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Electronic Supplementary Information

Conjugated microporous polymers based on biphenylene for CO_2 adsorption and luminescent detection of nitroaromatic compounds

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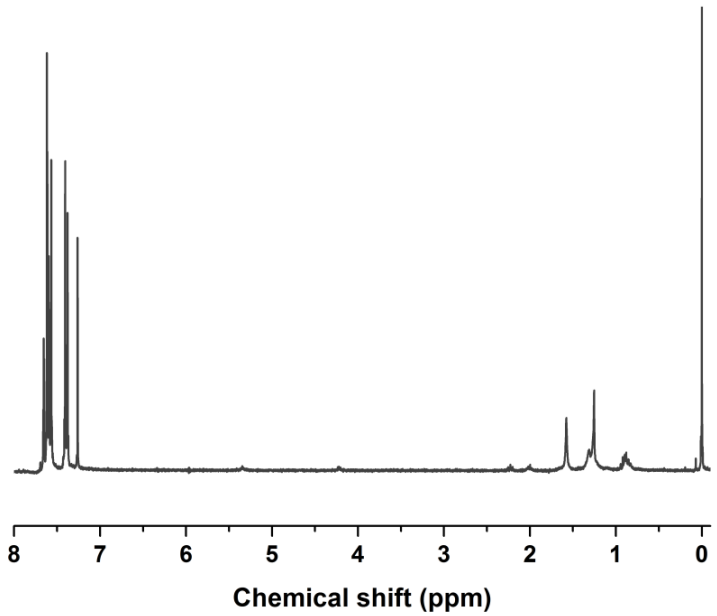

Fig. S1 ^{1}H NMR spectrum of 3,4',5-tribromobiphenyl in $CDCl_3$.

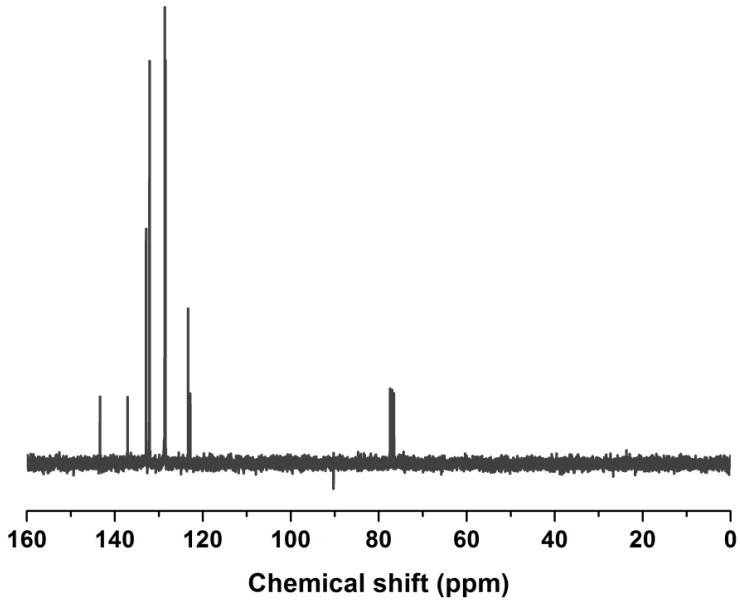

Fig. S2 ^{13}C NMR spectrum of 3,4',5-tribromobiphenyl in $CDCl_3$.

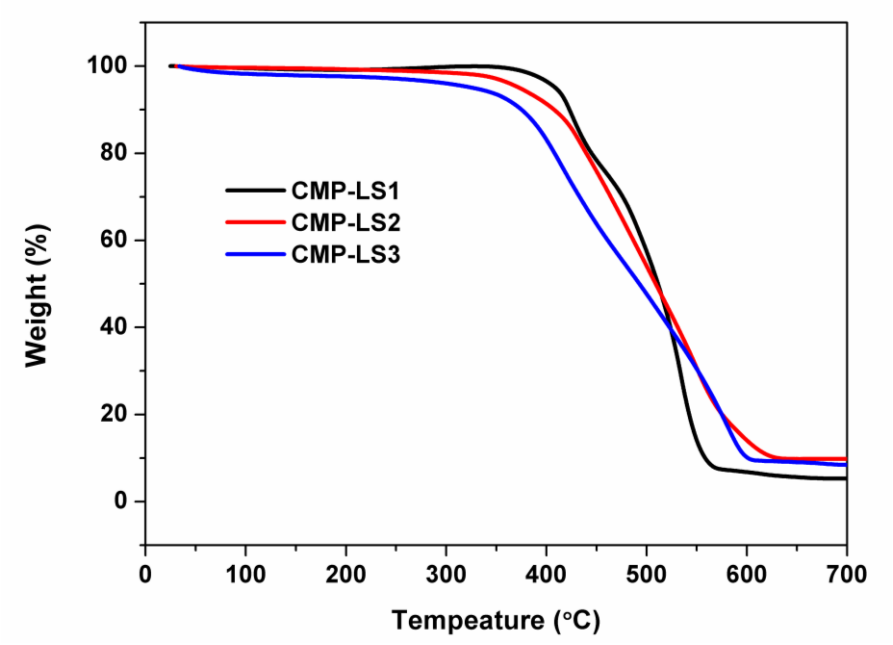

Fig. S3 TG curves of **CMP-LS1**–**3** under air atmosphere.

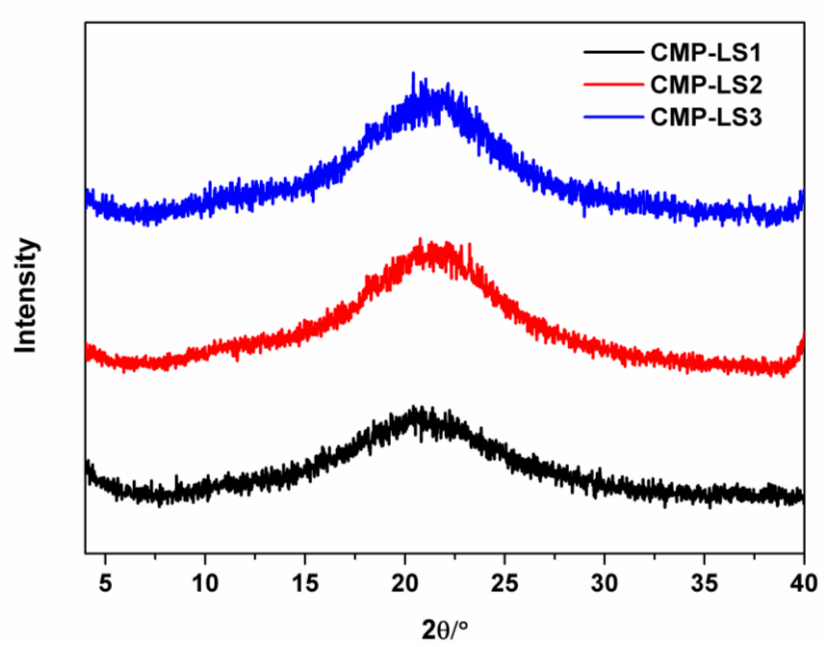

Fig. S4 Powder X-ray diffraction profiles of **CMP-LS1**–**3**.

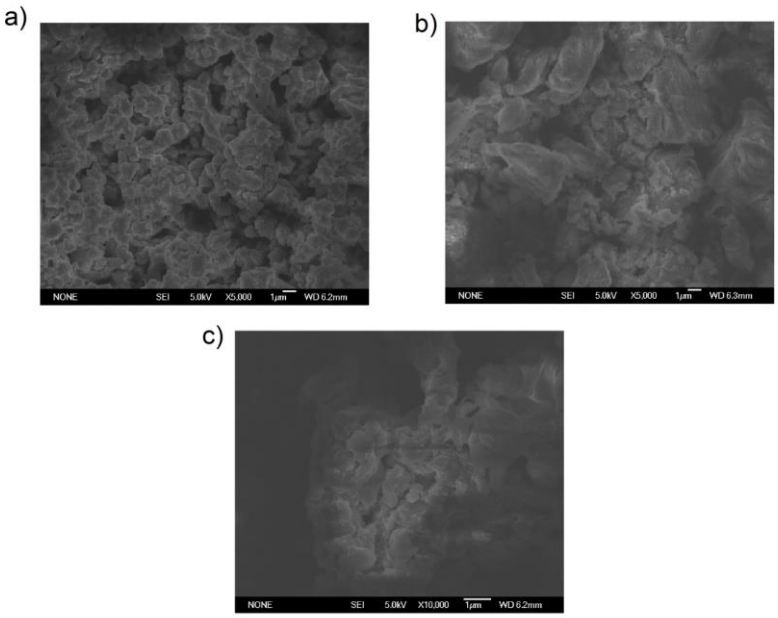

Fig. S5 FE-SEM images of (a) **CMP-LS1**, (b) **CMP-LS2** and (c) **CMP-LS3**.

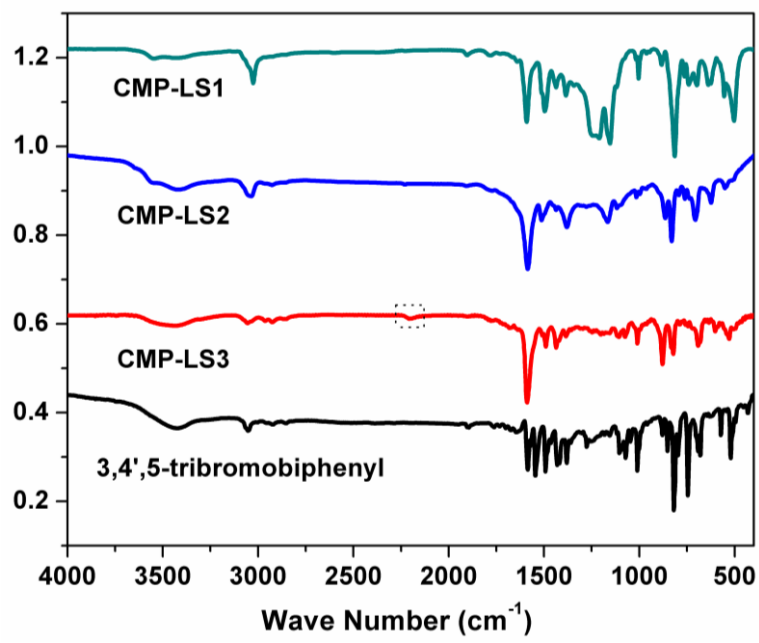

Fig. S6 IR spectra of 3,4',5-tribromobiphenyl and polymers.

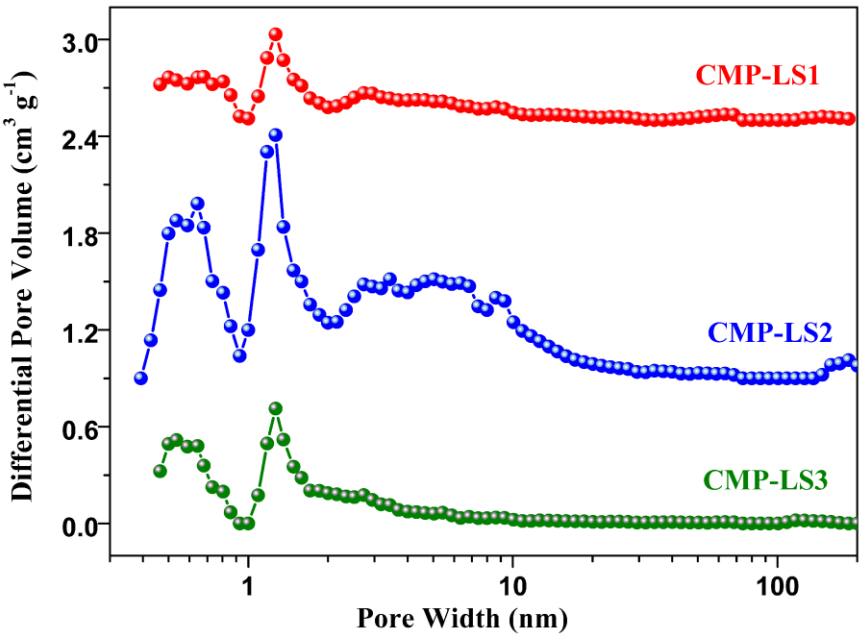

Fig. S7 Pore size distributions calculated using the non-local density functional theory (NLDFT) method.

Calculations of the Isosteric Heats of Gas Adsorption (Q_{st})

The isosteric heat was calculated using the Claussius - Clapeyron equation:

$$\ln P_1 - \ln P_2 = \frac{Qst}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

P_1 : pressure of the adsorption at T_1 = 273 K

P_2 : pressure of the adsorption at T_2 = 298 K

R : gas constant (8.314 kJ mol^{-1})

Q_{st} : isosteric heat which shows the interactions between the gas molecules and the framework

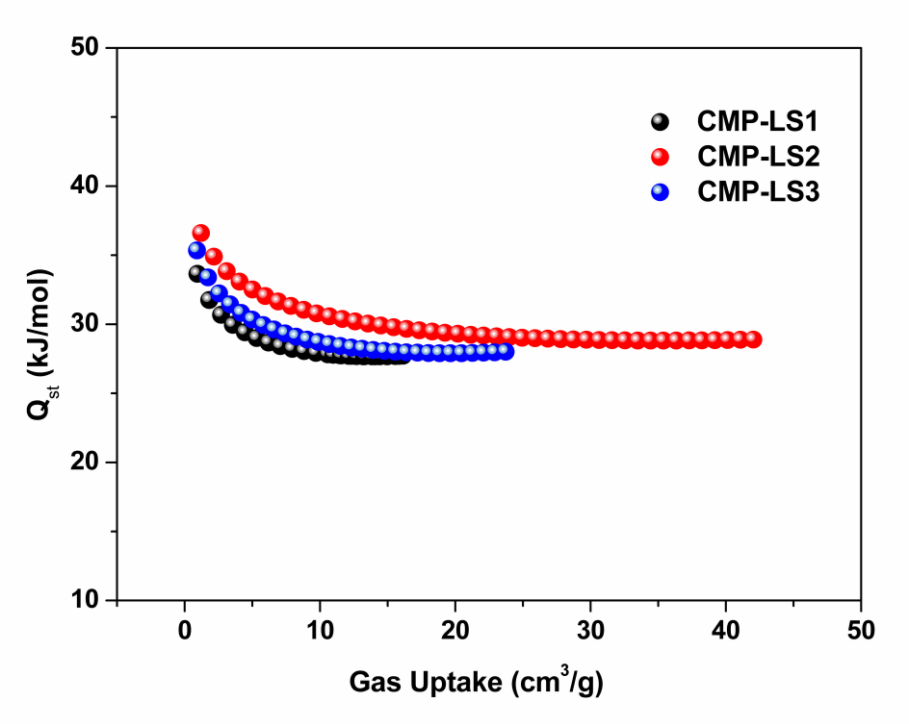

Fig. S8 Isosteric heats of adsorption of CO_2 for **CMP-LS1**–**3**.

Calculation procedures of selectivity from IAST

The excess adsorption data for pure gases measured at 273 K, were first converted to absolute loadings, along with Peng-Robinson equation. In order to perform the IAST calculations, the single-component isotherm was fitted by the dual-site Langmuir Freundlich (DSLF) adsorption model to correlate the pure-component equilibrium data and further predict the adsorption of mixtures. The DSLF model is described as:

$$y = a_1 \times \frac{b_1 \times x^{c1}}{1 + b_1 \times x^{c1}} + a_2 \times \frac{b_2 \times x^{c2}}{1 + b_2 \times x^{c2}}$$

Here x is the pressure of the bulk gas at equilibrium with the adsorbed phase, y is the adsorbed amount per mass of adsorbent, a_1 and a_2 are the saturation capacities of sites 1 and 2, b_1 and b_2 are the affinity coefficients of sites 1 and 2, c_1 and c_2 are the deviations from an ideal homogeneous surface. The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as:

$$S = \frac{y_1/y_2}{x_1/x_2}$$

y_1 and y_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of y_1 and y_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

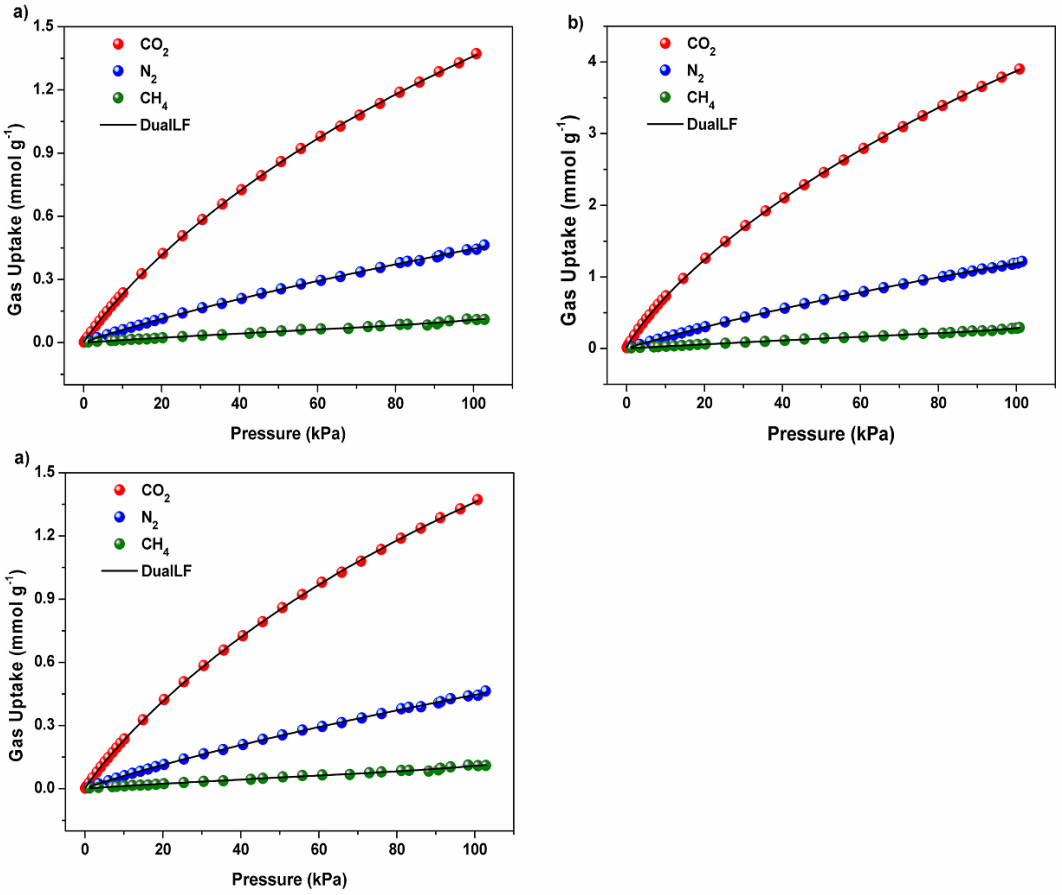

Fig. S9 Gas sorption isotherms of CO_2, CH_4 and N_2 along with the dual-site Langmuir-Freundlich (DSLF) fits for **CMP-LS1** (a), **CMP-LS2** (b) and **CMP-LS3** (c) at 273 K.

The experiment of luminescence detection

The micrometer-sized samples C**MP-LS1** and **CMP-LS2** were used for the detection experiments by taking advantage of their excellent dispersible nature, which might facilitate the close contact between the host frameworks and analytes. The sensing experiments were carried out as follows: C**MP-LS1** or **CMP-LS2** (5 mg) were well dispersed in ethanol (20 mL) with ultrasonic treatment for about 10 minutes; then various amounts of nitroaromatic compounds (analyte molecules) were added to a

quartz cuvette containing the suspension of **CMP-LS1** or **CMP-LS2** in 2 mL solution of ethanol for luminescence detection experiment. The emission spectra of these suspensions were recorded.

The cyclic detection experiment

C**MP-LS1** or **CMP-LS2** (5 mg) were dispersed in ethanol (20 mL) and the emission spectra without the addition of PA were recorded. Then the emission spectra with the addition of PA were recorded. The resulting suspension was transferred to a centrifuge tube. After being repeatedly washed by ethanol and centrifuged for three times, the materials were dried for another cyclic test.

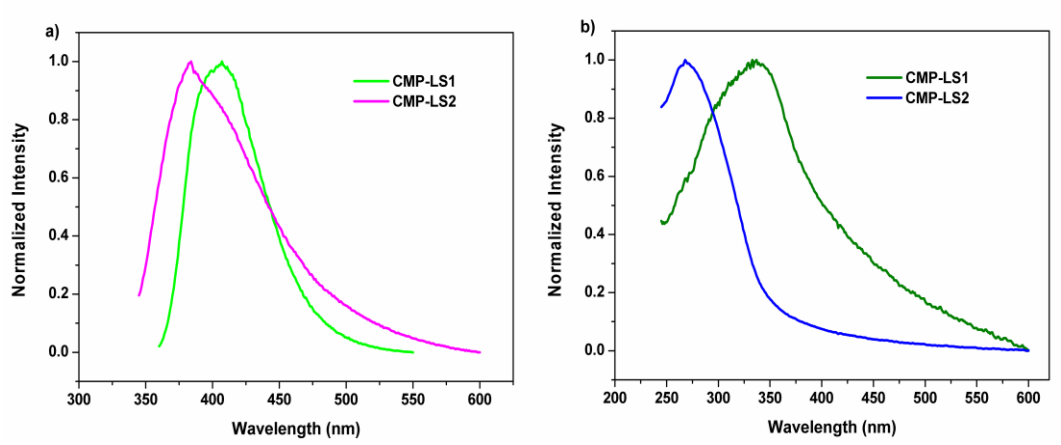

Fig. S10 Luminescent emission spectra of (0.25 mg mL^{-1}) (a), and the UV-vis absorption spectra of **CMP-LS1** and **CMP-LS2** in ethanol (0.05 mg mL^{-1}) (b).

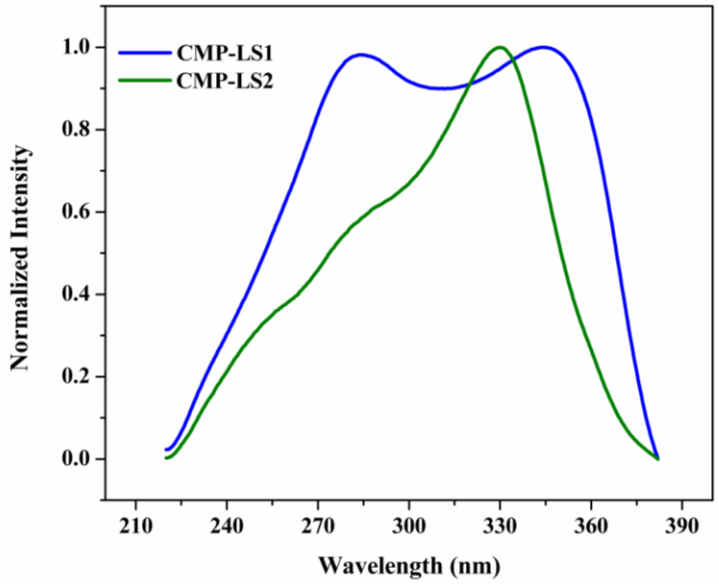

Fig. S11 Excitation spectra of **CMP-LS1** and **CMP-LS2** in ethanol (0.25 mg mL^{-1})

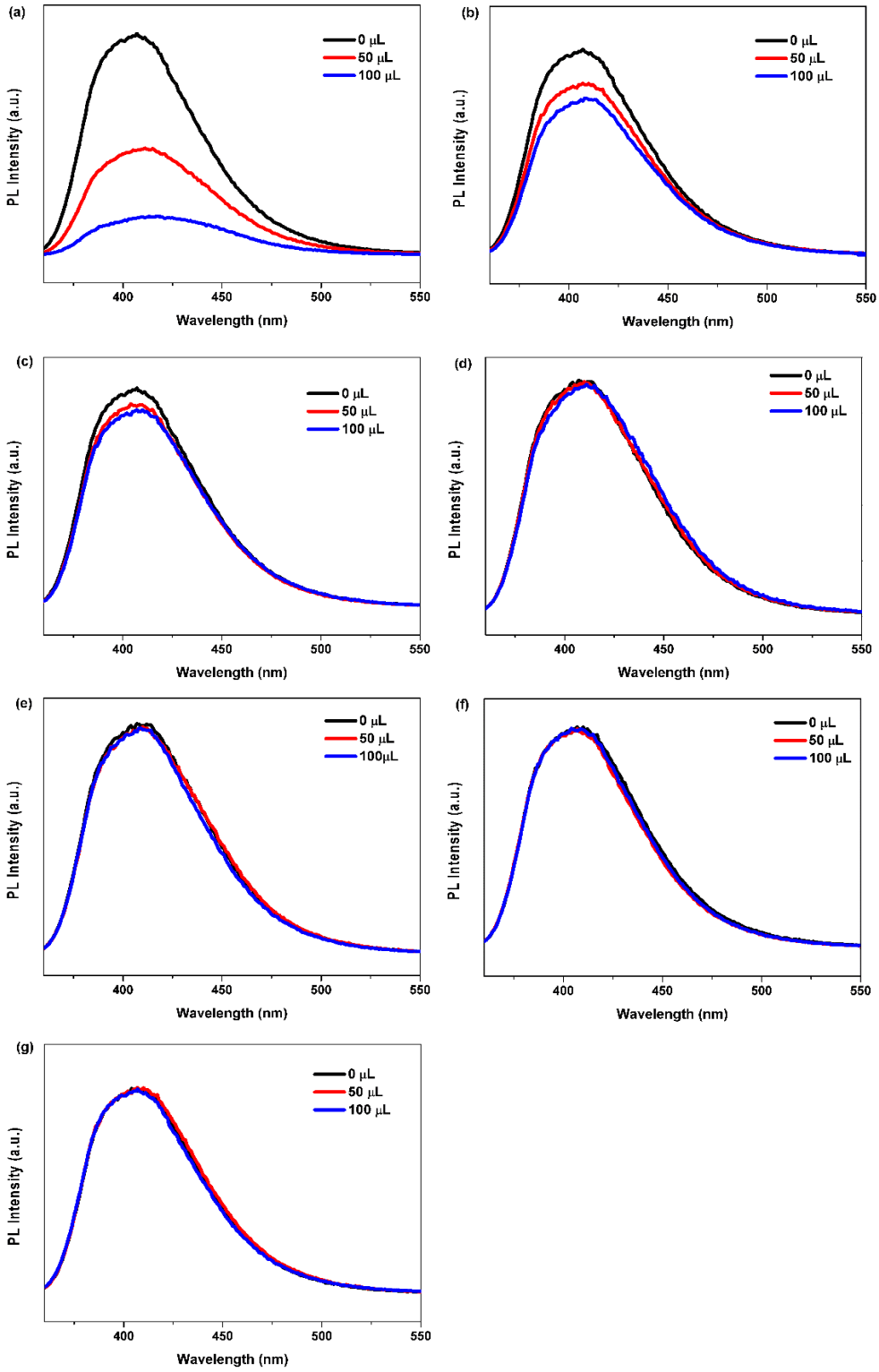

Fig. S12 Fluorescent Emission quenching observed for the suspension of **CMP-LS1** (0.25 mg mL^{-1} in ethanol, λ_{ex} = 345) upon addition of (a) PA, (b) NP, (c) ClDNB, (d) NT, (e) DNT, (f) ClNB and (g) NBA. The fluorescent emission spectra were recorded from 360 nm to 550 nm.

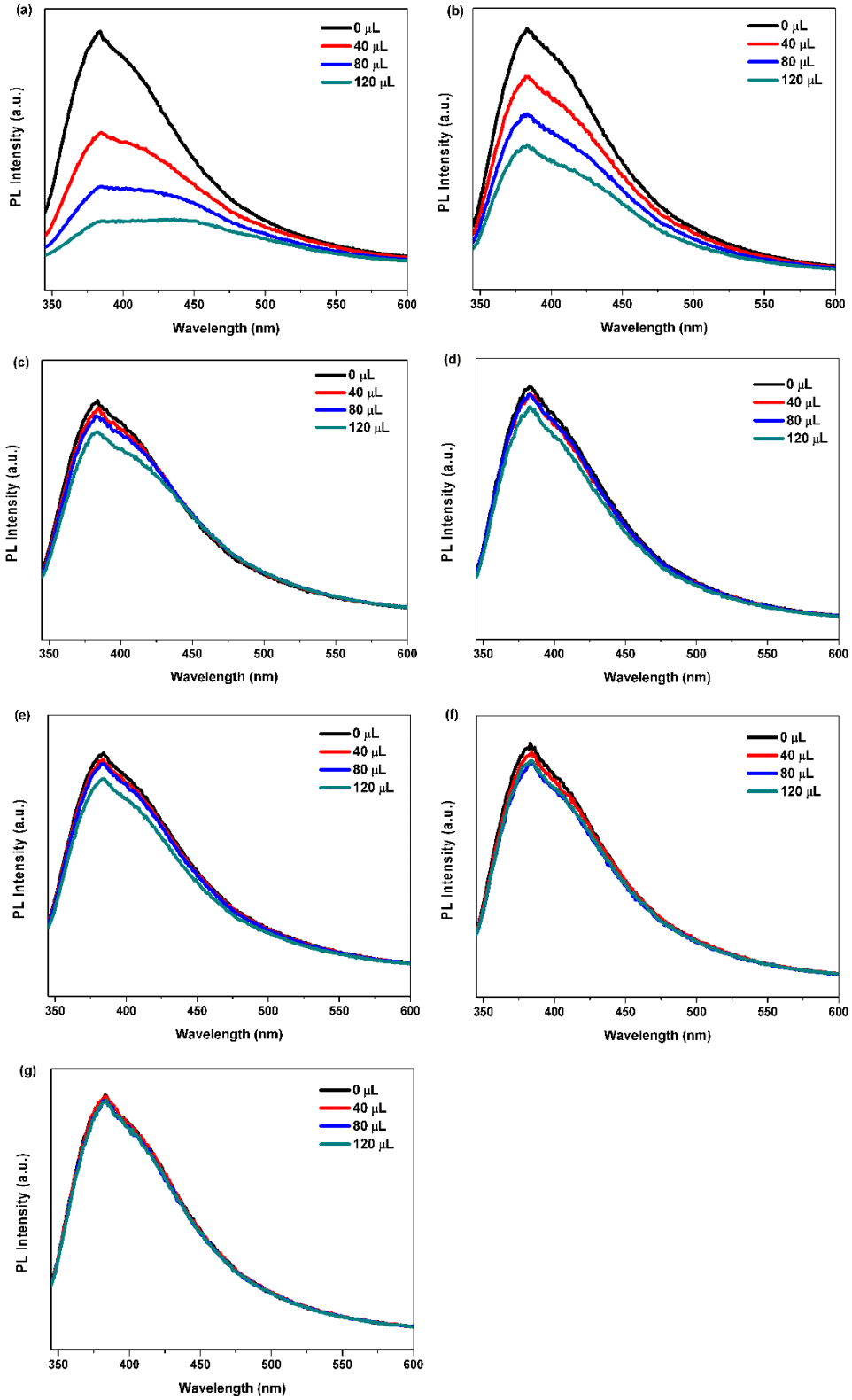

Fig. S13 Fluorescent emission quenching observed for the suspension of **CMP-LS2** (0.25 mg mL^{-1} in ethanol, λ_{ex} = 332) upon addition of (a) PA, (b) NP, (c) ClDNB, (d) NT, (e) DNT, (f) ClNB and (g) NBA. The fluorescent emission spectra were recorded from 350 nm to 600 nm.

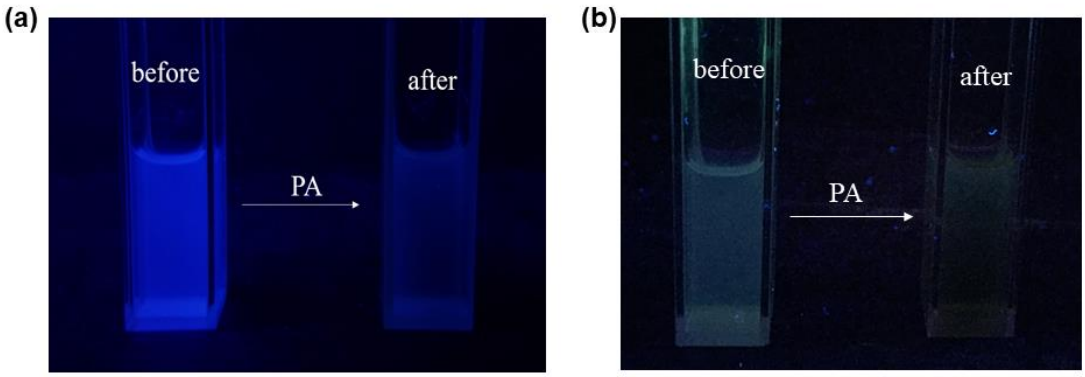

Fig. S14 The fluorescent visible color change of **CMP-LS1** (a) and **CMP-LS2** (b) dispersed in ethanol before and after addition of PA under UV light (365 nm).

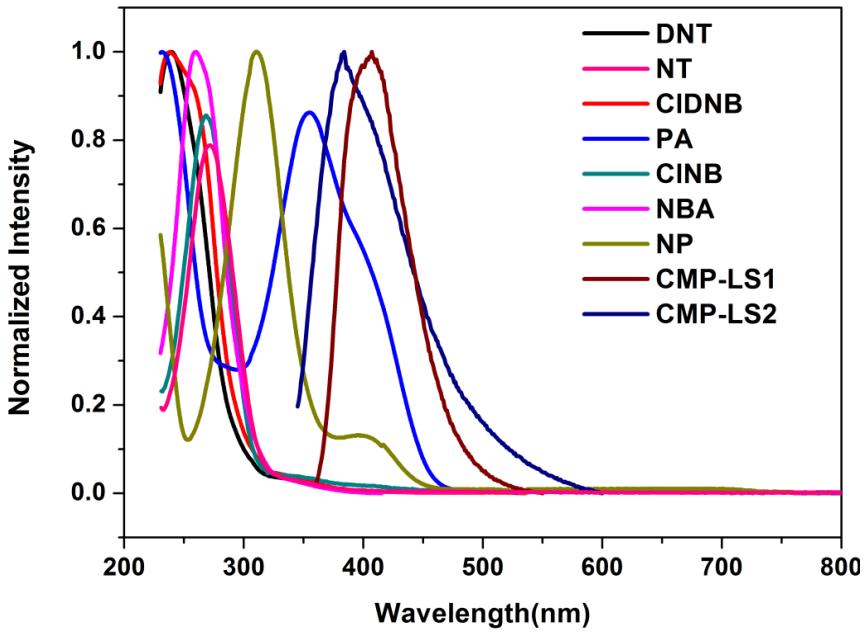

Fig. S15 Spectral overlap between the absorption spectra of analytes and the emission spectra of **CMP-LS1** and **CMP-LS2** in ethanol.

Table S1 Summary of CO_2 uptakes in porous organic polymers at 273 K and 1 atm.

POPs	CO_2 uptake (mmol/g)	Ref.	POPs	CO_2 uptake (mmol/g)	Ref.
CMP-LS2	3.90	our work	PAF-1	2.05	6
TCMP-0	2.38	1	PAF-3	3.48	
TCMP-2	2.62		PAF-4	2.41	
TCMP-3	2.25		A_6CMP-6	3.62	7
TCMP-5	1.22		A_6CMP-5	3.44	
CMP-1-NH_2	1.80	2	ZnP-5%F-CMPs	1.32	8
CMP-1-$(OH)_2$	1.60		ZnP-25%F-CMPs	1.91	
CMP-1-COOH	2.05		ZnP-50%F-CMPs	2.95	
Azo-POF-1	2.98	3	HCP-1	3.01	9
Azo-POF-2	1.92		HCP-2	3.30	
Ene-POF-1	2.19		HCP-3	3.24	
Ene-POF-2	1.61		HCP-4	3.92	
CPOP-16	2.34	4	CMP-YA	2.10	10
CPOP-17	2.50		CMP-SO-1B2	2.12	
CPOP-18	3.43		CMP-SO-1B3	2.09	
CPOP-19	3.80		PCP-Cl	2.31	11
POPs-B10	3.20	5	PCP-BF_4	2.20	
POPs-B20	3.29		PCP-BF_6	1.78	

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Table S2 The refined parameters for the Dual-site Langmuir-Freundlich equations fit

for the pure isotherms of CO_2, CH_4 and N_2 for **CMP-LS1**–**3** at 273 K.

		a_1	b_1	c_1	a_2	b_2	c_2	R^2
CMP-LS1	CO_2	4.08576	0.00349	1.01655	0.29860	0.04111	1.02293	0.99998
	CH_4	0.63615	0.01064	0.92436	6.83897	5.92E-05	1.32348	0.99985
	N_2	0.00132	0.00952	0.89513	1.80598	5.93E-04	1.01251	0.99597
CMP-LS2	CO_2	0.91006	0.05648	0.91237	14.06651	0.00357	0.95508	0.99999
	CH_4	0.06808	9.76E-04	2.05057	20.07398	9.50E-04	0.89834	0.99994
	N_2	1.47035	4.06E-05	1.66318	26.37054	2.04E-04	0.74075	0.99891
CMP-LS3	CO_2	4.09365	0.00352	1.01516	0.29474	0.04119	1.02448	0.99998
	CH_4	0.37402	0.01614	0.94159	10.04345	8.42E-05	1.23457	0.99985
	N_2	3.31061	3.70E-04	0.78279	9.80042	1.57E-04	0.95190	0.99799

Table S3 Comparison of the selectivity for different adsorbents.

POPs	CO_2/CH_4	CO_2/N_2	Ref.
CMP-LS1	4.5	23.2	This work
CMP-LS2	5.6	27.9	
CMP-LS3	4.5	19.8	
SCMP-COOH@1	4.4	24.9	1
SCMP-COOH@2	5.2	30.5	
SCMP-COOH@3	4.5	36.2	
BILP-3	8.1	59.0	2
BILP-6	8.4	63.0	
BILP-7	9.0	62.0	3
PCTF-1	5.0	13.0	4
PCTF-3	6.0	25.0	5
NPC-1-600	7.0	37.0	6

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Table S4 Summary of K_{sv} of polymers.

polymers	$K_{SV}/M^{-1}(10^4)$	Ref.
CMP-LS1	5.05	our work
CMP-LS2	3.70	
1'	2.90	1
compound 1’	3.50	2
1'	6.39	3
2'	7.18	
LMOP-15	2.60	4
PP_C-PPy_S-PAF-2	2.42	5
DBQP	9.02	6
DBQN	1.79	
DTF	2.08	7
Zn-TCPP′	3.59	8

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