Supporting Information

Functionalizing the pore wall of chiral porous metal-organic frameworks by distinct -H, -OH, -NH_2, -NO_2, -COOH shutters showing selective adsorption of CO_2, tunable photoluminescence, and direct white-light emission

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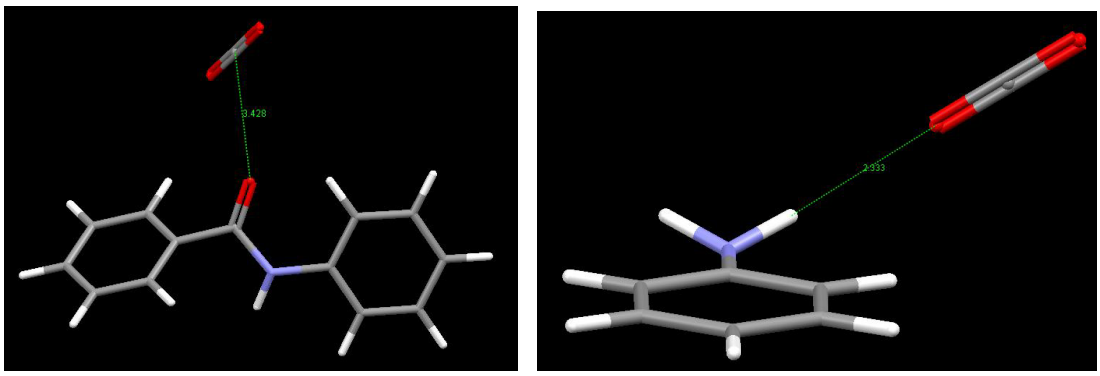
The syntheses of 1-5. A DMF/H_2O solution (6mL, 5:1) of $Zn(NO_3)_2$, L, multi-caroxylate ligand (H_2ip (isophthalic acid), or H_3BTC (1, 3, 5-benzenetricarboxylic acid), or H_2aip (5-aminoisophthalic acid), or H_2hip (5-hydroxyisophthalic acid), or H_2nip (5-nitroisophthalic acid)) in a ratio of 1:1:1 was sealed in a Teflon reactor, and heated at 120 ˚C for 2 days, and then cooled to room temperature at 3 ˚C/h. Subsequently, hexagonal crystals were obtained in 90%-**1**, 88%-**2**, 93%-**3**, 89%-**4**, 92%-**5**, yield based on Zn, respectively. The CCDC number of these polymers is 871159 - 871168 for compounds 1, 1a, 2, 2a...6, 6a, respectively.

EA, TG and XRD studies. The amount of guest molecule is estimaed by EA and TG analysis. For **1**, the experimental EA analysis is C/56.86, H/3.95, N/9.03, which suggests the Zn(L)(ip)·(DMF)$(H_2O)_{1.5}$ molecular formula (cal: C/56.37, H/4.07, N/9.13). The TG studies suggest the loss of DMF and water molecule is at 30-240 °C (exp. 13.3%, calc. 13.1%) (Figure S1). And the skeleton of it can be maintained about 300°C, which is supported by XRD research, see Figure S2. For **2**, the experimental EA analysis is C/57.27, H/4.26, N/9.56, which suggests the Zn(L)(hip)·(DMF)(H_2O) molecular formula (cal: C/57.5, H/4.27, N/9.57). The TG studies suggest the loss of water molecule is at 30-250 °C (exp. 11.6%, calc. 12.4%) (Figure S1). And the skeleton of it can be maintained about 300 °C, which is supported by XRD research (Figure S2). For **3**, the experimental EA analysis is C/58.41, H/3.79, N/10.46, which suggests the Zn(L)(aip)·(H_2O) molecular formula (cal: C/58.50, H/3.83, N/10.66). The TG studies suggest the loss of water molecule is at 30-150 °C (exp. 3.0%, calc. 2.7%) (Figure S1). And the skeleton of it can be maintained about 270 °C, which is supported by XRD research (Figure S2). The amount of guest molecules found in **3** is litter than that found in other polymers, due to the laggardly efflorescence

that often lose guest molecules spontaneity. For **4**, the experimental EA analysis is C/55.88, H/3.50, N/10.34, which suggests the Zn(L)(nip)·$(DMF)_{0.5}(H_2O)_{0.5}$ molecular formula (cal: C/56.95, h/3.67, N/10.58). The TG studies suggest the loss of water molecule is at 30-215 °C (exp. 6.5%, calc. 6.2%) (Figure S1). And the skeleton of it can be maintained about 290 °C, which is supported by XRD research (Figure S2). For **5**, the experimental EA analysis is C/55.69, H/3.79, N/8.16, which suggests the Zn(L)(HBTC)·$(H_2O)_2$ molecular formula (cal: C/56.30, H/3.72, N/7.95). The TG studies suggest the loss of water molecule is at 30-220 °C (exp. 4.9%, calc. 5.1%) (Figure S1). And the skeleton of it can be maintained about 320 °C, which is supported by XRD research (Figure S2).

DFT studies.

Optimization of geometries were preformed using Gaussian 03 program[1], employing the hybrid density functional theory (B3LYP) at the restricted B3LYP/6-31G (d, p) level. Single-pointed energy and the frequency calculations were also done on the optimized geometries at the same level, and the change of enthalpy energies (ΔH) in the reactions were obtained using the frequency calculations at room temperature and 1 atm. The zero-point energy (ZPE) and thermal energy corrections without scale were also made at the B3LYP/6-31G (d, p) level. All the reactants and products are characterized to be minima on potential energy surface by the vibrational frequency analysis. The selected mode, the final structure after optimized geometry, as well as the closest contact between CO_2 molecule and acylamide (-NHCO-), amide (NH_2-) groups is shown below:



Reference

1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,

V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.

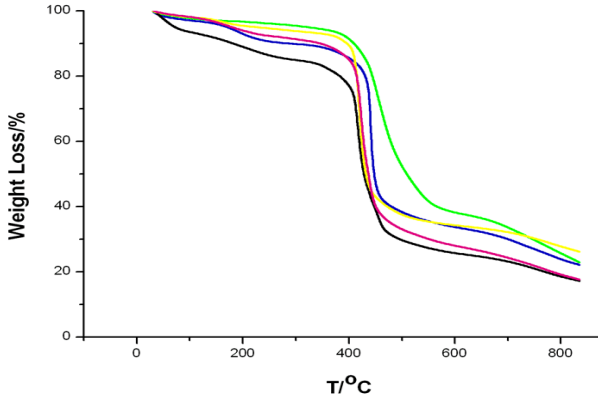
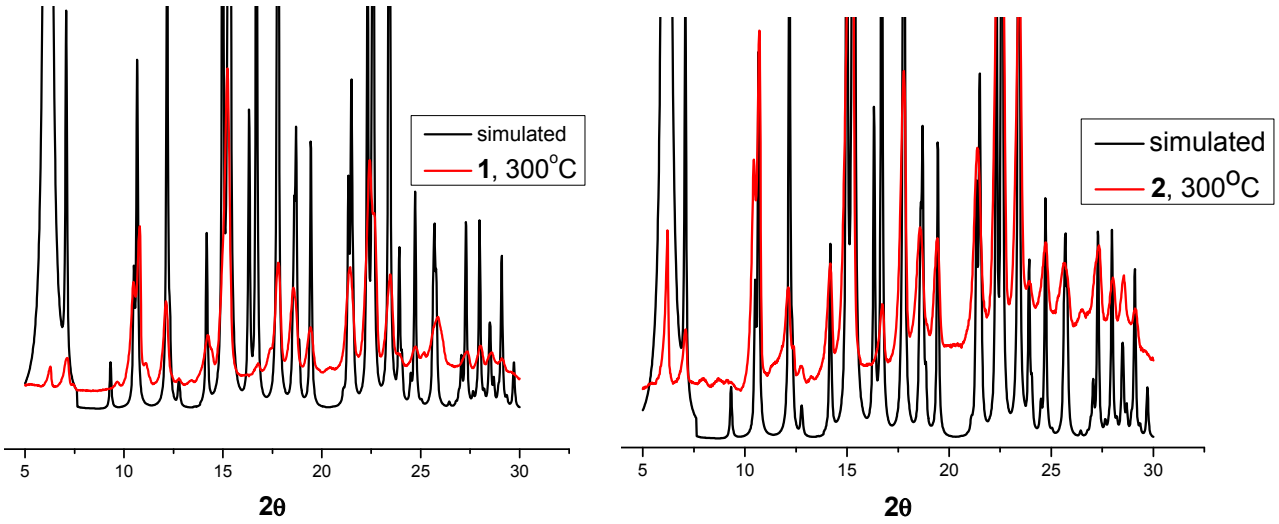


Figure S1. The TG studies of **1**-**5**: black/**1**, blue/**2**, green/**3**, red/**4**, yellow/**5**.



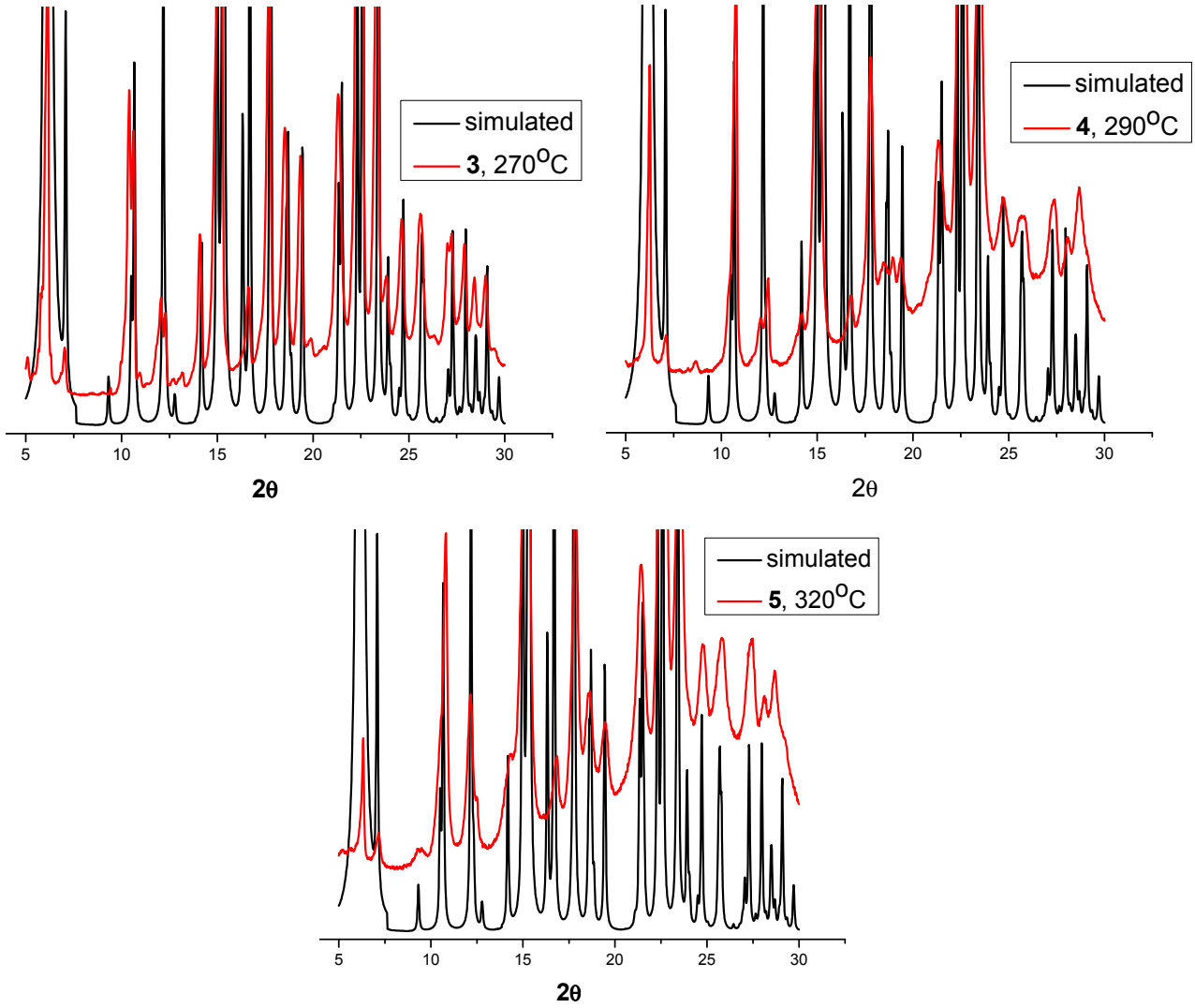
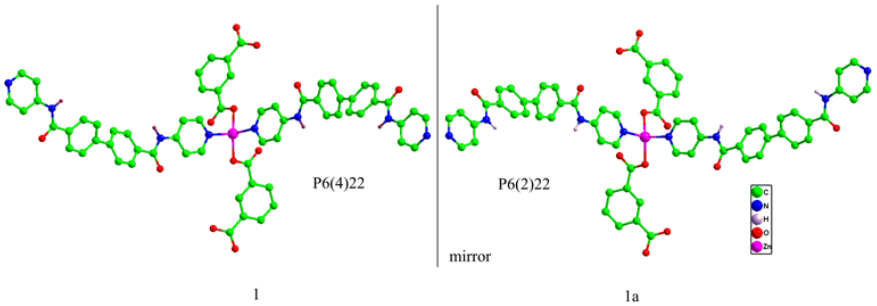


Figure S2. The experimental/red and simulated/black XRD patterns: **1** (after calcination at 300 °C), **2** (after calcination at 300 °C), **3** (after calcination at 270 °C), **4** (after calcination at 290 °C), **5** (after calcination at 320 °C).



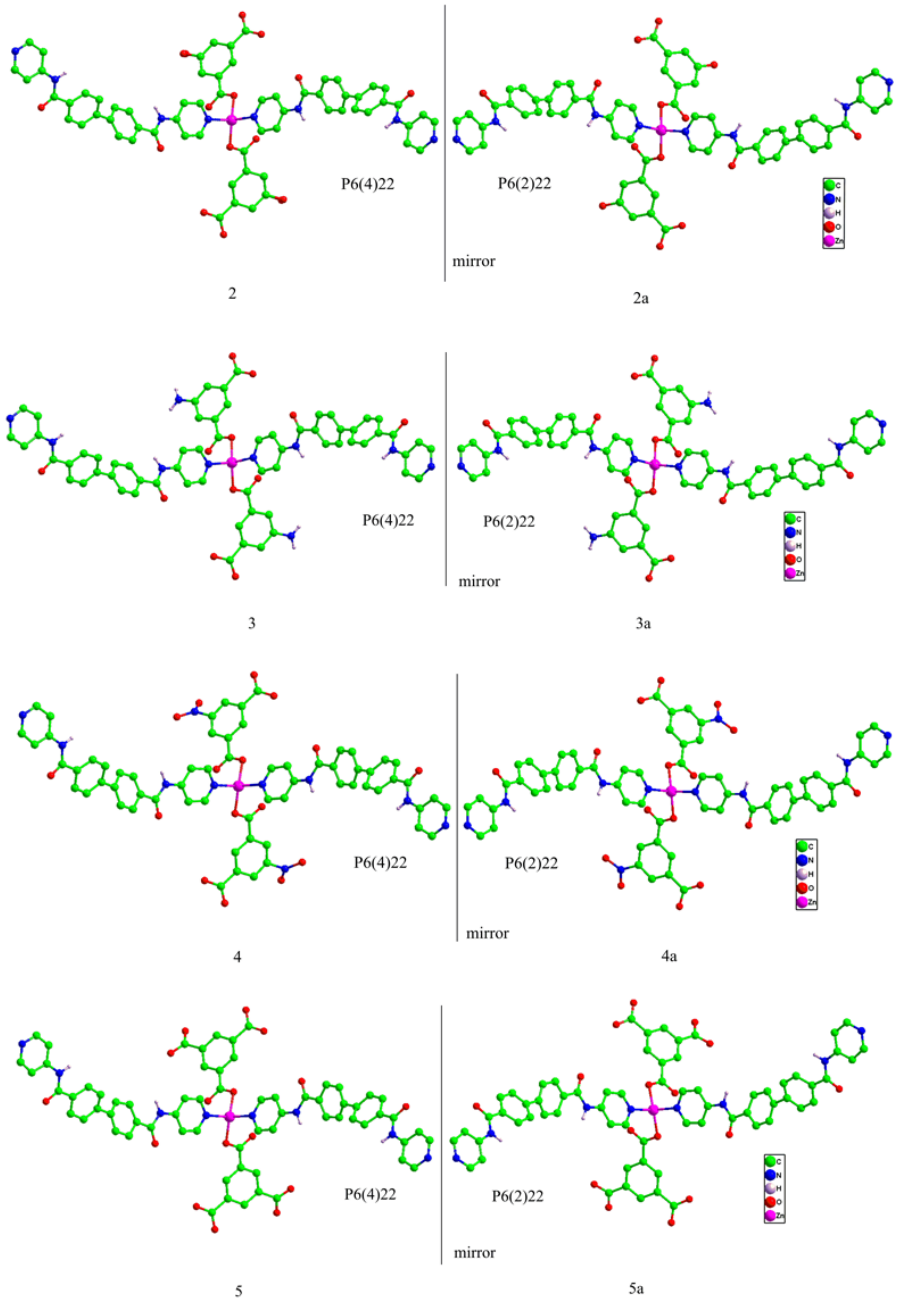


Figure S3. The asymetrical unit and the coordination surrounding around metal ion for **1-5**.

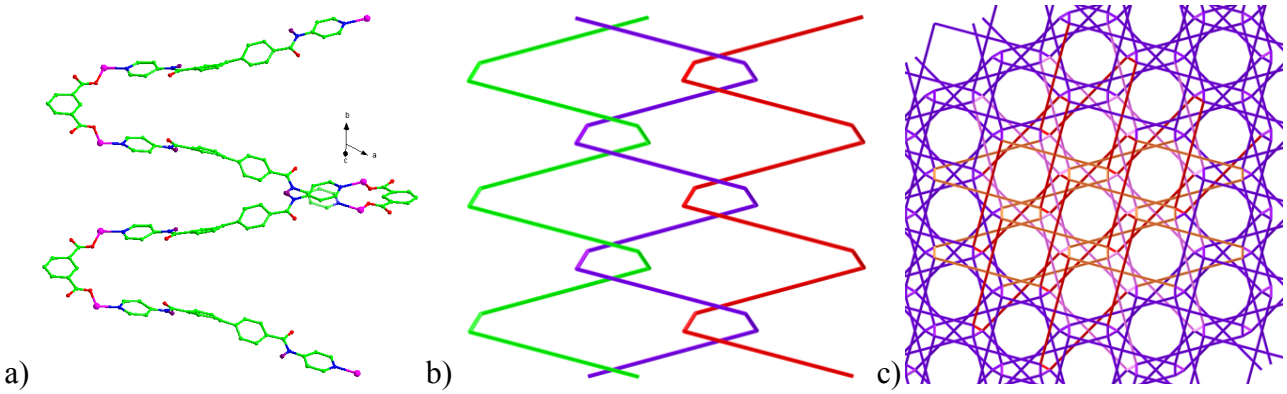


Figure S4. a) View of 1-D helical chain composed of Zn(II), multi-carboxylate ligand, and L; b) Schematic description of the unprecedented 2-D molecule braid; c) the four-connecting self-penetrating net bulit on the special 2-D molecule braid.

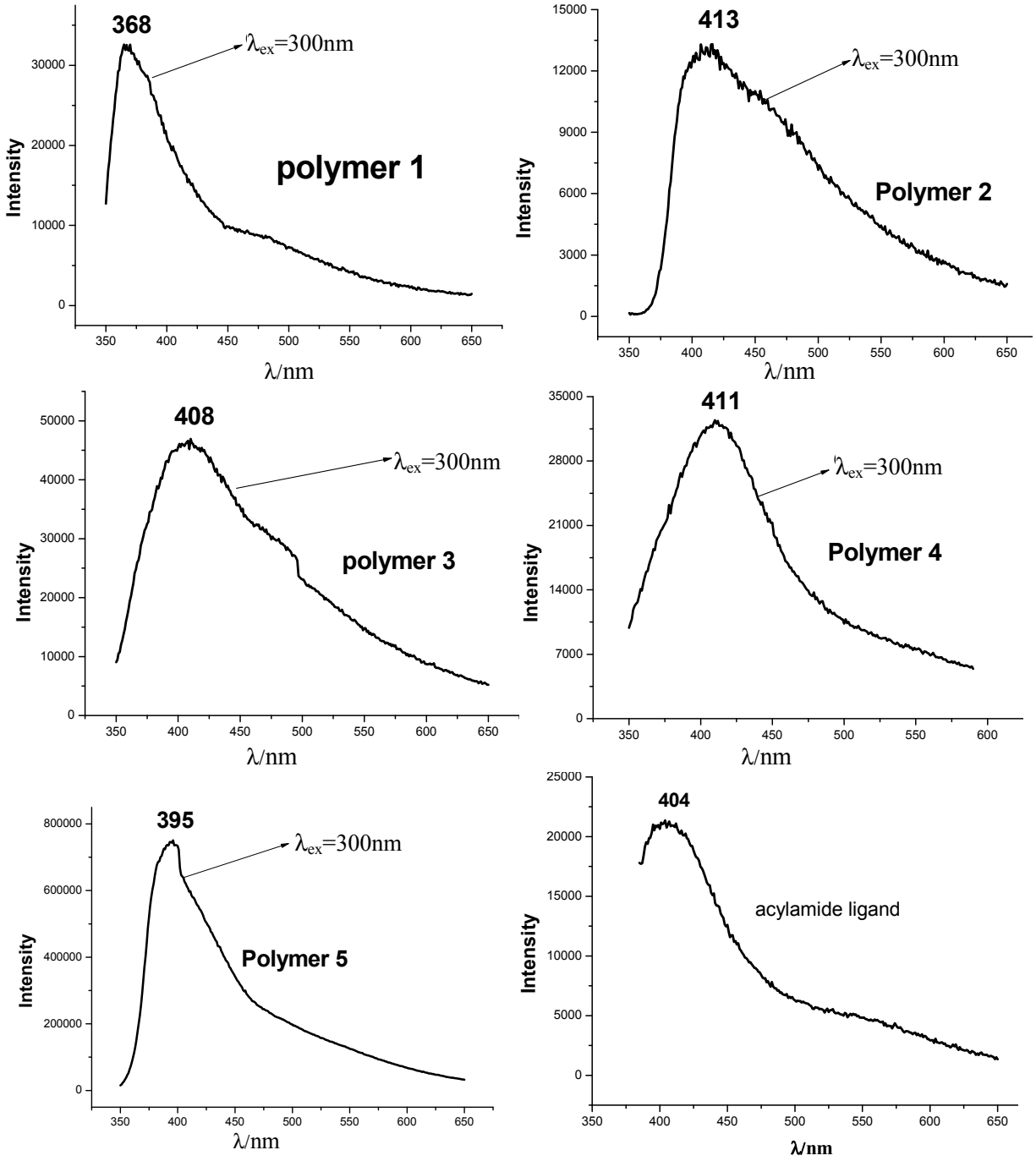


Figure S5. Solid-state PL spectra of **1-5** and acylamide ligand L.

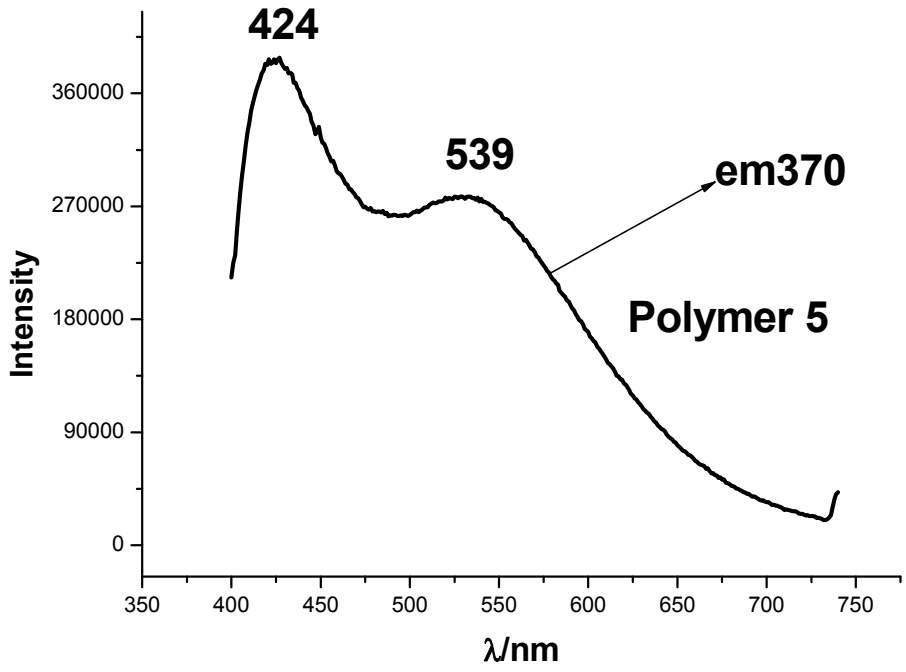


Figure S6. Solid-state PL spectrum of **5** excited at 370 nm.

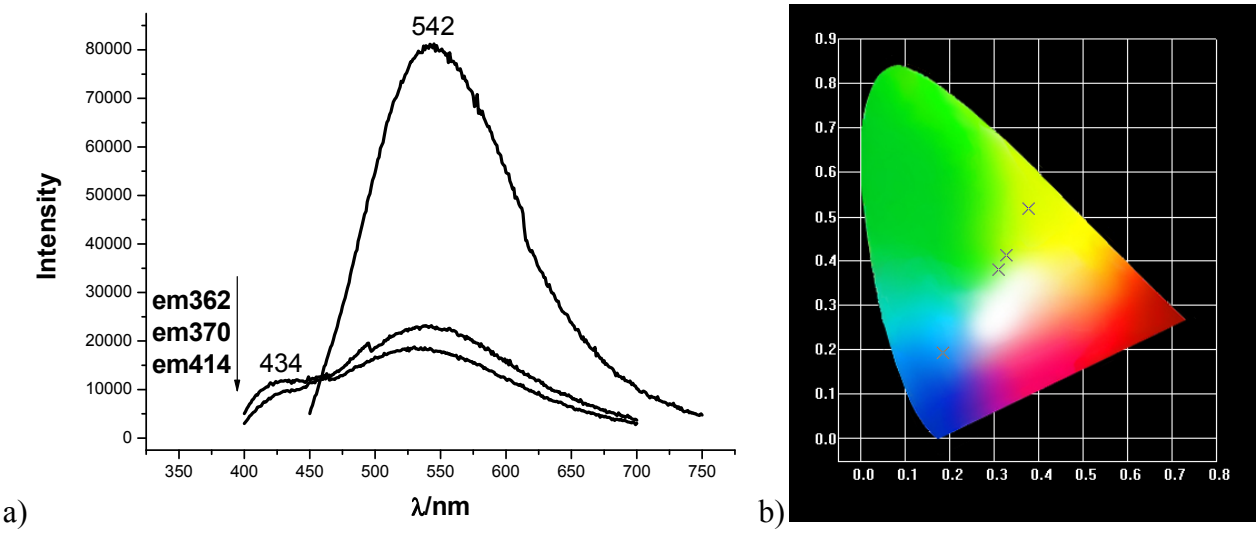


Figure S7. a) Solid-state PL spectra of **4** by variation of excitation light under the same metrical condition; b) A photograph of the CIE color coordinates of tunable PL properties from yellow to blue by means of the variation of excitation light.

Table 1. A simple crystallography summarization of **1**-**5**.

Compounds	Space group	Flack factor	Pore diameter(Å)	Inner surface character	Solvent-accessible volume(Å^3)
Zn(L)(ip)·solvents (**1**)	*P6$_4$22*	-0.02(2)	9.4	Acylamide+-H	2314.5, 38.5%

	P6$_2$22	0.019(3)			
Zn(L)(hip)·solvents(**2**)	*P6$_4$22* *P6$_2$22*	-0.01(4) 0.05(5)	8.0	Acylamide+-OH	2239.3, 37.3%
Zn(L)(aip)·solvents (**3**)	*P6$_4$22* *P6$_2$22*	0.00(3) 0.05(3)	7.5	Acylamide+-NH_2	2083.6, 34.9%
Zn(L)(nip)·solvents(**4**)	*P6$_4$22* *P6$_2$22*	0.01(3) 0.00(4)	7.3	Acylamide+-NO_2	2061.9, 34.0%
Zn(L)(HBTC)·solvents(**5**)	*P6$_4$22* *P6$_2$22*	0.05(3) 0.04(4	7.0	Acylamide+-COOH	1971.6, 32.8%

Table 2. The CIE color coordinates based on different excitation light.

Compound	CIE color coordinates	Excitation wavelength (nm)
5	0.21, 0.21	300
	0.21, 0.22	314
	0.22, 0.20	350
	0.21, 0.20	354
	0.22, 0.21	359
	0.26, 0.30	370
	0.28, 0.32	371
	0.28, 0.32	372
	0.29, 0.34	373
	0.29, 0.35	374
	0.30, 0.36	375
	0.30, 0.37	376
	0.31, 0.38	377
	0.31, 0.38	378
	0.31, 0.38	379
	0.32, 0.39	380
	0.32, 0.40	381
4	0.18, 0.19	300
	0.30, 0.38	362

0.32, 0.41	370
0.38, 0.52	414