Supramolecular organic frameworks of a Schiff-base showing selective guest adsorption

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Supporting information

S1. Synthesis and characterization for 1

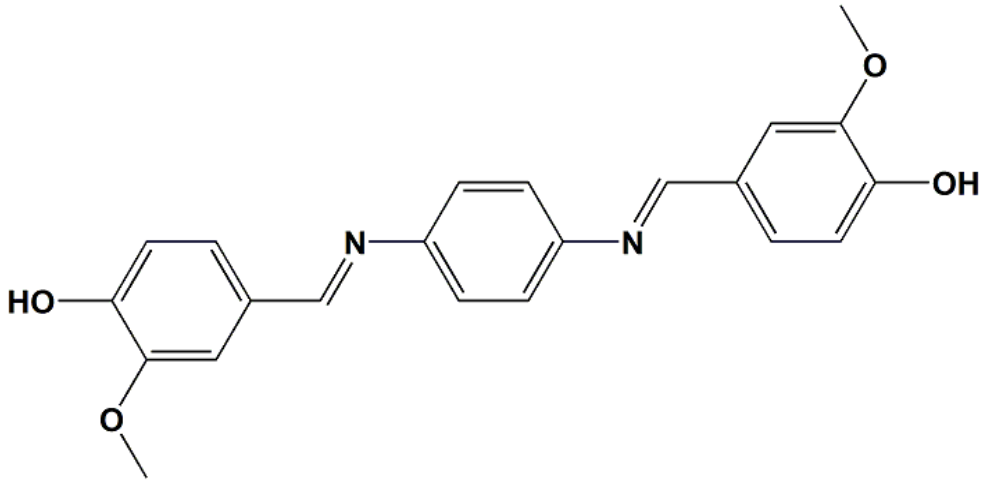

Figure S1 The chemical structure of the Schiff base compound **1**

Organic synthesis of **1**: 4-hydroxy-3-methoxybenzaldehyde (3.04 g, 20 mmol) and *p*-phenylenediamine (1.06 g, 9.8 mmol) was added to a 100 ml round bottom flask, to which 50 ml of methanol was added and the reaction mixture was refluxed for overnight under nitrogen before allowed to cool to room temperature. The reaction progress was monitored by TLC. After completion the volume of reaction mixture was reduced to half by rotary evaporation. Large amount solids appeared upon adding 15 ml of CH_2Cl_2-Et_2O (4:1, v/v). The solids were filtered and washed with ethanol and ether followed by column chromatography on silica gel with dicloromethane as eluent to afford the product as a pale yellow solid. Yield: 3.51g, 95%.

Procedure for crystal growth: single crystals were obtained using the vapour diffusion method.

1-2CHCl3: Vapour diffusion of diethyl ether into concentrated chloroform solution of 1.

1-THF (THF = tetrahydrofuran): Vapour diffusion of diethyl ether into a concentrated THF solution of 1.

1-C6H6 (C6H6 = benzene): Vapour exchange between benzene and a chloroform solution of 1 afforded single crystals 1-C6H6.

1-bpy (bpy = 4,4′ -bipyridine): Vapour diffusion of diethyl ether into a concentrated chloroform solution of 1 and 4,4′ -bipyridine (in a 1:1 molar ratio).

1-py (py = pyridine): Vapour diffusion of diethyl ether into a concentrated pyridine solution of 1.

1: ^{1}H NMR (500 MHz, DMSO): δ = 9.73 (s, 2H), 8.513 (s, 2H), 7.542 (s, 2H), 7.349 (d, J = 8.0 Hz, 2H), 7.279 (s, 4H), 6.908(d, J = 8.0 Hz, 2H), 3.857 (s, 6H). ^{13}C NMR (500 MHz, DMSO): δ = 164.1, 155.1, 153.1, 134.3, 129.5, 126.9, 120.1, 115.0, 60.5, 59.3. MS: m/z (%): 376.2 (100) [M^{+}]; elemental analysis (%): calcd for $C_{22}H_{20}N_2O_4$: C: 70.20, H: 5.36, N: 7.44; found: C: 69.73, H: 5.62, N: 7.17.

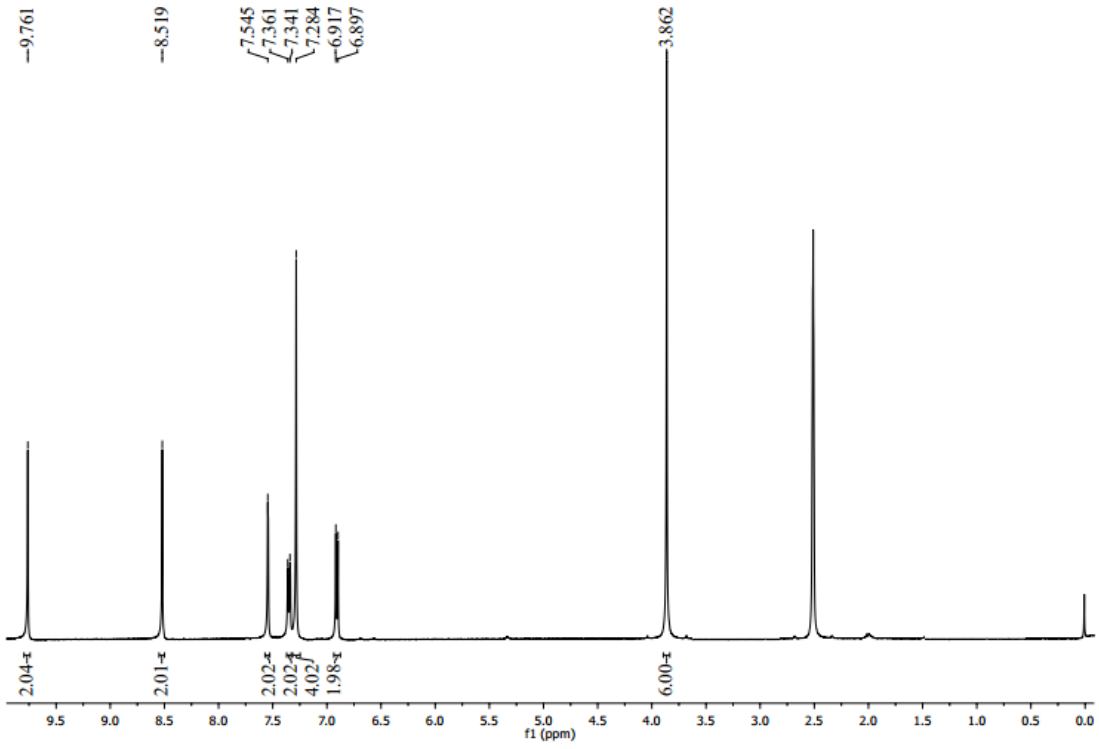

Figure S2 1H NMR spectrum of the Schiff base compound **1**

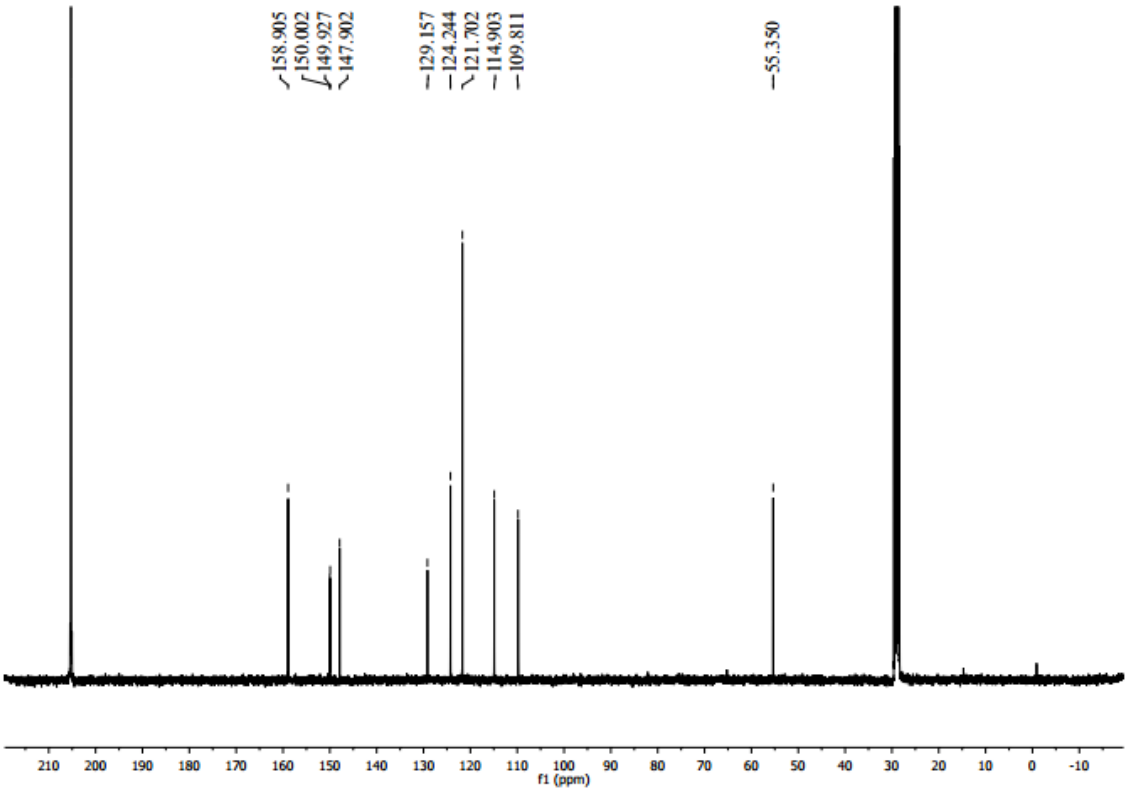

Figure S3 13C NMR spectrum of the Schiff base compound **1**

S2. Crystallographic data and drawings

Crystal data for **1**-C_6H_6: $C_{28}H_{26}N_2O_4$, M = 454.51, monoclinic, space group $P2_1/n$, a = 5.9038 (4), b = 10.7455 (8), c = 19.4895 (11) Å, β = 90.263 (2)° (10), V = 1236.39 (14) Å^3, Z = 2, μ(MoK$_\alpha$) = 0.082 mm^{-1}, F(000) = 480, 10582 total reflections, 2813 independent reflections, R_1 = 0.0555 (all data), wR_2 = 0.1164 (all data), GOF(F^2) = 0.986.

Crystal data for **1**-2$CHCl_3$: $C_{24}H_{22}N_2O_4Cl_6$, M = 615.4, monoclinic, space group $P2_1/n$, a = 6.8524 (3), b = 11.9655 (5), c = 17.3274 (8) Å, β = 99.6780° (11), V = 1400.50 (11) Å^3, Z = 2, μ(MoK$_\alpha$) = 0.646 mm^{-1}, F(000) = 628, 8217 total reflections, 3190 independent reflections, R_1 = 0.099 (all data), wR_2 = 0.182 (all data), GOF(F^2) = 0.933.

Crystal data for **1**-THF: $C_{26}H_{28}N_2O_5$, M = 448.50, monoclinic, space group $P2_1/c$, a = 13.2363 (9), b = 11.7650 (8), c = 17.6353 (9) Å, β = 103.2810° (10), V = 2672.8 (3) Å^3, Z = 4, μ(MoK$_\alpha$) = 0.078 mm^{-1}, F(000) = 952, 17652 total reflections, 6100 independent reflections, R_1 = 0.1243 (all data), wR_2 = 0.3038 (all data), GOF(F^2) = 1.109.

Crystal data for **1**-BPY: $C_{32}H_{28}N_4O_4$, M = 532.6, monoclinic, space group P2/c, a = 12.8209(9), b = 7.0395(4), c = 14.7623(7) Å, β = 96.820°(3), V = 1322.91(13) Å^3, Z = 2, μ(MoK$_\alpha$) = 0.090 mm^{-1},

F(000) = 560, 2967 independent reflections, R_1 = 0.108 (all data), wR_2 = 0.195 (all data), GOF(F^2) = 1.049.

All of the crystallographic data collection was performed on an MAR diffractmeter with a 300 mm image plate detector(λ = 0.71073 Å).

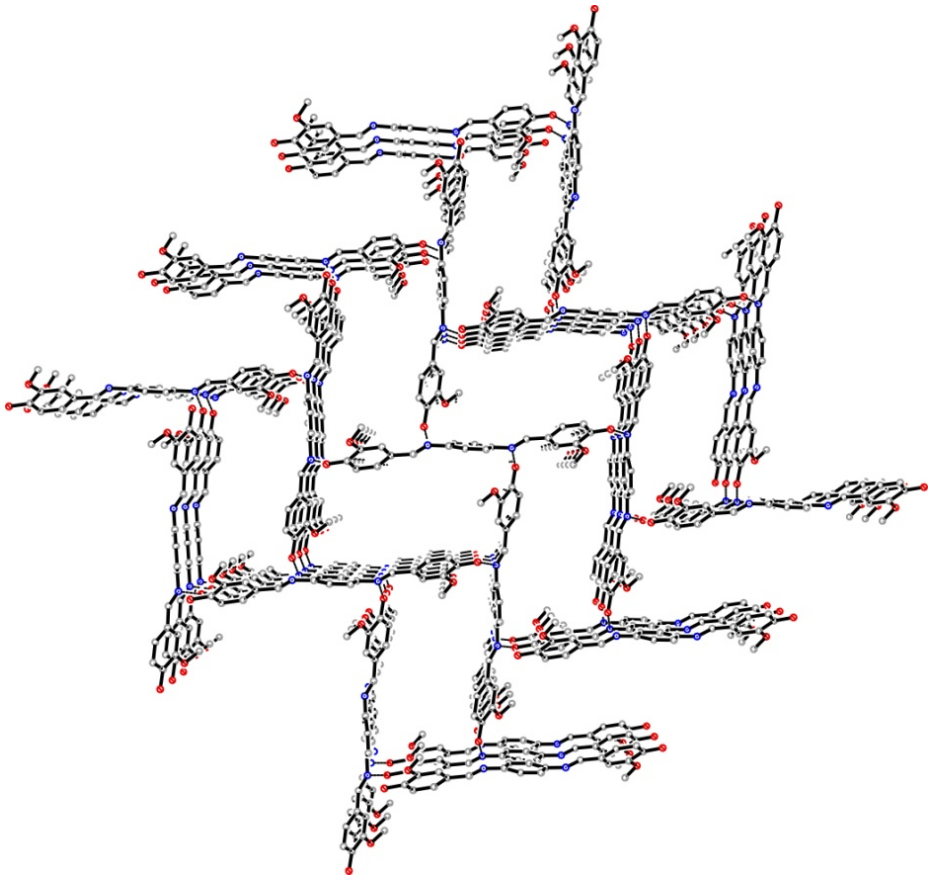

Figure S4 The supramolecular two-dimensional crystal lattice packed by **1**, The guest molecules and hydrogen atoms were omitted for clarity

S2.1. 1-2$CHCl_3$ (CCDC 212053)

Table S1 Crystal data and structure refinement for **1**-2$CHCl_3$

Empirical formula	$C_{24}H_{22}Cl_6N_2O_4$
Formula weight	615.14
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 6.8524(3) Å α= 90º

	b = 11.9655(5) Å β= 99.6780(11)º
	c = 17.3274(8) Å γ= 90º
Volume	1400.50(11) $Å^3$
Z, Calculated density	2, 1.459 Mg/m^3
Absorption coefficient	0.646 mm^{-1}
F(000)	628
Crystal size	0.36 x 0.25 x 0.20 mm
θ range for data collection	2.08º - 27.46º
Limiting indices	0<=h<=8, 0<=k<=15, -22<=l<=22
Reflections collected / unique	8217 / 3190 [R(int) = 0.0240]
Completeness to θ = 27.46	99.5 %
Max. and min. transmission	0.8816 and 0.8006
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3190 / 0 / 231
Goodness-of-fit on F^2	0.933
Final R indices [I>2sigma(I)]	R1 = 0.0592, wR2 = 0.1657
R indices (all data)	R1 = 0.0990, wR2 = 0.1826
Largest diff. peak and hole	0.562 and -0.404 e. $Å^{-3}$

Table S2 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**-2$CHCl_3$

Bond Distances (Å)

Cl(1)-C(12)	1.705(14)	Cl(2)-C(12)	1.877(14)
Cl(3)-C(12)	1.793(13)	O(1)-C(1)	1.351(3)
O(2)-C(6)	1.360(3)	O(2)-C(11)	1.412(3)
N(1)-C(7)	1.272(3)	N(1)-C(8)	1.421(3)
C(1)-C(2)	1.368(4)	C(1)-C(6)	1.407(3)
C(2)-C(3)	1.380(4)	C(4)-C(7)	1.451(3)

Bond Angles (°)

C(6)-O(2)-C(11)	118.2(2)	C(7)-N(1)-C(8)	118.0(2)
O(1)-C(1)-C(2)	119.0(2)	O(1)-C(1)-C(6)	122.0(2)

C(2)-C(1)-C(6)	119.0(2)	C(1)-C(2)-C(3)	120.6(3)
O(2)-C(6)-C(5)	125.9(2)	O(2)-C(6)-C(1)	114.1(2)
C(10)-C(8)-N(1)	123.3(2)	C(9)-C(8)-N(1)	117.8(2)

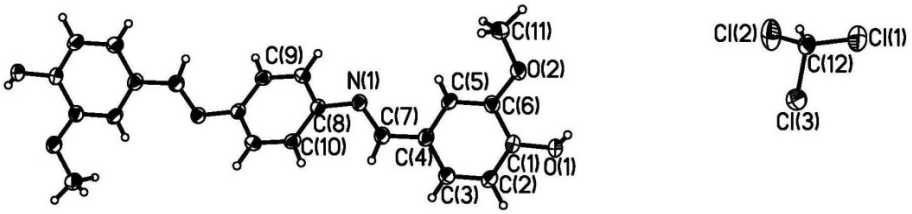

Figure S5 Perspective drawing of **1**-2$CHCl_3$ with atomic numbering scheme

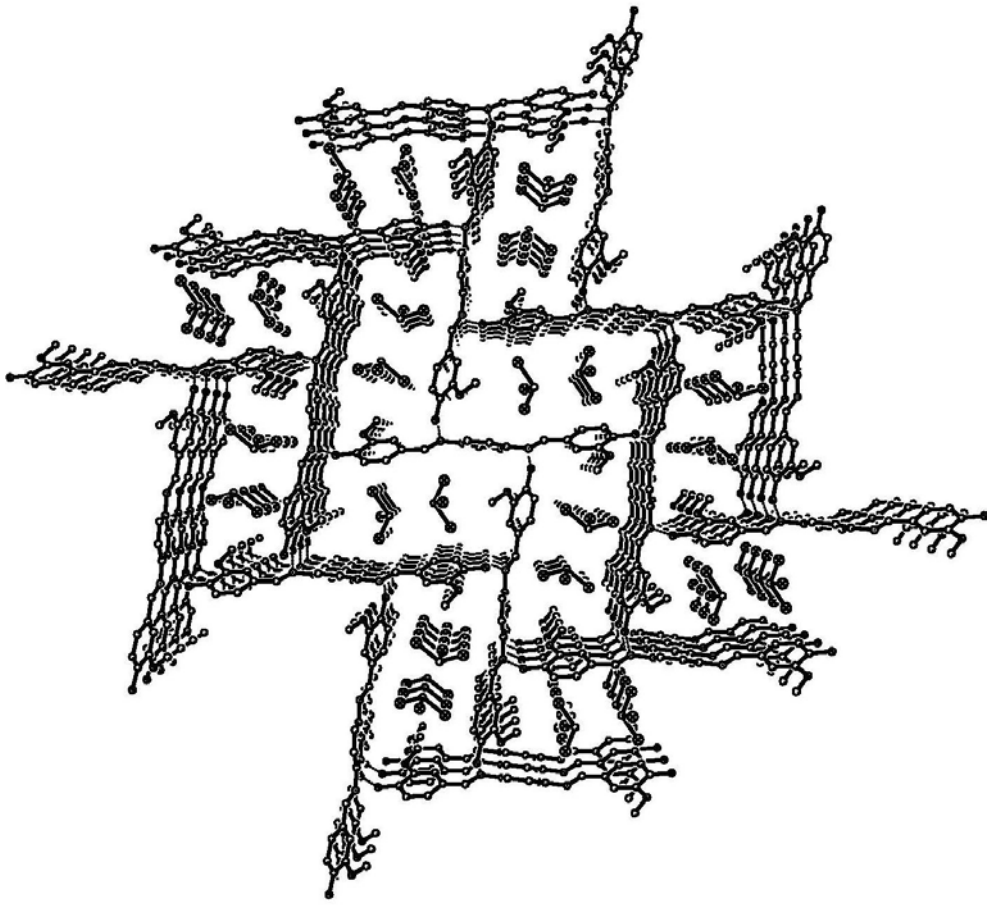

Figure S6 The packing diagram of **1**-2$CHCl_3$, the hydrogen atoms were omitted for clarity

S2.2. 1-THF (CCDC 212054):

Table S3 Crystal data and structure refinement for **1**-THF

Empirical formula	$C_{26}H_{28}N_2O_5$
Formula weight	448.50
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/ c
Unit cell dimensions	a = 13.2363(9) Å α= 90º
	b = 11.7650(8) Å β= 103.2810(10)º
	c = 17.6353(9) Å γ= 90º
Volume	2672.8(3) $Å^3$
Z, Calculated density	4, 1.115Mg/m^3
Absorption coefficient	0.078 mm^{-1}
F(000)	952
Crystal size	0.42 x 0.41 x 0.39 mm
θ range for data collection	2.34º ~ 27.48º
Limiting indices	0<=h<=17, 0<=k<=15, -22<=l<=22
Reflections collected / unique	17652 / 6100 [R(int) = 0.0281]
Completeness to θ = 27.46	99.5 %
Max. and min. transmission	0.9706 and 0.9683
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6100 / 0 / 378
Goodness-of-fit on F^2	1.109
Final R indices [I>2sigma(I)]	R1 = 0.1015, wR2 = 0.2874
R indices (all data)	R1 = 0.1243, wR2 = 0.3038
Largest diff. peak and hole	1.541 and -0.408 e. $Å^{-3}$

Table S4 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**-THF

Bond Distances (Å)

O(1)-C(11)	1.357(3)	O(2)-C(1)	1.412(4)
O(3)-C(31)	1.353(3)	O(4)-C(4)	1.417(4)

O(5)-C(44)	1.448(6)	N(1)-C(2)	1.279(4)
N(1)-C(21)	1.430(3)	N(2)-C(3)	1.276(4)
C(3)-C(34)	1.465(4)	C(11)-C(16)	1.381(4)
C(31)-C(36)	1.377(4)	C(42)-C(43)	1.533(8)

Bond Angles (°)

C(12)-O(2)-C(1)	117.9(2)	C(41)-O(5)-C(44)	112.5(4)
N(1)-C(2)-C(14)	125.6(2)	O(1)-C(11)-C(12)	121.4(2)
C(12)-C(13)-C(14)	120.2(3)	C(22)-C(21)-N(1)	119.2(2)
C(26)-C(21)-N(1)	121.7(2)	O(4)-C(32)-C(33)	125.4(2)
O(4)-C(32)-C(31)	114.6(2)	C(44)-C(43)-C(42)	102.6(4)

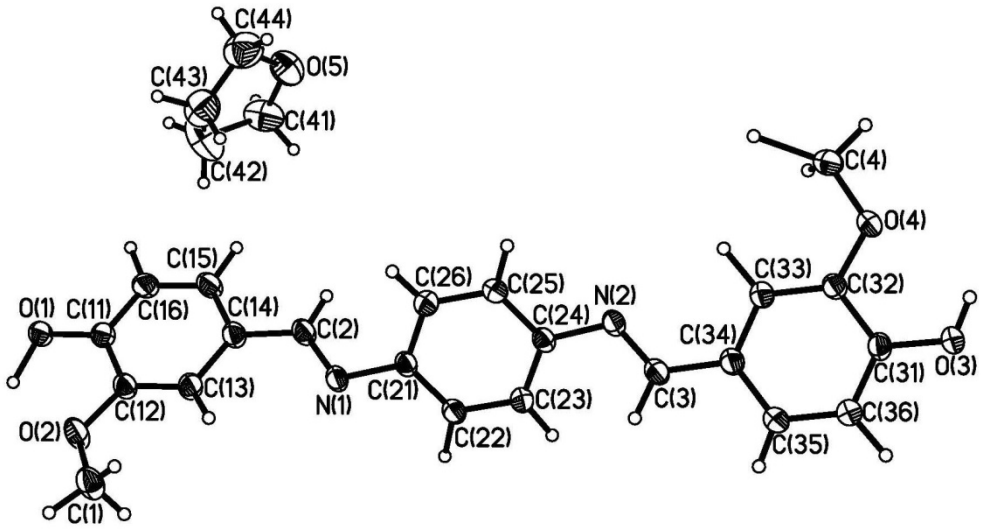

Figure S7 Perspective drawing of **1**-THF with atomic numbering scheme

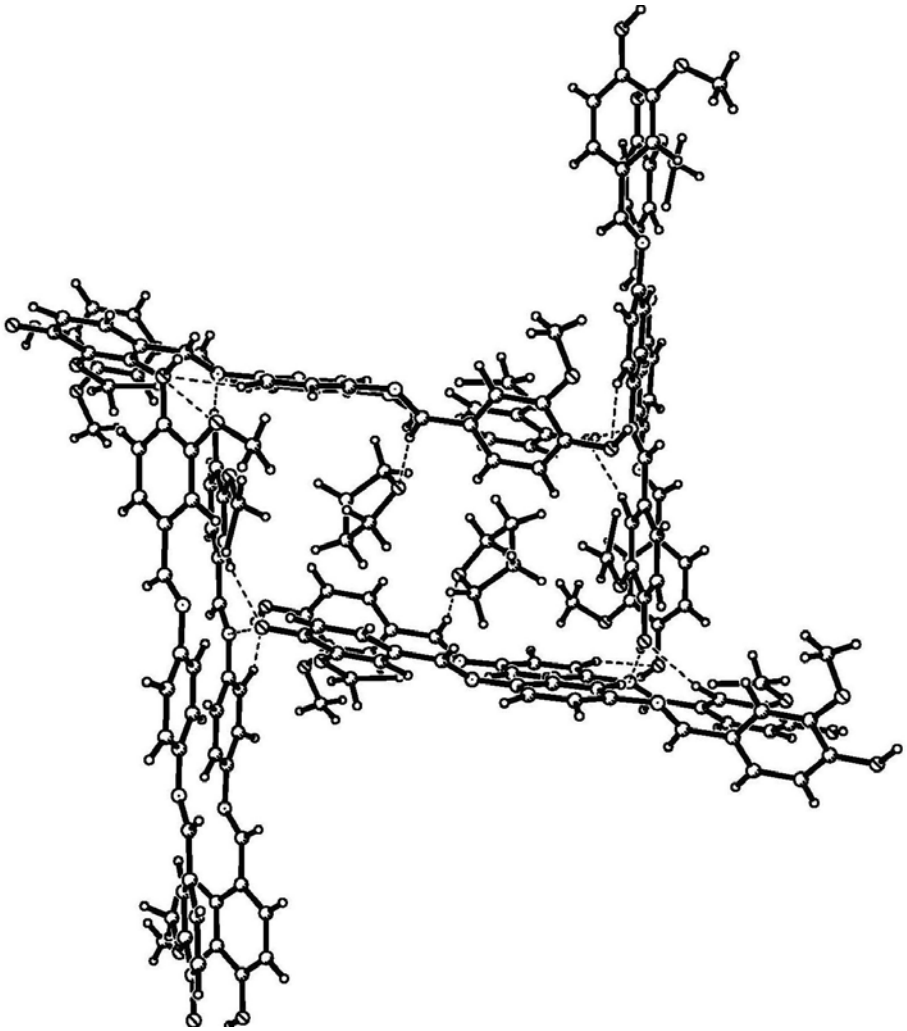

Figure S8 The two-dimensional sheets of **1**-THF, it shows two array of guest THF arranged in the two-dimensional channel and every THF twisted to occupy two layers

S2.3. 1·C_6H_6 (CCDC 212052):

Table S5 Crystal data and structure refinement for **1**-C_6H_6

Empirical formula	$C_{28}H_{26}N_2O_4$
Formula weight	454.51
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 5.9038(4)Å α= 90º
	b = 10.7455(8)Å β= 90.263(2)º
	c = 19.4895(11)Å γ= 90º
Volume	1236.39(14) $Å^3$
Z, Calculated density	2, 1.221 Mg/m^3

Absorption coefficient	0.082 mm^{-1}
F(000)	480
Crystal size	0.51 x 0.37 x 0.24 mm
θ range for data collection	2.82º - 27.48º
Limiting indices	0<=h<=7, 0<=k<=13, -25<=l<=25
Reflections collected / unique	10582 / 2813 [R(int) = 0.0429]
Completeness to θ = 27.46	99.1 %
Max. and min. transmission	0.9806 and 0.9593
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2813 / 0 / 206
Goodness-of-fit on F^2	0 .986
Final R indices [I>2sigma(I)]	R1 = 0 .0421 , wR2 = 0.1110
R indices (all data)	R1 = 0.0555, wR2 = 0.1164
Largest diff. peak and hole	0.177 and -0.215 e. $Å^{-3}$

Table S6 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**-C_6H_6

Bond Distances (Å)

O(1)-C(1)	1.3577(13)	O(2)-C(11)	1.4303(17)
O(2)-C(6)	1.3668(14)	N(1)-C(7)	1.2823(15)
N(1)-C(8)	1.4209(14)	C(1)-C(2)	1.3811(16)
C(1)-C(6)	1.4079(16)	C(4)-C(7)	1.4563(16)
C(12)-C(13)	1.369(4)	C(13)-C(14)	1.355(4)
C(12)-C(14)#2	1.379(4)	C(14)-C(12)#2	1.379(4)

Bond Angles (°)

C(6)-O(2)-C(11)	116.89(10)	C(7)-N(1)-C(8)	118.25(9)
O(1)-C(1)-C(2)	119.28(10)	O(1)-C(1)-C(6)	121.42(10)
O(2)-C(6)-C(5)	125.08(11)	C(6)-C(5)-C(4)	120.24(11)
O(2)-C(6)-C(1)	114.52(10)	N(1)-C(7)-C(4)	123.54(10)
C(9)-C(8)-N(1)	122.64(10)	C(14)-C(13)-C(12)	121.1(3)

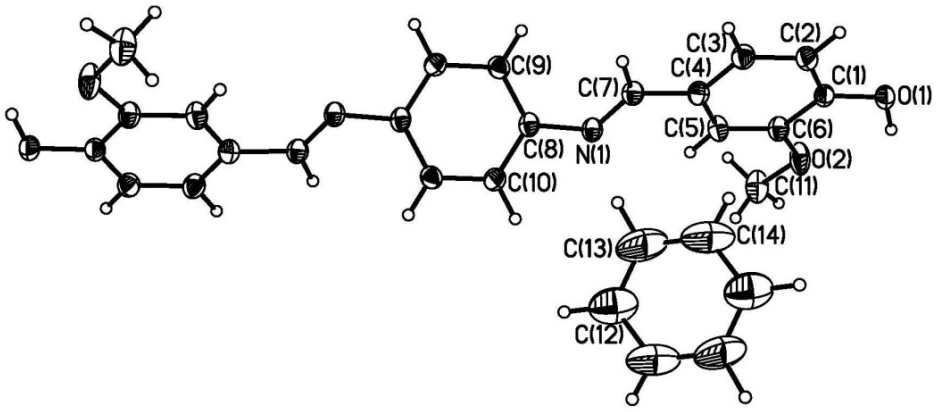

Figure S9 Perspective drawing of **1**-C_6H_6 with atomic numbering scheme

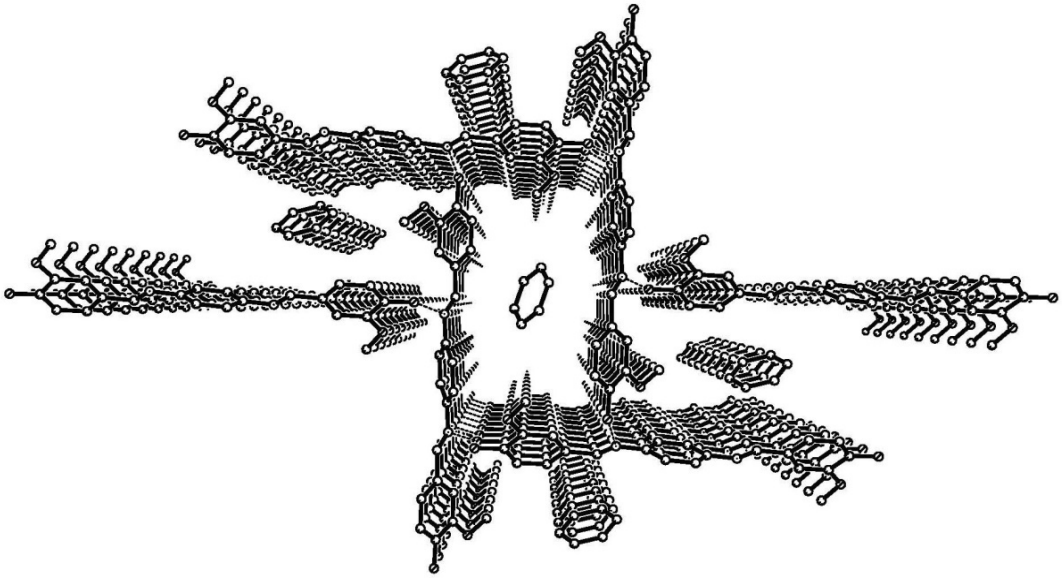

Figure S10 The packing diagram of **1**-C_6H_6, the hydrogen atoms were omitted for clarity

S2.4. 1·BPY (CCDC 1012199):

Table S7 Crystal data and structure refinement for **1**-BPY

Empirical formula	$C_{32}H_{28}N_4O_4$
Formula weight	532.58
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2/c
Unit cell dimensions	a = 12.8209(9)Å α= 90º

	b = 7.0395(4) Å β= 96.820(3)º
	c = 14.7623(7) Å γ= 90º
Volume	1322.91(13) $Å^3$
Z, Calculated density	2, 1.337Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	560
Crystal size	0.48 x 0.25 x 0.23 mm
θ range for data collection	1.60º ~ 27.48º
Limiting indices	0<=h<=16, 0<=k<=9, -19<=l<=18
Reflections unique	2967 [R(int) = 0.0000]
Completeness to θ = 27.46	97.6 %
Max. and min. transmission	0.9796 and 0.9582
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2967 / 0 / 234
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0727, wR2 = 0.1769
R indices (all data)	R1 = 0.1084, wR2 = 0.1953
Extinction coefficient	0.012(3)
Largest diff. peak and hole	0.313 and -0.205 e. $Å^{-3}$

Table S8 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for **1**-BPY

Bond Distances (Å)

O(1)-C(1)	1.361(4)	O(2)-C(6)	1.379(3)
O(2)-C(11)	1.420(3)	N(1)-C(7)	1.273(4)
N(1)-C(9)	1.414(4)	C(1)-C(2)	1.382(5)
C(1)-C(6)	1.411(4)	C(2)-C(3)	1.380(5)
C(4)-C(5)	1.399(4)	C(14)-C(15)	1.361(4)
C(14)-C(14)#2	1.485(7)	C(4)-C(7)	1.468(4)

Bond Angles (°)

C(6)-O(2)-C(11)	116.6(2)	C(7)-N(1)-C(9)	118.6(3)

C(12)-N(2)-C(16)	113.5(4)	O(1)-C(1)-C(2)	119.6(3)
C(3)-C(2)-C(1)	120.7(3)	C(5)-C(6)-O(2)	125.4(2)
O(2)-C(6)-C(1)	113.7(3)	C(8)-C(9)-N(1)	123.4(3)
C(15)-C(14)-C(13)	115.9(4)	N(2)-C(16)-C(15)	125.0(4)

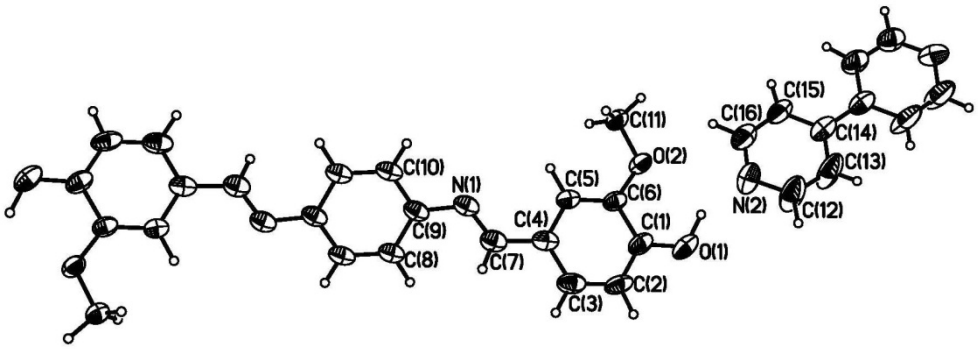

Figure S11 Perspective drawing of **1**-BPY with atomic numbering scheme

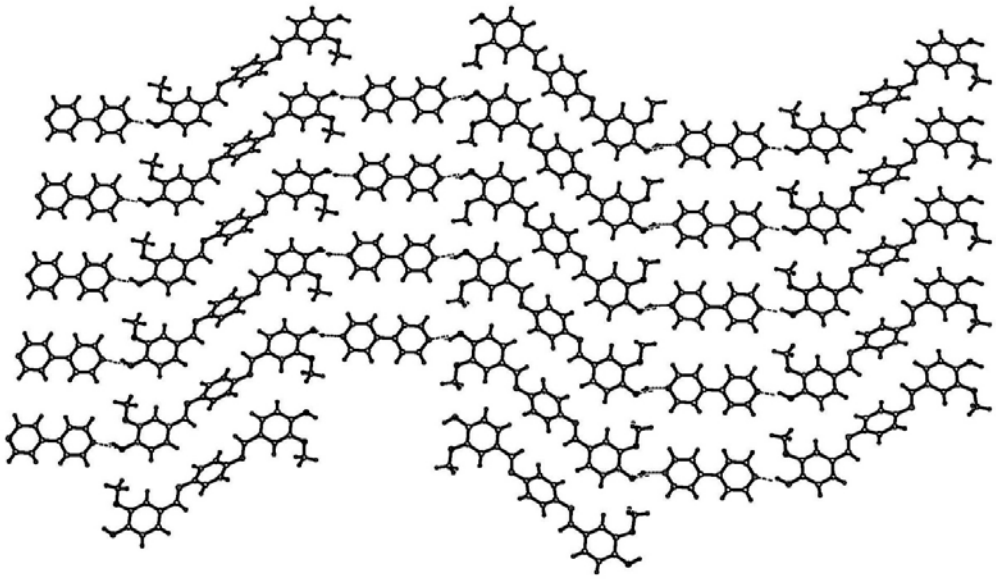

Figure S12 The one-dimensional chains of **1**-BPY, the hydrogen atoms were omitted for clarity

S2.5. 1-2PY:

1-2PY:(The following are preliminary results according to the single crystal contains some defects)

Table S9 Crystal data and structure refinement for **1**-2PY

Empirical formula	$C_{32}H_{30}N_4O_4$

Formula weight	534.60
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 12.8857(7)Å α= 90º
	b = 7.0971(3)Å β=100.7700(10)º
	c = 15.2576(8) Å γ= 90º
Volume	1370.75(12) $Å^3$
Z, Calculated density	2, 1.295 Mg/m^3
Absorption coefficient	0.087 mm^{-1}
F(000)	564
Crystal size	0.38 x 0.22 x 0.18 mm
θ range for data collection	1.90º ~ 27.48º
Limiting indices	0<=h<=16, 0<=k<=9, -19<=l<=19
Reflections unique	3128 [R(int) = 0.0329]
Completeness to θ = 27.46	99.5 %
Max. and min. transmission	0.9845 and 0.9675
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3128 / 0 / 237
Goodness-of-fit on F^2	0.901
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0845
R indices (all data)	R1 = 0.0641, wR2 = 0.1056
Largest diff. peak and hole	0.151 and -0.217 e. $Å^{-3}$

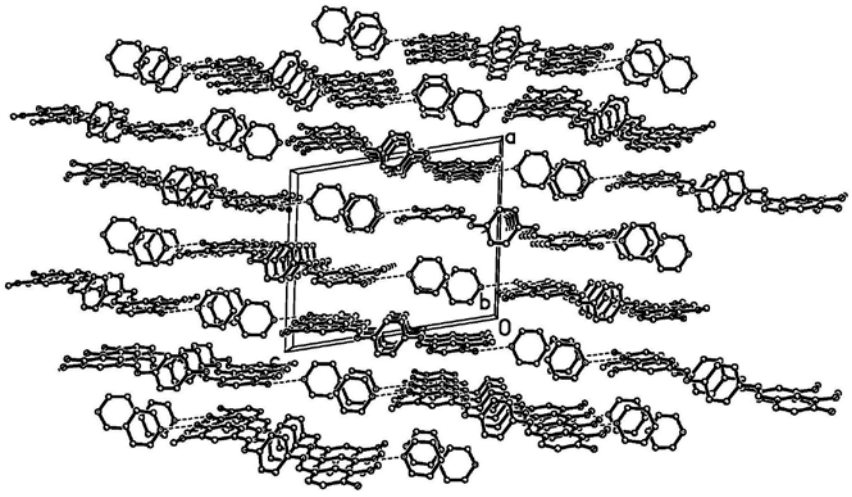

Figure S13 The one-dimensional chains of **1**-2PY, the hydrogen atoms were omitted for clarity

S3. Crystallographic data in CIF format

Crystallographic data in CIF format for **1**-C_6H_6, **1**-2$CHCl_3$, **1**-THF, and **1**-BPY, CCDC 212052 – 212054, 1012199, respectively are also available.