC-707606-707610 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

2. **Synthesis and Guest Exchange**.

2.1 ***Synthesis of Complexes***

1a·benzene: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (14.9 mg, 0.05 mmol) and H_2**L** (32.0mg, 0.05 mmol) was placed in a small vial containing DMF (1 mL), water (0.1 mL) and benzene (1 mL). The *vial* was sealed, heated at 80 ºC for one day, and allowed to cool to room temperature, and light yellow rod-like crystal was collected, washed with ether, and dried in air. Yield: 25.7 mg, 66.2 % (based on Zn).

1a·toluene: The complex was obtained in a similar procedure to **1a**·benzene by using toluene instead of benzene or from **1a** (see below). Yield: 23.1 mg, 60.1 % (based on Zn). It can also be obtained by using a guest-exchange procedure from **1a**.

1b·benzene*:* The complex was obtained in a similar procedure to **1a**·benzene by heating at 100 ºC instead of 80 ºC or from **1a** or **1a**·benzene (see below). Yield: 24.3 mg, 63.2 % (based on Zn). It can also be obtained by using a guest-exchange procedure from **1a** or by heating **1a**·benzene at 100 ºC in benzene vapor.

1b·toluene*:* The complex was obtained in a similar procedure to **1b**·benzene by using toluene instead of benzene or from **1a** or **1a**·toluene (see below). Yield: 23.7 mg, 62.3 % (based on Zn). It can also be obtained by using a guest-exchange procedure from **1a** or by heating **1a**·toluene at 100 ºC in toluene vapor.

2.2. ***Guest-Exchange Experiment****.*

From **1a**·G (G = benzene or toluene) to **1a**: The crystal of **1a** was obtained by directly heating crystals of **1a**·benzene at 373 K under vacuum for 2 hours, as confirmed by single crystal X-ray crystallography, TGA and microanalysis. Similarly, heating other **1a**·toluene**, 1b**·benzene **or 1b**·toluene can also afford crystalline samples of **1a**.

From **1a** to **1a**·G (G = benzene or toluene): A typical guest-exchange experiment: Freshly evaculated crystals of **1a** (14.0 mg) were placed in corresponding guest vapor at 80 ºC for one day. The resulting crystalline samples were then washed several times with ether. Based on the results of microanalysis, TGA and powder XRD diffraction experiments, the product can be formulated as **1a** · benzene and **1a** · toluene.

From **1a** to **1b**·G (G = benzene or toluene): A typical guest-exchange experiment: Freshly evaculated crystals of **1a** (14.0 mg) were placed in corresponding guest vapor at 100 ºC for one day. The resulting crystalline samples were then washed several times with ether. Based on the results of microanalysis, TGA and powder XRD diffraction experiments, the product can be formulated as **1b** · benzene and **1b** · toluene.

From **1a**·G to **1b**·G (G = benzene or toluene): A typical guest-exchange experiment: Crystals of **1a**·G (14.0 mg) were placed in corresponding guest vapor at

100 ºC for one day. The resulting crystalline samples were then washed several times with ether. Based on the results of TGA and powder XRD diffraction experiments, the product can be formulated as **1b** · benzene and **1b** · toluene.

Elemental Analysis data of **1a**·benzene: Anal (%) Calcd for C48H48N4O2Zn1 C 74.07, H6.22, N7.20; Found: C 73.47, H 6.12, N 7.12.
IR of **1a** · benzene (KBr, cm^{-1}): 3556.27(m), 3482.98(s), 3413.56(s), 2952.63(w), 2952.63(m), 2204.35(m), 1619.99(m), 1589.14(m), 1525.49(m), 1440.64(m), 1384.71(m), 1378.92(m), 1334.56(m), 1168.71(m), 1141.71(m), 1024.07(w), 837.00(w), 624.85(w).

Elemental Analysis data of **1b**·benzene:
Anal (%). Calcd for C48H48 N4O2Zn1: C, 74.07; H, 6.22; N, 7.20. Found: C, 73.44; H, 6.13; N, 7.14.
IR of **1b**·benzene: (KBr, cm^{-1}): 3445.90(b), 2940.67(w), 2190.35(m), 1627.73(s), 1587.49(s), 1522.92(m), 1438.47(m), 1384.04(s), 1353.75(m), 1199.82(m), 1138.03(m), 1019.74(w), 836.64(w), 524.15(m)

Elemental Analysis data of **1a**: Anal (%). Calcd for C42H42N4O2Zn1: C, 72.04; H, 6.05; N, 8.00. Found: C, 71.64; H, 6.01; N, 7.94.
IR of **1a**, (KBr, cm^{-1}): 3440.34(b), 2936.70(w), 2196.95(m), 1621.99(s), 1565.42(s), 1531.59(m), 1446.64(w), 1384.46(s), 1353.02(m), 1175.22(m), 1139.71(m), 1018.98(m), 829.11(w), 526.41(w)

Elemental Analysis data of **1a**·toluene: Anal (%). Calcd for C49H50N4O2Zn1: C, 74.28; H, 6.36; N, 7.07. Found: C, 73.94; H, 6.28; N, 7.00.
IR of **1a**·toluene, (KBr, cm^{-1}): 3446.95(b), 2942.63(w), 2193.64(m), 1624.69(s), 1567.17(s), 1524.49(m), 1439.27(m), 1382.82(s), 1355.02(m), 1189.65(m), 1136.71(m), 1020.47(w), 838.31(w), 524.54(w).

Elemental Analysis data of **1b**·toluene: Anal (%). Calcd for C49H50N4O2Zn1: C, 74.28; H, 6.36; N, 7.07. Found: C, 73.81; H, 6.30; N, 6.97.
IR of **1b**·toluene: (KBr, cm^{-1}): 3455.66(b), 2932.64(w), 2201.45(m), 1626.37(s), 1568.87(m), 1527.59(m), 1441.75(m), 1384.17(s), 1348.56(m), 1190.71(m), 1137.78(m), 1019.54(w), 834.31(w), 523.33(m)

3. **Selective binding and Separation experiment**.

A typical Selective binding and Separation experiment: Evacuated sample of **1a** (50 mg) and a mixture of cyclohexane (5 mL) and benzene (5 mL) was put in a sealed vial at 80 ºC for two days. The solid sample was filtered, washed with diethyl ether, and then loaded into a distillation setup and gently heated to under vacuum while the volatiles were collected with a liquid nitrogen bath (see our recent report *Angew. Chem. Int. Ed*. 2008, **47**, 1245 –1249). The recycling and reused experiment was done in the same way.

The molar ratio of desorbed benzene and cyclohexane from **1a** was determined to be 97:3 by using gas chromatography (GC). Conditions Column: SE-54 by Lunan Ruihong Company (30 m × 0.3 mm I.D.). injection port temperature: 120℃; flame ionization detector: 150℃; Column temperature: 36℃. Carrier gas: N2 5.0 mL/min, H2 2.5 mL/min. Retention time were 8.91 min for benzene, 9.48 min for cyclohexane.

The molar ratio of the desorbed toluene and cyclohexane from **1a** was determined to be 98:2 by using GC. Conditions Column: SE-54 by Lunan Ruihong Company (30 m × 0.3 mm I.D.). injection port temperature: 120℃; flame ionization detector: 150℃; Column temperature: 40℃. Carrier gas: N2 5.0 mL/min, H2 2.5 mL/min. Retention time were 6.55 min for cyclohexane, 12.19 min for toluene.

The molar ratio of desorbed toluene and n-heptane from **1a** was determined to be 94:6 by using GC. Conditions Column: SE-54 by Lunan Ruihong Company (30 m × 0.3 mm I.D.). injection port temperature: 120℃; flame ionization detector: 150℃; Column temperature: 42℃. Carrier gas: N2 5.0 mL/min, H2 2.5 mL/min. Retention time were 8.39 min for n-heptane, 11.92 min for toluene.

The molar ratio of desorbed toluene and benzene from **1a** was determined to be 62:38 by using (GC). Conditions Column: SE-54 by Lunan Ruihong Company (30 m × 0.3 mm I.D.). injection port temperature: 120℃; flame ionization detector: 150℃; Column temperature: 40℃. Carrier gas: N2 5.0 mL/min, H2 2.5 mL/min. Retention time were 6.10 min for benzene, 12.36 min for toluene. The result was not reported in the text.

Table S1. Crystal data and structure refinement for **1a**·benzene, **1a**·toluene, **1b** · benzene, **1b**·toluene and **1a**.

Identification code	**1a**·benzene	**1b**·benzene	**1a**·toluene	**1b**·toluene	**1a**
Empirical formula	$C_{96}H_{96}N_8O_4Zn_2$	$C_{96}H_{96}N_8O_4Zn_2$	$C_{91}H_{92}N_8O_4Zn_2$	$C_{94.5}H_{96}N_8O_4Zn_2$	$C_{84}H_{84}N_8O_4Zn_2$
Formula weight	1556.55	1556.55	1492.47	1538.53	1400.33
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	C2	C2	C2	C2	C2
Unit cell dimensions	a = 15.611(3) Å b = 29.312(6) Å c = 18.931(4) Å beta = 103.05(3) º	14.4846(14) 25.908(3) 22.624(2) 92.096(2)	15.5160(14) 28.981(3) 19.4548(18) 103.236(2)	14.929(7) 25.901(12) 22.477(10) 90.000(5)	15.531(2) 29.200(4) 18.945(3) 102.634(2)
Volume ($Å^3$), Z	8439(3), 4	8484.6(14), 4	8515.9 (13), 4	8691(7), 4	8384(2), 4
Density (calculated) (mg/m^3)	1.225	1.219	1.164	1.176	1.109
Absorption coefficient (mm^{-1})	0.624	0.621	0.616	0.605	0.621
F(000)	3280	3280	3144	3244	2944
Theta range for data collection (º)	2.99 to 25.00	2.38 to 25.00	2.03 to 25.00	2.87 to 25.00	2.04 to 25.00
Limiting indices	-18 < h < 17, -34 < k < 34, -22 < l < 22	-17 < h < 13, -29 < k < 30, -23 < l < 26	-18 < h < 18, -31 < k < 34, -14 < l < 23	-17 < h < 16, -27 < k < 30, -26 < l < 26	-18 < h < 18, -34 < k < 24, -22 < l < 22
Reflections collected	29712	22741	22174	18748	21732
Independent reflections	14237 (R_{int} = 0.0660)	14483 (R_{int}= 0.0227)	13580 (R_{int} = 0.0499)	10558 (R_{int} = 0.0620)	10662 (R_{int} = 0.0375)
Completeness to theta	25.00/98.7%	25.00/99.7%	25.00/99.7%	25.00/86.7%	25.00/99.8%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	14237/24/791	14483/17/793	13580/9/797	10558/62/753	10662/8/777
Goodness-of-fit on F^2	1.091	1.095	1.065	0.905	1.126
Final R indices [I>2sigma(I)]	R1=0.0788,wR2=0.1994	R1=0.0673,wR2=0.1588	R1=0.0719,wR2=0.1587	R1=0.0686,wR2=0.1413	R1=0.0622,wR2=0.1681
R indices (all data)	R1=0.1124,wR2=0.2233	R1=0.1143,wR2=0.1863	R1=0.1386,wR2=0.1951	R1=0.1881,wR2=0.1769	R1=0.0864,wR2=0.1866
Absolute structure parameter	0.008(19)	0.09(2)	0.01(2)	0.08(3)	0.014(18)
Largest diff. peak and hole ($e.Å^{-3}$)	0.771 and -0.948	0.612 and -0.358	0.491 and -0.347	0.331 and -0.217	0.812 and -0.528

Table S2. Selected bond lengths [Å] and angles [º] for **1a** · benzene.

Zn(1)-O(1)	1.971(5)
Zn(1)-O(2)	1.995(5)
Zn(1)-N(2)	2.082(7)
Zn(1)-N(3)	2.098(7)
Zn(1)-N(5)#1	2.111(4)
Zn(2)-O(4)	1.950(6)
Zn(2)-O(3)	1.979(5)
Zn(2)-N(6)	2.084(7)
Zn(2)-N(7)	2.101(6)
Zn(2)-N(1)	2.123(4)
O(1)-Zn(1)-O(2)	96.6(2)
O(1)-Zn(1)-N(2)	155.1(2)
O(2)-Zn(1)-N(2)	87.0(2)
O(1)-Zn(1)-N(3)	88.3(2)
O(2)-Zn(1)-N(3)	155.2(2)
N(2)-Zn(1)-N(3)	78.8(2)
O(1)-Zn(1)-N(5)#1	99.7(2)
O(2)-Zn(1)-N(5)#1	99.8(2)
N(2)-Zn(1)-N(5)#1	104.0(2)
N(3)-Zn(1)-N(5)#1	103.3(2)
O(4)-Zn(2)-O(3)	98.6(2)
O(4)-Zn(2)-N(6)	167.5(2)
O(3)-Zn(2)-N(6)	86.8(2)
O(4)-Zn(2)-N(7)	89.3(2)
O(3)-Zn(2)-N(7)	139.0(2)
N(6)-Zn(2)-N(7)	79.4(2)
O(4)-Zn(2)-N(1)	94.4(2)
O(3)-Zn(2)-N(1)	105.7(2)
N(6)-Zn(2)-N(1)	94.9(2)
N(7)-Zn(2)-N(1)	113.8(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 x,y,z-1

Table S3. Selected bond lengths [Å] and angles [º] for **1b** · benzene.

Zn(1)-O(2)	1.959(6)
Zn(1)-O(1)	2.017(7)
Zn(1)-N(3)	2.098(8)
Zn(1)-N(2)	2.111(7)
Zn(1)-N(8)#1	2.11(5)
Zn(2)-O(3)	1.975(7)
Zn(2)-O(4)	2.000(6)
Zn(2)-N(6)	2.079(8)
Zn(2)-N(7)	2.108(7)
Zn(2)-N(1)	2.116(4)
O(2)-Zn(1)-O(1)	97.6(3)
O(2)-Zn(1)-N(3)	144.4(3)
O(1)-Zn(1)-N(3)	88.1(3)
O(2)-Zn(1)-N(2)	88.2(3)
O(1)-Zn(1)-N(2)	163.5(3)
N(3)-Zn(1)-N(2)	78.4(3)
O(2)-Zn(1)-N(8)#1	105(2)
O(1)-Zn(1)-N(8)#1	97(2)
N(3)-Zn(1)-N(8)#1	109(2)
N(2)-Zn(1)-N(8)#1	97(2)
O(3)-Zn(2)-O(4)	97.7(3)
O(3)-Zn(2)-N(6)	156.7(3)
O(4)-Zn(2)-N(6)	87.4(3)
O(3)-Zn(2)-N(7)	86.9(3)
O(4)-Zn(2)-N(7)	153.4(3)
N(6)-Zn(2)-N(7)	78.9(3)
O(3)-Zn(2)-N(1)	99.4(2)
O(4)-Zn(2)-N(1)	101.6(2)
N(6)-Zn(2)-N(1)	101.8(3)
N(7)-Zn(2)-N(1)	103.4(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 x,y,z+1
#3 -x+1,y,-z+1 #4 -x+1,y,-z+2

Table S4. Selected bond lengths [Å] and angles [º] for **1a** · toluene.

Zn(1)-O(1)	1.964(6)
Zn(1)-O(2)	2.003(7)
Zn(1)-N(4)	2.096(7)
Zn(1)-N(3)	2.100(7)
Zn(1)-N(5)#1	2.112(5)
Zn(2)-O(4)	1.970(6)
Zn(2)-O(3)	1.980(6)
Zn(2)-N(7)	2.071(7)
Zn(2)-N(6)	2.094(8)
Zn(2)-N(1)	2.126(5)
O(1)-Zn(1)-O(2)	97.8(3)
O(1)-Zn(1)-N(4)	87.9(3)
O(2)-Zn(1)-N(4)	155.3(3)
O(1)-Zn(1)-N(3)	152.5(3)
O(2)-Zn(1)-N(3)	86.2(3)
N(4)-Zn(1)-N(3)	78.2(3)
O(1)-Zn(1)-N(5)#1	101.2(3)
O(2)-Zn(1)-N(5)#1	99.9(3)
N(4)-Zn(1)-N(5)#1	102.5(3)
N(3)-Zn(1)-N(5)#1	104.9(3)
O(4)-Zn(2)-O(3)	97.7(3)
O(4)-Zn(2)-N(7)	89.1(3)
O(3)-Zn(2)-N(7)	142.2(3)
O(4)-Zn(2)-N(6)	166.3(3)
O(3)-Zn(2)-N(6)	88.3(3)
N(7)-Zn(2)-N(6)	78.8(3)
O(4)-Zn(2)-N(1)	93.9(3)
O(3)-Zn(2)-N(1)	105.3(3)
N(7)-Zn(2)-N(1)	111.3(3)
N(6)-Zn(2)-N(1)	96.3(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 x,y,z+1

Table S5. Selected bond lengths [Å] and angles [º] for **1b** · toluene.

Zn(1)-O(4)	1.944(12)
Zn(1)-O(3)	2.014(12)
Zn(1)-N(1)	2.075(7)
Zn(1)-N(7)	2.078(15)
Zn(1)-N(6)	2.082(13)
Zn(2)-O(1)	1.873(14)
Zn(2)-O(2)	2.009(11)
Zn(2)-N(3)	2.070(17)
Zn(2)-N(2)	2.102(13)
Zn(2)-N(5)#1	2.131(8)
O(4)-Zn(1)-O(3)	94.5(5)
O(4)-Zn(1)-N(1)	96.8(5)
O(3)-Zn(1)-N(1)	102.1(4)
O(4)-Zn(1)-N(7)	91.9(5)
O(3)-Zn(1)-N(7)	153.0(5)
N(1)-Zn(1)-N(7)	103.2(5)
O(4)-Zn(1)-N(6)	153.2(5)
O(3)-Zn(1)-N(6)	87.3(5)
N(1)-Zn(1)-N(6)	109.0(5)
N(7)-Zn(1)-N(6)	75.6(6)
O(1)-Zn(2)-O(2)	98.5(6)
O(1)-Zn(2)-N(3)	146.0(6)
O(2)-Zn(2)-N(3)	87.5(6)
O(1)-Zn(2)-N(2)	86.8(6)
O(2)-Zn(2)-N(2)	162.7(5)
N(3)-Zn(2)-N(2)	79.2(6)
O(1)-Zn(2)-N(5)#1	104.0(5)
O(2)-Zn(2)-N(5)#1	98.2(4)
N(3)-Zn(2)-N(5)#1	108.2(6)
N(2)-Zn(2)-N(5)#1	96.4(4)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 x,y,z-1
#3 -x+1,y,-z+1

Table S6. Selected bond lengths [Å] and angles [º] for **1a**.

Zn(1)-O(1)	1.944(5)
Zn(1)-O(2)	1.998(5)
Zn(1)-N(2)	2.089(6)
Zn(1)-N(3)	2.089(6)
Zn(1)-N(5)#1	2.113(4)
Zn(2)-O(3)	1.959(5)
Zn(2)-O(4)	1.962(5)
Zn(2)-N(7)	2.082(6)
Zn(2)-N(6)	2.086(6)
Zn(2)-N(1)	2.094(4)
O(1)-Zn(1)-O(2)	96.7(2)
O(1)-Zn(1)-N(2)	154.5(2)
O(2)-Zn(1)-N(2)	87.2(2)
O(1)-Zn(1)-N(3)	88.8(2)
O(2)-Zn(1)-N(3)	155.3(2)
N(2)-Zn(1)-N(3)	78.1(2)
O(1)-Zn(1)-N(5)#1	100.3(2)
O(2)-Zn(1)-N(5)#1	99.4(2)
N(2)-Zn(1)-N(5)#1	103.9(2)
N(3)-Zn(1)-N(5)#1	103.3(2)
O(3)-Zn(2)-O(4)	98.2(2)
O(3)-Zn(2)-N(7)	140.4(2)
O(4)-Zn(2)-N(7)	88.8(2)
O(3)-Zn(2)-N(6)	88.1(2)
O(4)-Zn(2)-N(6)	166.6(2)
N(7)-Zn(2)-N(6)	78.9(2)
O(3)-Zn(2)-N(1)	105.2(2)
O(4)-Zn(2)-N(1)	95.2(2)
N(7)-Zn(2)-N(1)	113.0(2)
N(6)-Zn(2)-N(1)	94.6(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 x,y,z-1

Table S7. A comparison of chain repeated periods and turning angles of 1D polymer in **1**.

	Adjacent Zn···Zn separation (Å)[a]	repeated period (Å) [b]	turning angle (°)	Chain diameter (Å)
1a·benzene	14.466(2) 14.477(2)	18.931(4)	81.703(3)	36.99
1a·toluene	14.522(1) 14.540(1)	19.455(2)	84.047(1)	36.59
1a	14.423(2) 14.410(2)	18.945(3)	82.155(2)	36.50
1b·benzene	14.598(1) 14.607(1)	22.624(2)	101.552(1)	35.83
1b·toluene	14.524(5) 14.531(5)	22.477(10)	101.358(7)	35.08

Table S8. A comparison of twisted angles and lengths of Zn**L** ligands in **1**.

	lengths of Zn**L** (Å)	twisted angles N (°)	dihedral angles of two pyridines (°)
1a·benzene	24.442(4) 24.451(4)	160.441(4) 160.223(4)	37.32 35.85
1a·toluene	24.617(2) 24.628(2)	163.824(2) 164.405(2)	17.78 19.94
1a	24.414 (3) 24.364 (3)	163.287(3) 160.609(3)	21.22 20.73
1b·benzene	23.991(2) 24.067(2)	147.763(3) 148.675(2)	9.81 7.02
1b·toluene	23.890(8) 24.107(8)	150.907(10) 154.575(10)	10.25 14.14

Figure S1. Ball-and-stick (top) and space-filling (bottom) representations of a 1D zigzag chain of **1a**.

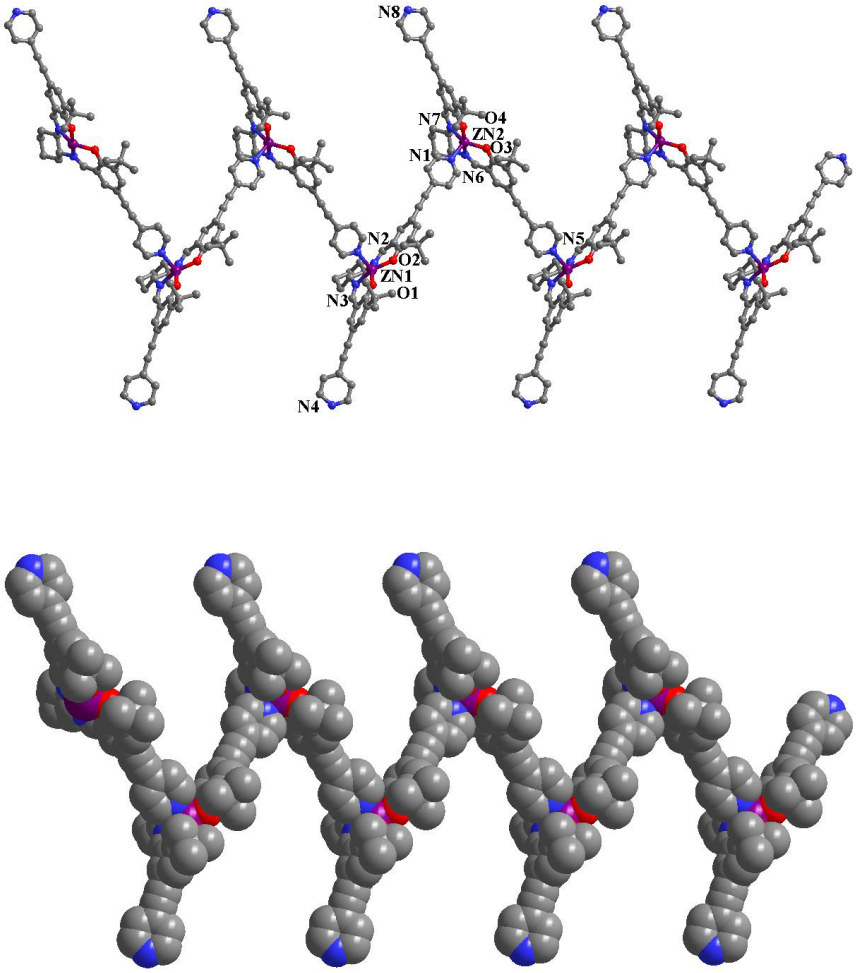

Figure S2. Ball-and-stick representations of a 1D zigzag chain of **1a**·benzene.

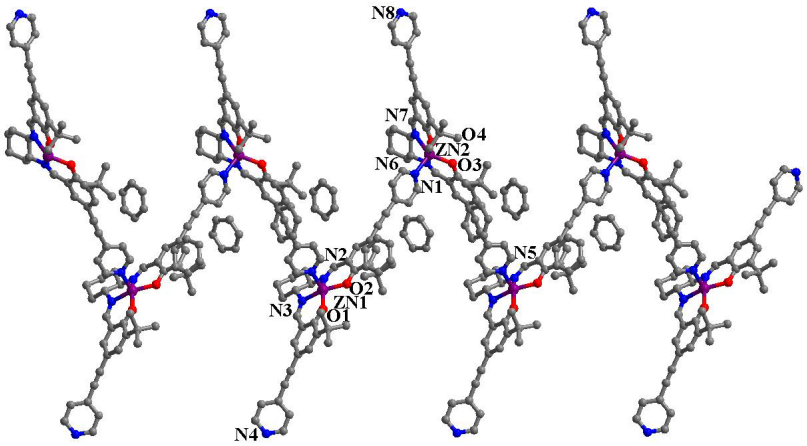

Figure S3. Ball-and-stick representations of a 1D zigzag chain of **1a**·toluene.

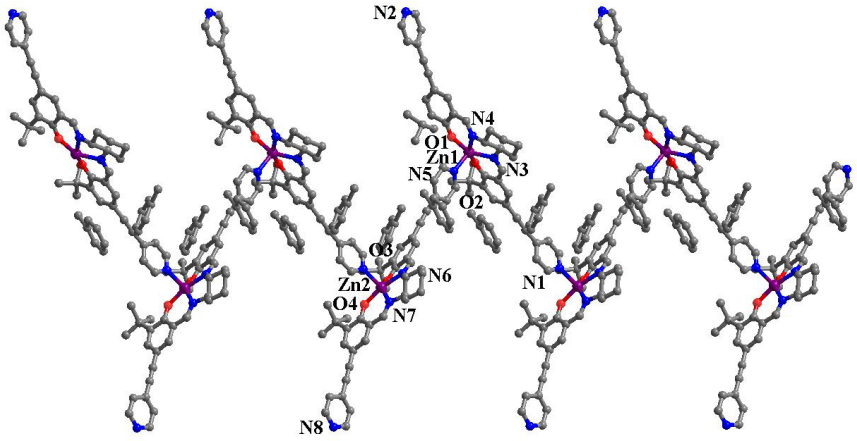

Figure S4. Ball-and-stick representations of a 1D zigzag chain of **1b**·benzene.

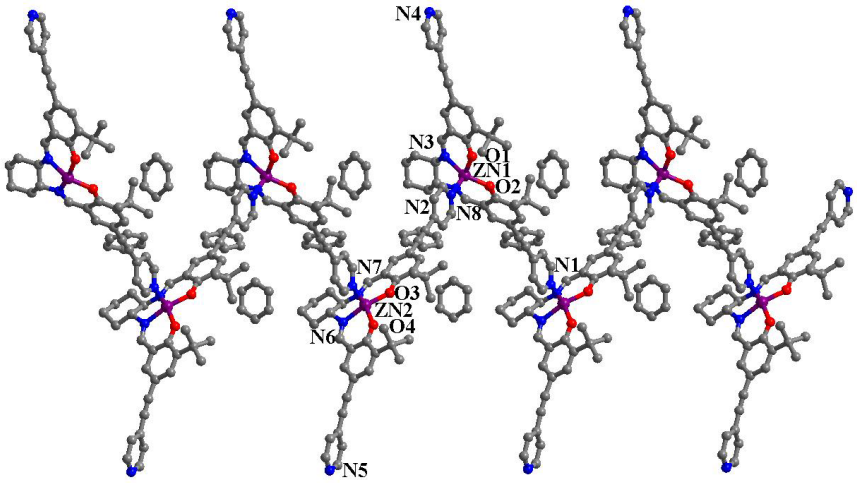

Figure S5. Ball-and-stick representations of a 1D zigzag chain of **1b**·toluene.

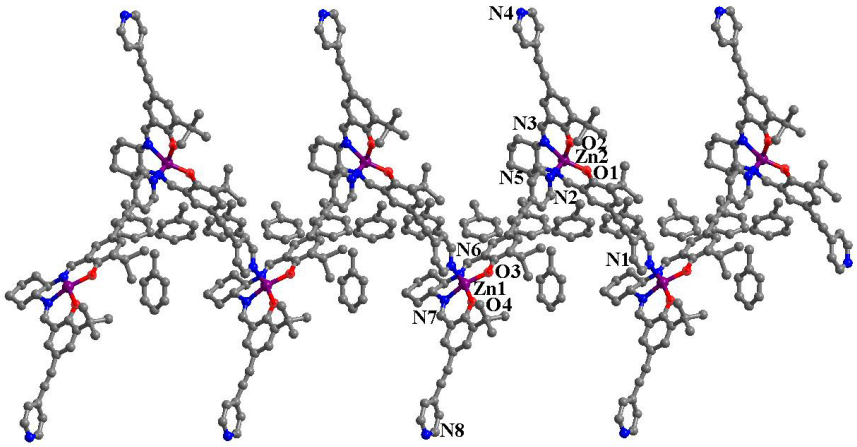

Figure S6. CH · · · π interactions between the Zn**L** ligand and the guest benzene in **1a**·benzene.

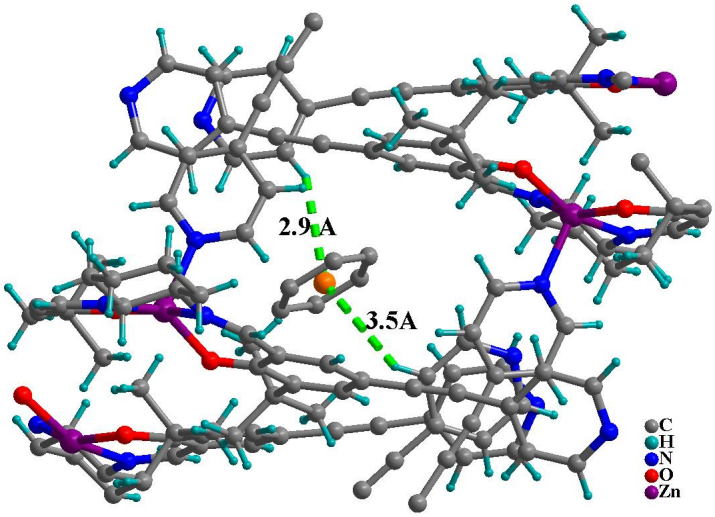

Figure S7. CH · · · π interactions between the Zn**L** ligand and the guest toluene in **1a**·toluene.

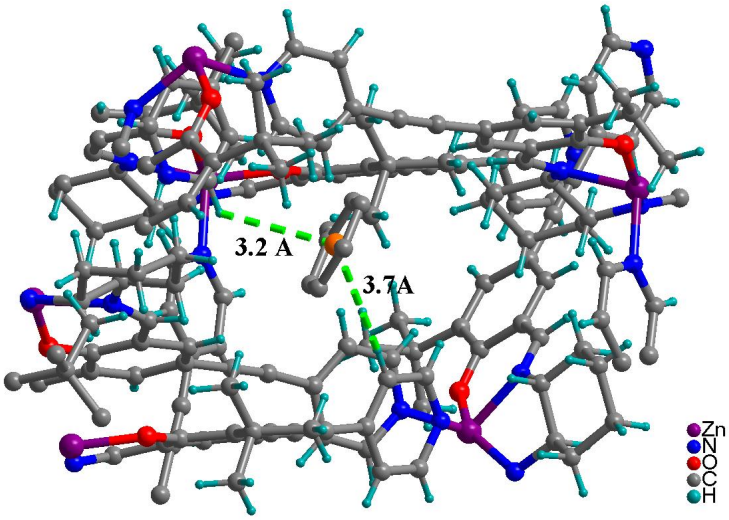

Figure S8. CH · · · π interactions between the Zn**L** ligand and the guest benzene in **1b**·benzene.

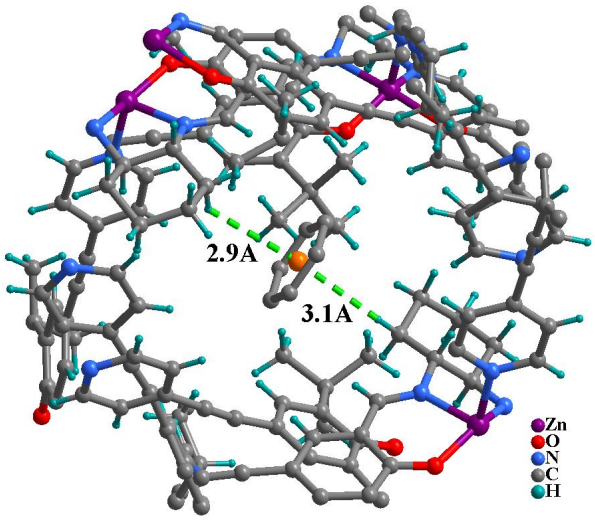

Figure S9. CH···π interactions between the Zn**L** and the guest toluene of **1b**·toluene.

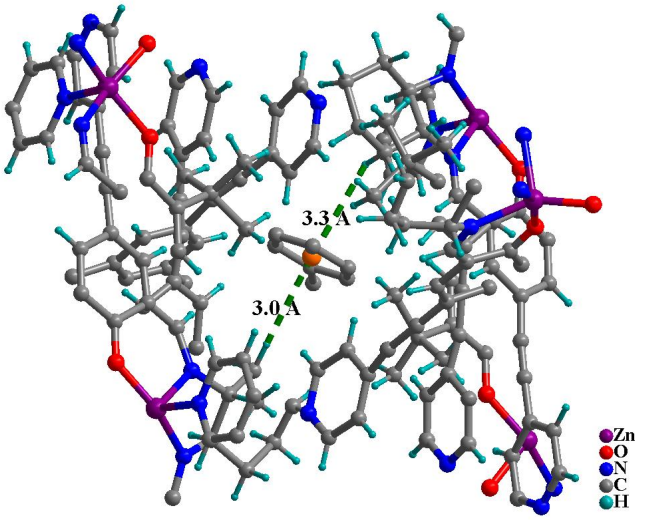

Figure S10. Intermolecular π-π interaction between **1a** in the three compounds.

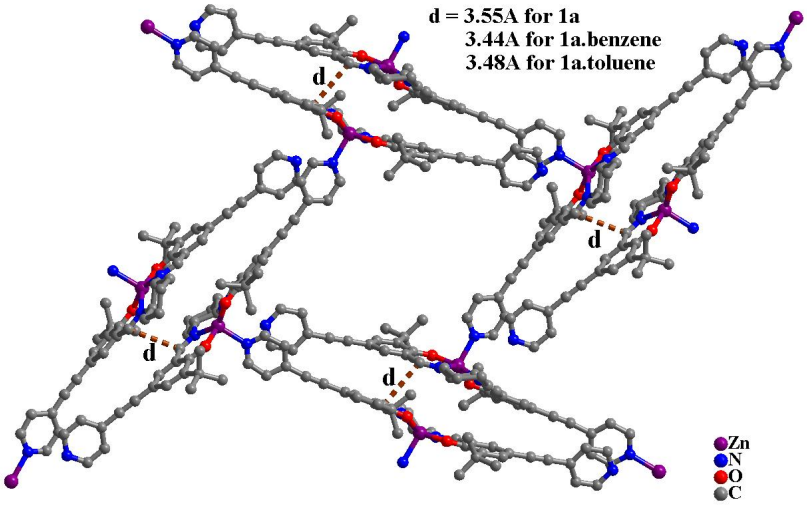

Figure S11. Intermolecular π-π interaction between **1b** in the two compounds.

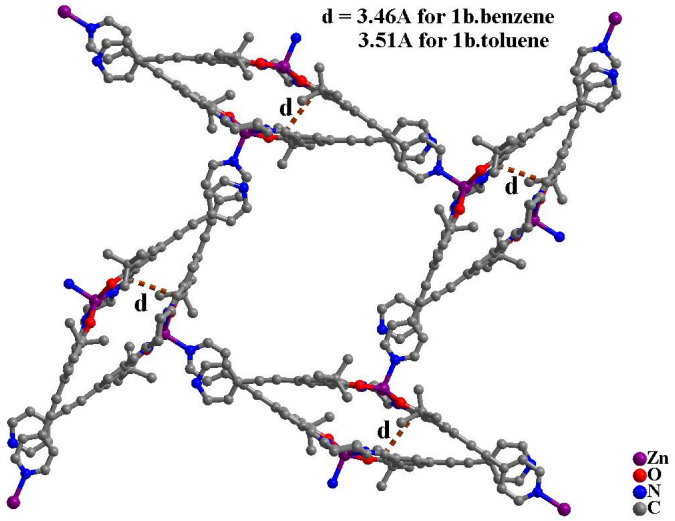

Figure S12. interlamellar C≡C···C≡C interactions between **1a** in the three compounds.

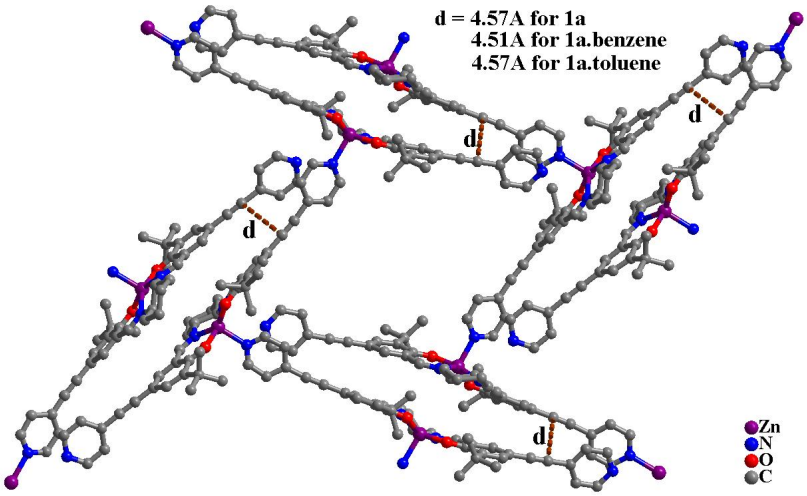

Figure S13. interlamellar C≡C···C≡C interactions between **1b** in the two compounds.

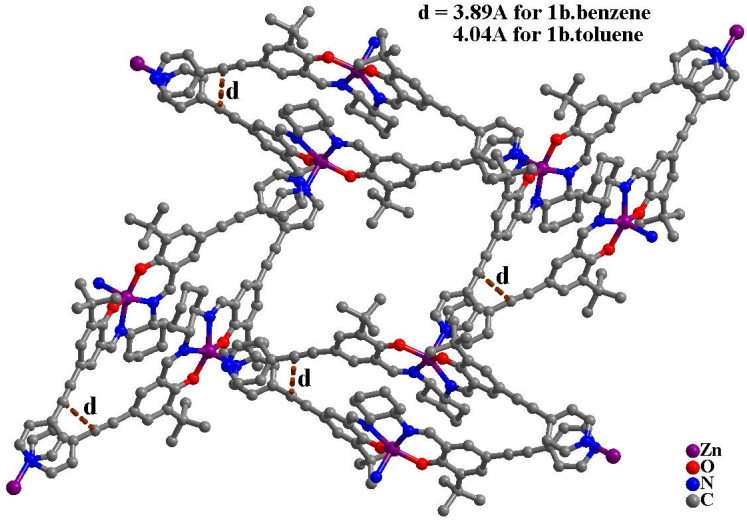

Figure S14. A view of the packing of **1a** along the a-axis forming 2D structures and its space-filling mode.

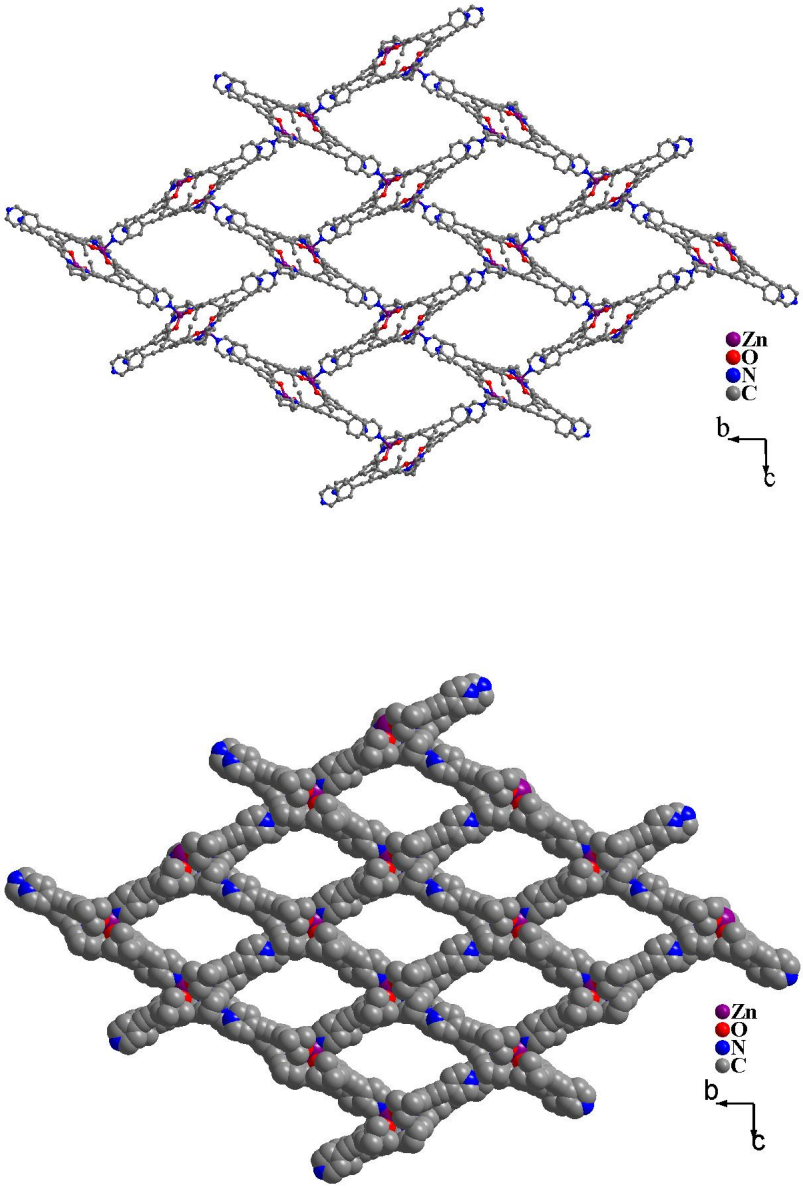

Figure S15. A view of the packing of **1b** along the a-axis forming 2D structures and its space-filling mode.

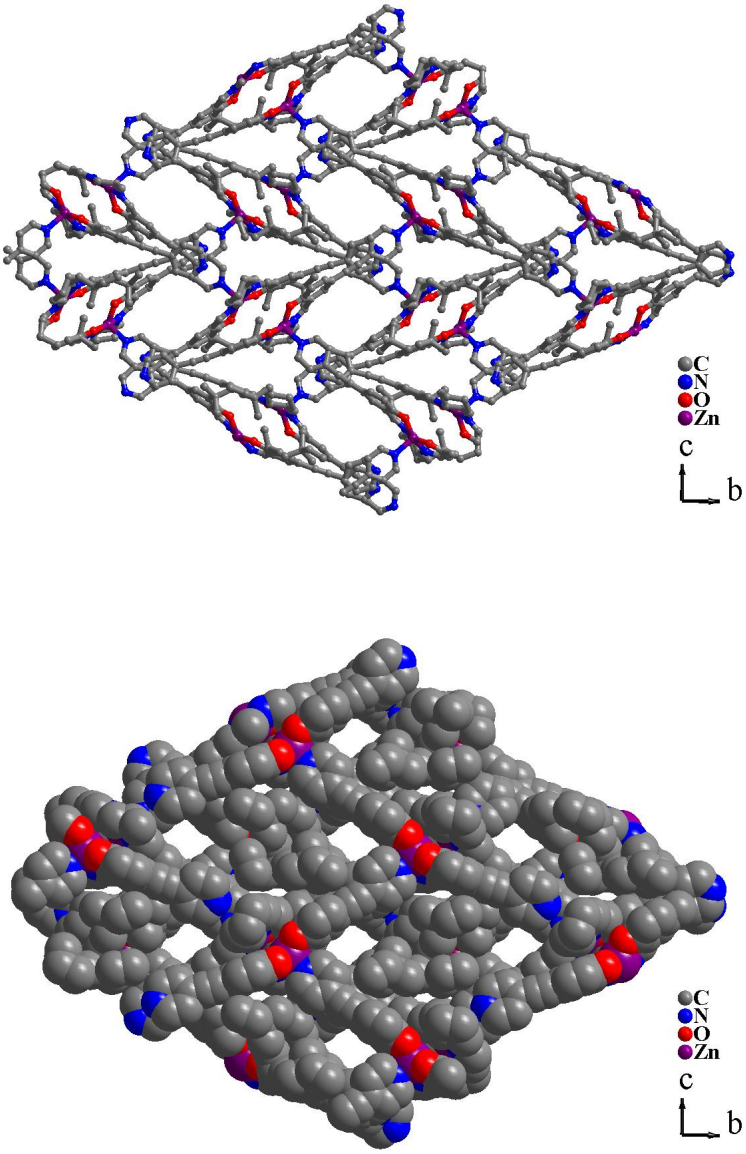

Figure S16. A view of 3D structure of **1a**·toluene along the a-axis and its space-filling mode.

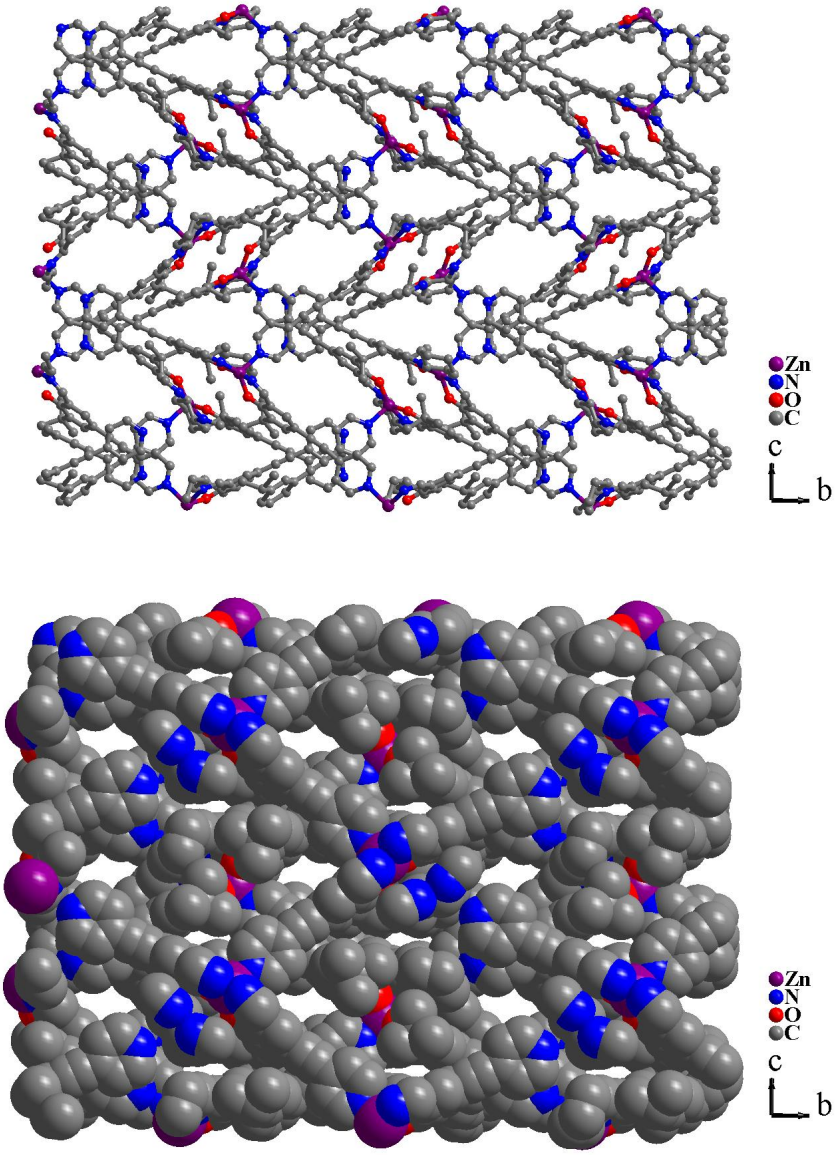

Figure S17. A view of 3D structure of **1b**·toluene along the a-axis and its space-filling mode.

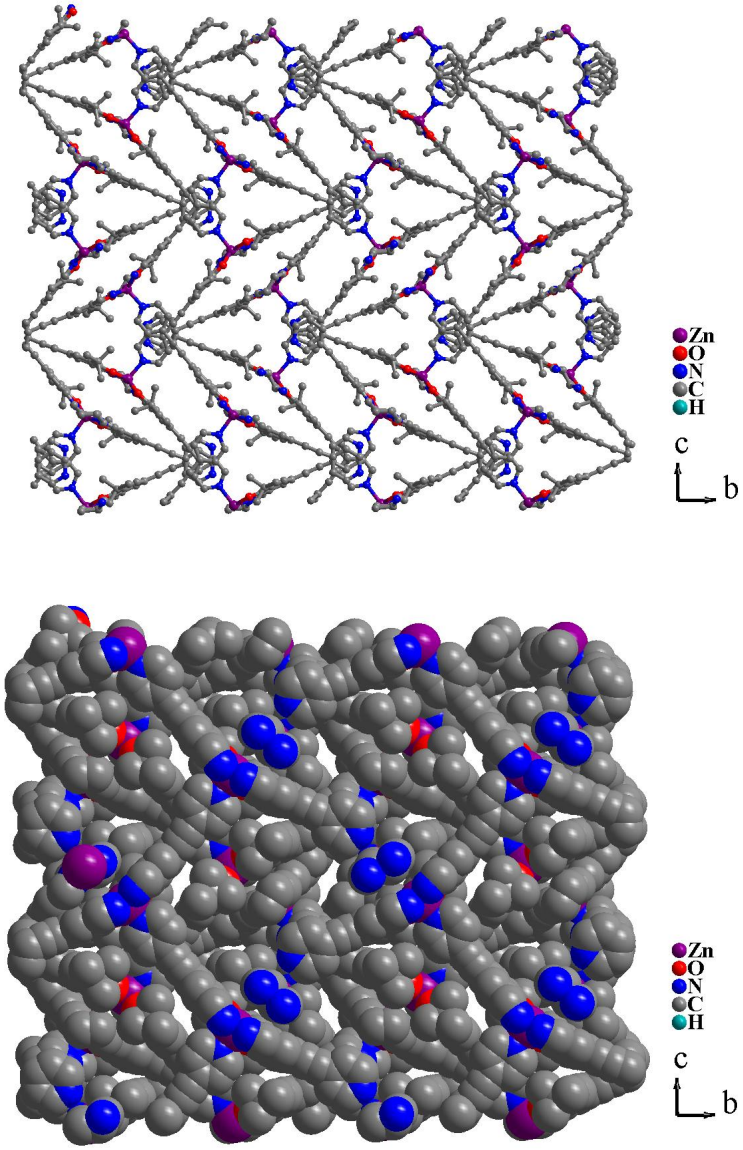

Figure S18. The PXRD pattern and the simulated PXRD pattern of **1a**.

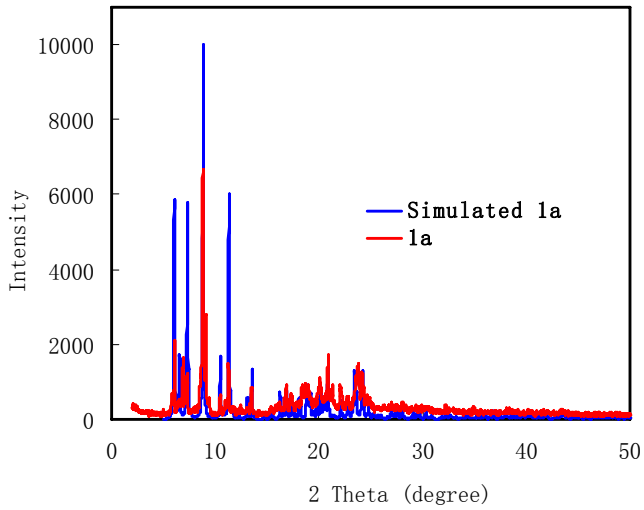

Figure S19. The PXRD pattern and the simulated PXRD pattern of **1a**·benzene.

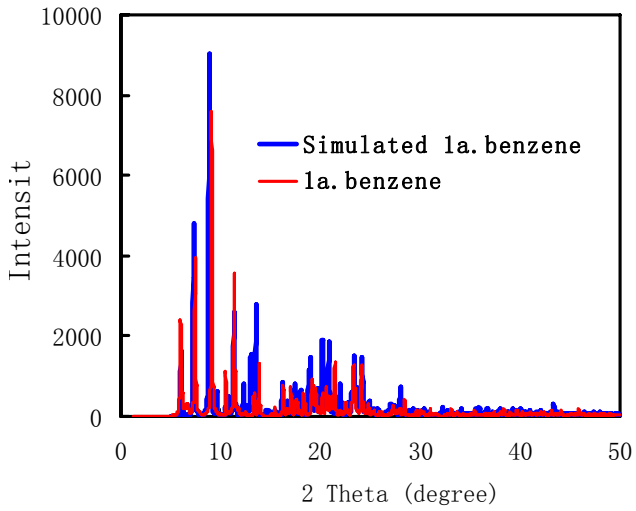

Figure S20. The PXRD pattern and the simulated PXRD pattern of **1a**·toluene.

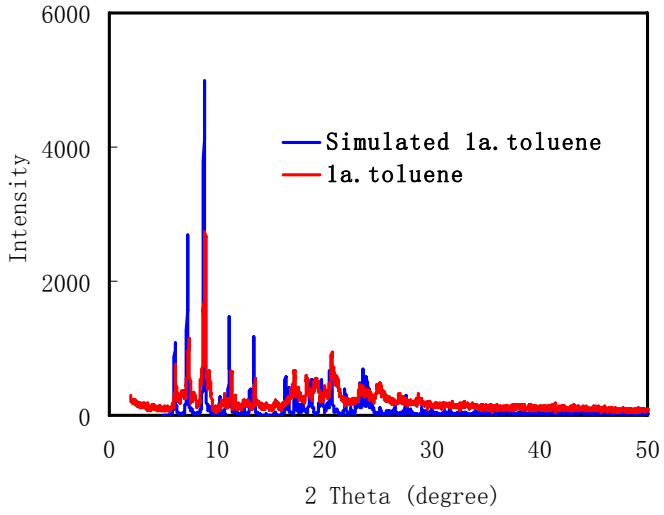

Figure S21. The PXRD pattern and the simulated PXRD pattern of **1b**·benzene.

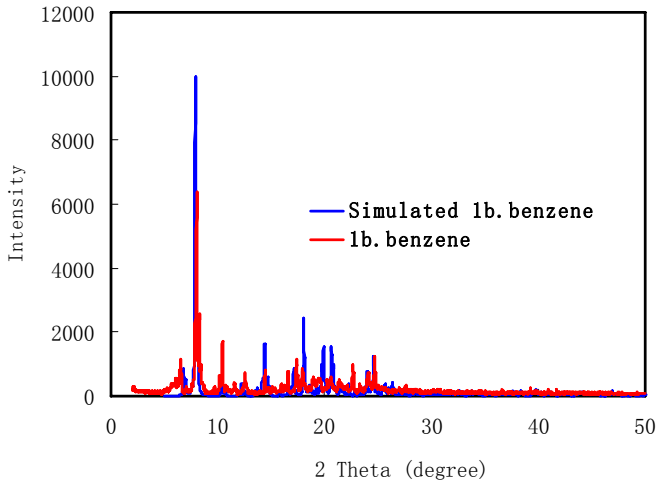

Figure S22. The PXRD pattern and the simulated PXRD pattern of **1b**·toluene.

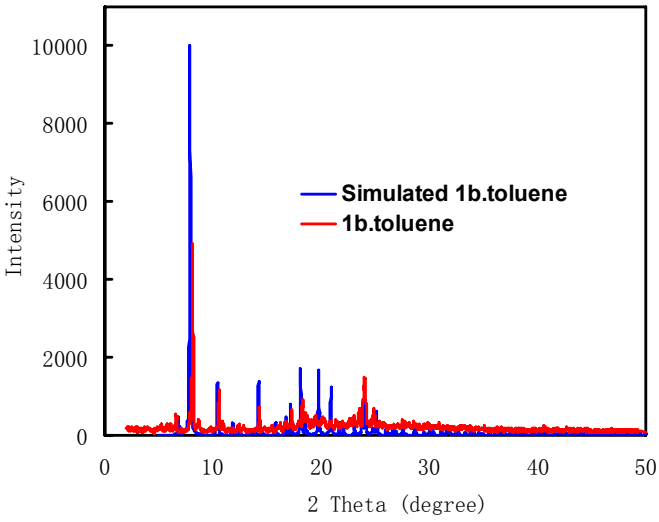

Figure S23. TGA curve of **1a**, **1a**·benzene, **1a**·toluene**, 1b**·benzene and **1b**·toluene.

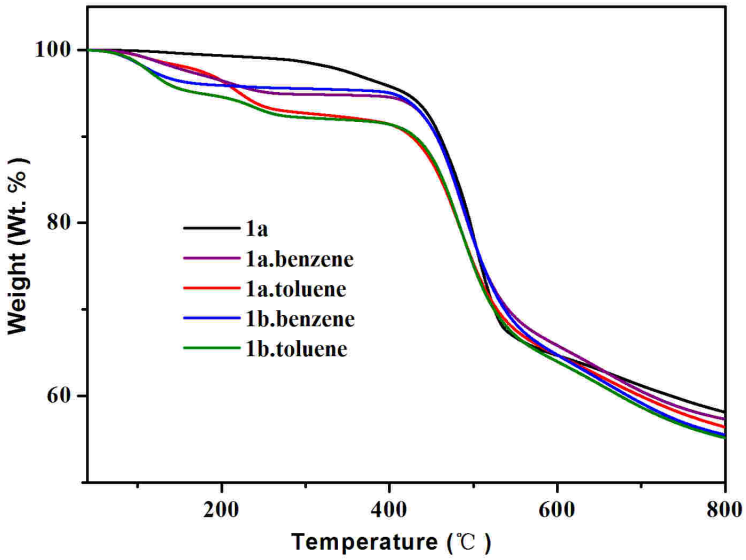

Figure S24. GC result of competing binding experimental of **1a** for benzene /cyclohexane, toluene/cyclohexane, toluene/heptane and benzne.toluene.

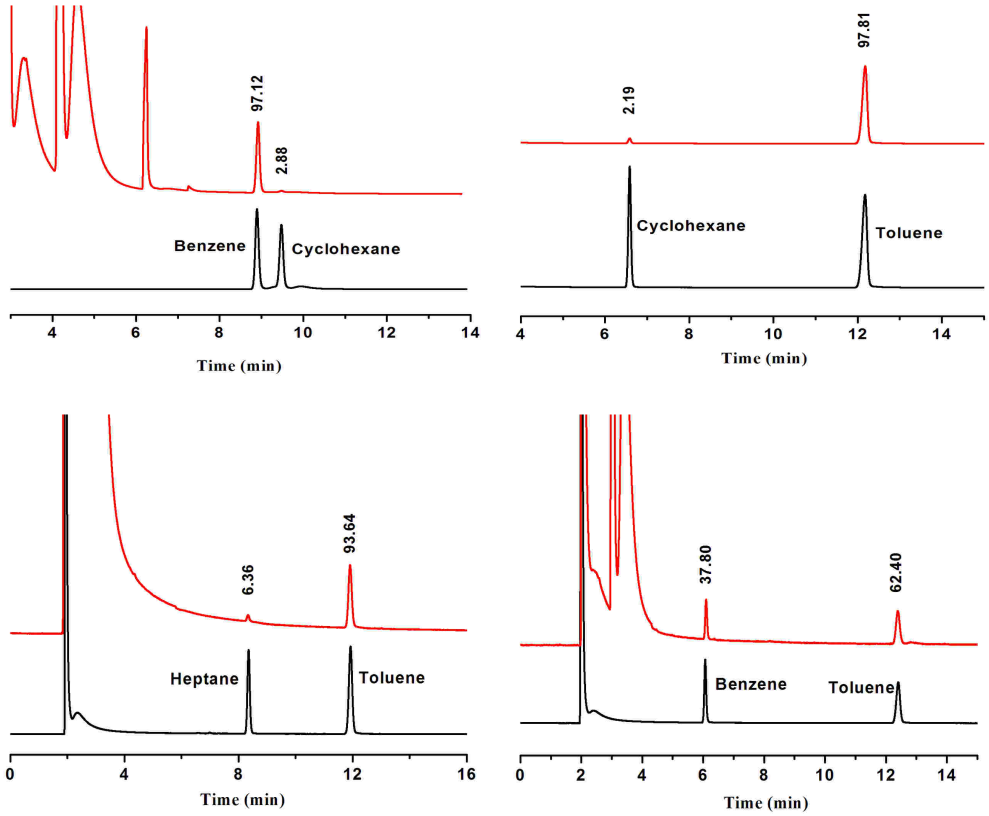

Figure S25. GC results of recycling and reuse of **1a** for adsorption separation of benzene and cyclohexane.

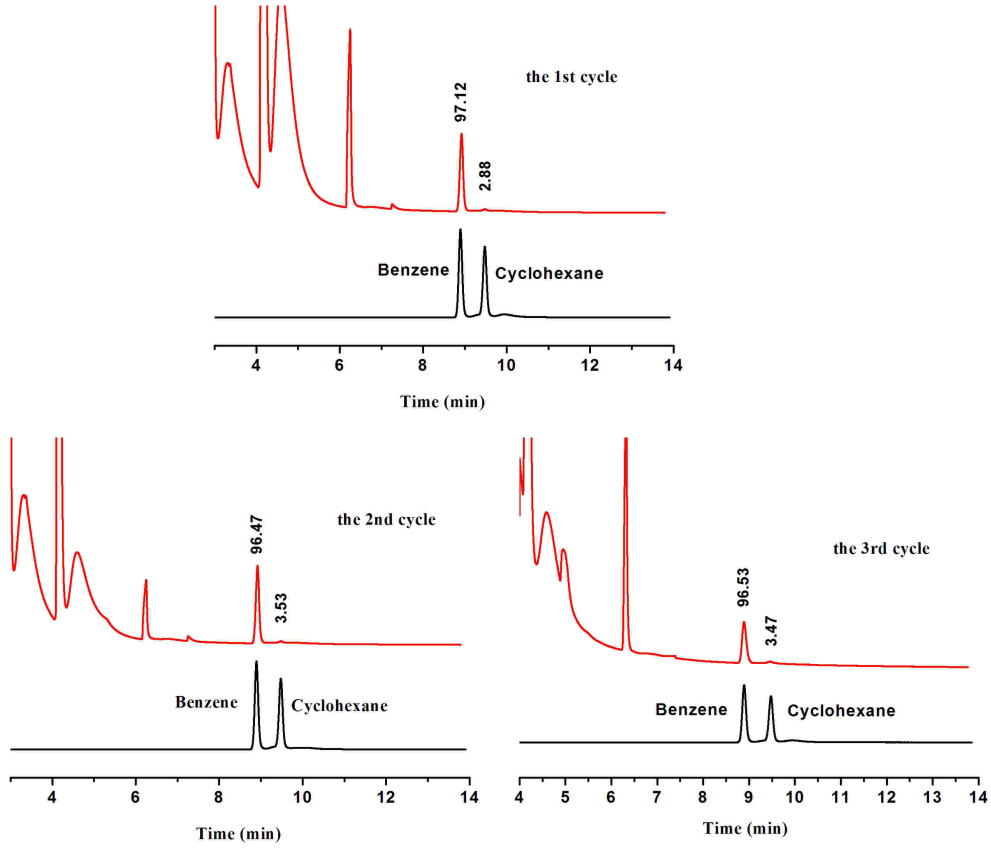

Figure S26. GC result of competing binding experimental of **1a** in the mixture ratios (1:10) of the benzene/cyclohexane.

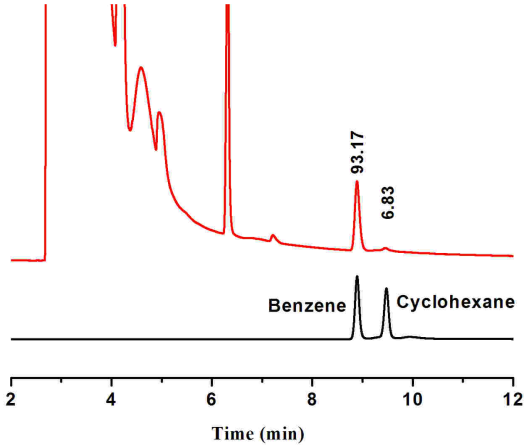

Figure S27. BET data of **1a**.

Relative Pressure (P/Po)	Quantity Adsorbed (cm^2/g)	1/[Q(Po/P - 1)]
0.058180934	0.1298	0.475864
0.100267346	0.1697	0.656644
0.169071019	0.1752	1.161275
0.219039482	0.1442	1.944540
0.269000174	0.0997	3.691935

BET Surface Area: 0.3240 m^2/g
Langmuir Surface Area: 0.4369 m^2/g

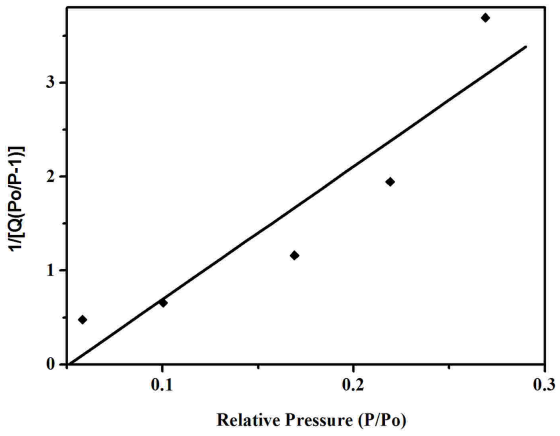

Figure S28. Adsorption and desorption isotherms for Cyclohexane, Benzene and Toluene in **1a**.