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Electronic Supplementary Information (ESI)

Supramolecular Recognition of Benzene Homologues in a 2D Coordination Polymer through Variable Inter-layer π-π Interaction

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Materials and measurements

The Single X-ray diffraction spectra were recorded on a Rigaku XtalAB PRO MM007 DW diffractometer at 77K with a Cu-target. Fluorescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer. The Power X-ray diffraction (PXRD) spectra were recorded on a Rigaku MiniFlex 600 diffractometer at 40 kV, 15 mA with a Cu-target tube. Thermal gravimetric analysis (TGA) was carried out on a Rigaku TG8121 analyzer in air atmosphere with a heating rate of 10 ℃/min from ambient temperature to 800 ℃ using an empty Al_2O_3 crucible as the reference. The infrared (IR) spectra were recorded on a TENSOR 37 (Bruker) Fourier transform infrared (FT-IR) spectrometer using KBr pellets within the 4000–400 cm^{-1} region. Elemental analysis (C, H, N) was performed on a Vairo EL Cube (Elementar) analyzer. Simulation of the PXRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org.

(1,1'-biphenyl)-2,2',6,6'-tetracarboxylic acid Synthesis:

To pyrene (6.00 g, 29.7 mmol) in CH_2Cl_2 (120 mL) was added MeCN (120 mL) and water (180 mL). To the resulting biphasic solution was added $NaIO_4$ (60 g, 280 mmol) followed by Ru(III)Cl_3 (240 mg, 1.16 mmol). The solution warmed somewhat as the reaction began but was not vigorous. The reaction was run overnight (~ 16 h) with stirring and was filtered to give a yellow solid. The mixed solid (tetraacid/$NalO_4$) was extracted with acetone (750 mL) and the acetone was refiltered to yield a yellow solution. Upon evaporation the product was identified as a mixture of the desired tetraacid and the corresponding dianhydride. The crude product was ground to a fine powder and was refluxed for 1 h in CH_2Cl_2 before being filtered hot. The tetraacid was collected as a white powder. (^{1}H NMR (300 MHz, DMSO) δ 8.32 (s, 1H), 8.29 (s, 1H), 7.74 (s, 1H), 7.72 (s, 1H), 7.69 (s, 1H).) (Fig. S1)

Complex 1 synthesis

The mixture of $Cd(NO_3)_2·4H_2O$(0.0313 g, 0.1 mmol), H_4bpta(0.0165 g, 0.05 mmol) and 3-tpt(0.0156g, 0.05mmol) in DMF–H_2O-Ethanol mixed solvents (6ml, v:v:v = 1:1:1) were ultrasonicated in an ultrasonic bath at room temperature and atmospheric pressure for 20 min in a 10 ml glass vials upon heating at 100°C for 4 days. The resulting yellow crystal was isolated by centrifugation, washed with DMF for three times.

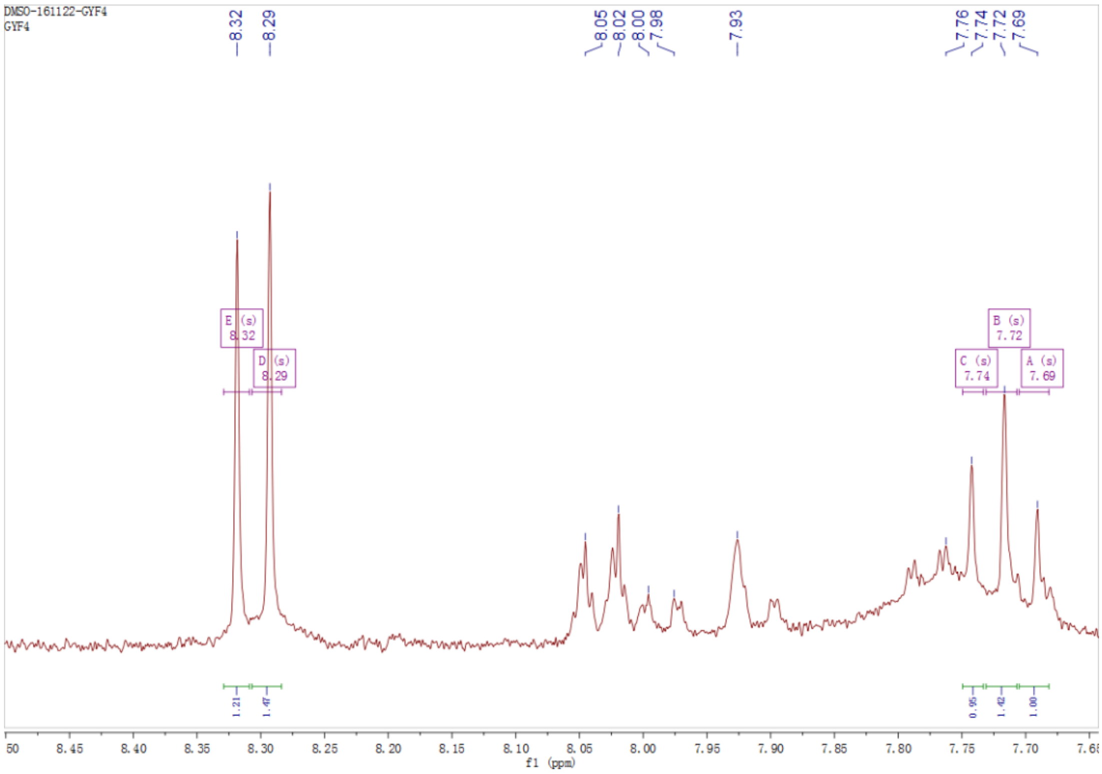

Fig. S1. The ^{1}H NMR Spectrum of (1,1'-biphenyl)-2,2',6,6'-tetracarboxylic acid

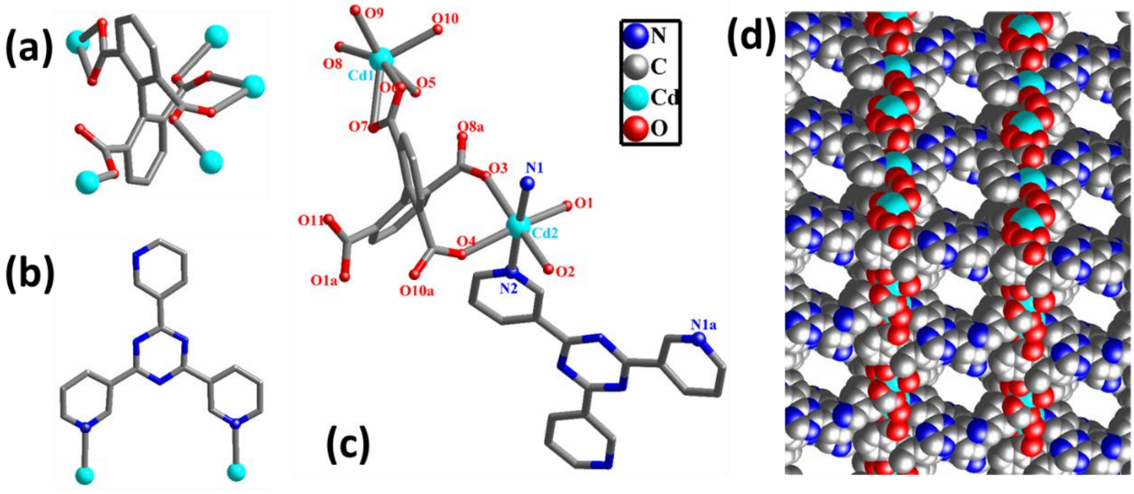

Fig. S2 Coordination environment of (a) bpta^{4-}, (b) 3-tpt and (c) complex **1.** And the 3D deposition of complex **1** (d). H atoms are omitted for clarity.

Table S1. Crystal data and structure refinement summary for complex **1**, complex **2**, and complex **3.**

	1		**2**		**3**	
Formula	$C_{34}H_{24}N_6O_{11}Cd_2$		$C_{41}H_{32}N_6O_{11}Cd_2$		$C_{42}H_{34}N_6O_{11}Cd_2$	
M**r (g mol^{-1})**	**911.36**		**1003.5**		**1017.5**	
Space group	$P2_1/c$		$P2_1/c$		$P2_1/c$	
Crystal system	**Monoclinic**		**Monoclinic**		**Monoclinic**	
a **(Å)**	**16.830(3)**		**16.0536(2)**		**17.1153(1)**	
b **(Å)**	**18.059(4)**		**17.8754(2)**		**18.1270(1)**	
c **(Å)**	**15.756(3)**		**17.8754(2)**		**15.6893(1)**	
α**(°)**	**90**		**90**		**90**	
β**(°)**	**98.82(3)**		**102.7310(10)**		**94.978(1)**	
γ**(°)**	**90**		**90**		**90**	
V **(Å^3)**	**4732.1(17)**		**4393.27(8)**		**4849.23(5)**	
Z	**4**		**4**		**4**	
Dc **(gcm^{-3})**	**1.279**		**1.517**		**1.394**	
R_{int}	**0.1792**		**0.0277**		**0.0268**	
	-21<=h<=21		***-20<=h<=20***		***-21<=h<=21***	
limiting indices	***-23<=k<=23***		***-22<=k<=22***		***-22<=k<=22***	
	-20<=l<=20		***-19<=l<=19***		***-19<=l<=19***	
Reflns collected	**44550**		**24705**		**28188**	
Reflns unique	**10729**		**8700**		**9618**	
GOF on F^2	**0.954**		**0.910**		**1.011**	
$R1$, $wR2$ [$I>2\sigma(I)$]	**0.0910**	**0.2218**	**0.0279**	**0.0838**	**0.0287**	**0.0633**
$R1$, $wR2$ [*all data*]	**0.1771**	**0.1858**	**0.0313**	**0.0851**	**0.0308**	**0.0642**

$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. The elemental analysis results of complex**1**, **2,** and **3.**

	Calculated (%)			Found (%)		
	C	H	N	C	H	N
Complex **1**	44.8	2.0	9.2	42.7	2.2	9.7
Complex **2**	49.1	2.6	8.4	46.2	2.7	8.8
Complex **3**	49.6	2.8	8.3	46.7	2.8	8.5

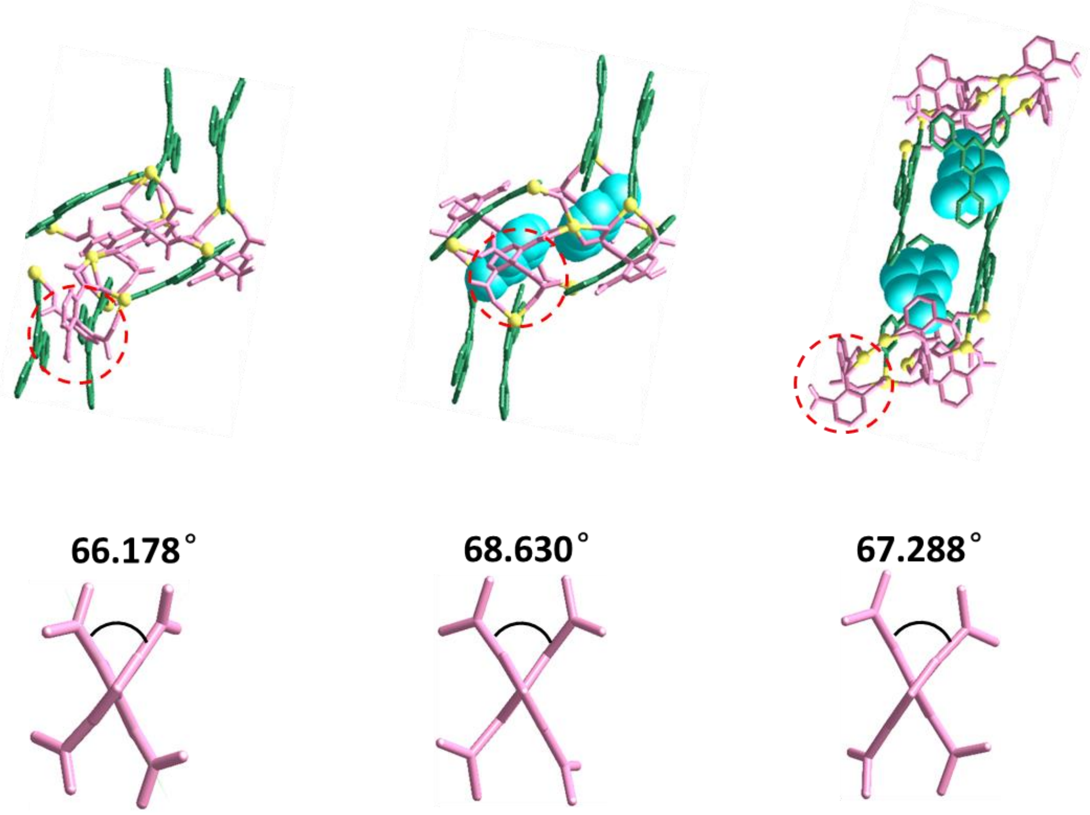

Fig. S3. The torsion angle between the two benzene ring in one bpta^{4-} of complex **1**, complex **2,** and complex **3.**

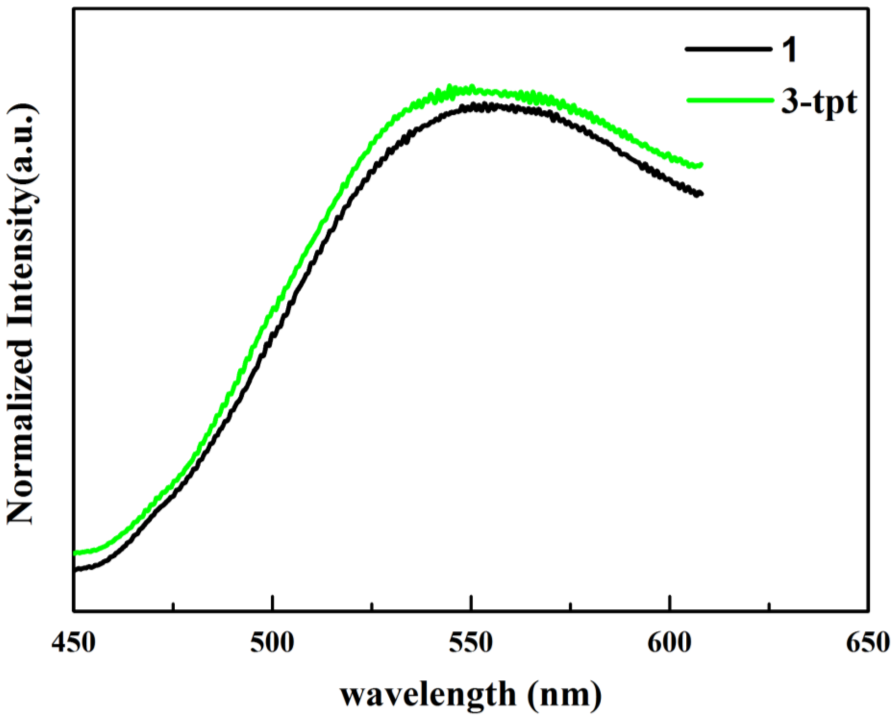

Fig. S4. The solid-state fluorescent spectra of complex 1 and 3-tpt, investigated in room temperature, and the emission peak appears at 554 nm (λ = 418 nm).

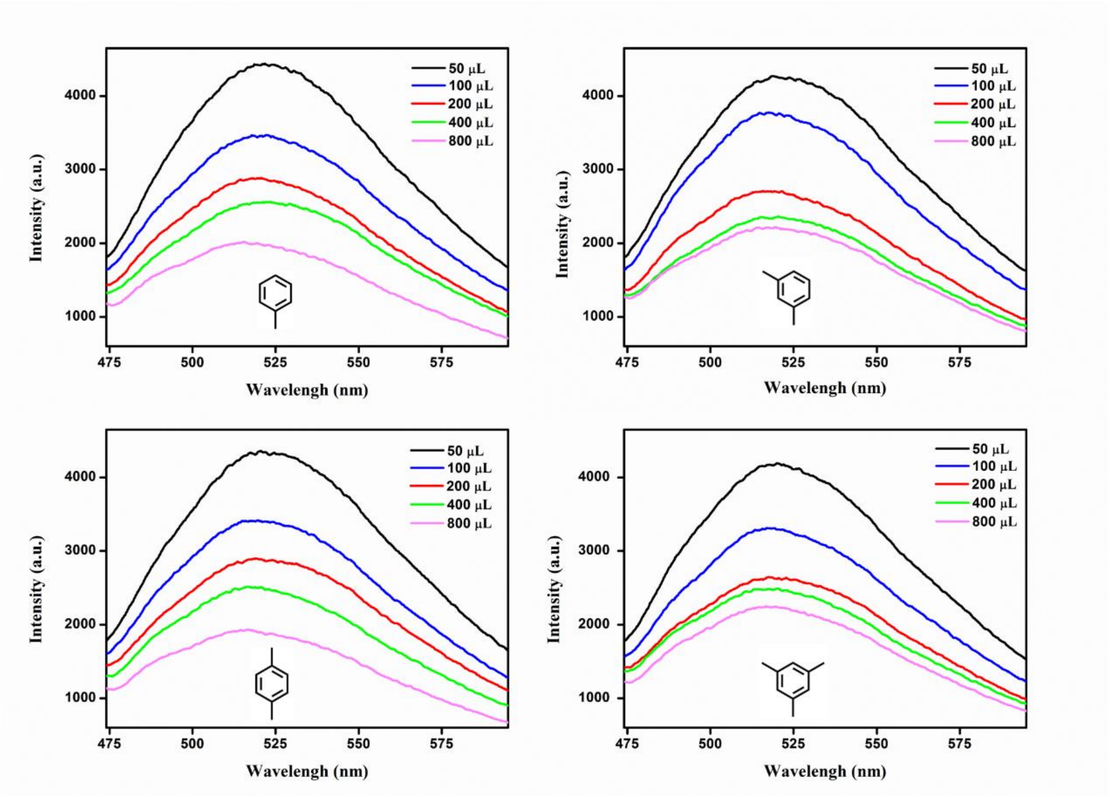

Fig. S5. The intensity of the fluorescence emission in response to different concentration of benzene homologues.