Supporting information

Multifunctional Microporous Organic Polymers

Buyi Li^{a†}, Zhenhong Guan^{b†}, Xinjia Yang^a, Wei David Wang^c, Wei Wang^c, Irshad Hussain^d, Kunpeng Song ^b, Bien Tan^{a*} and Tao Li^{b*}

^a Institute of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road No. 1037, Wuhan, 430074, China

^b Key Laboratory for Large-Format Battery Materials and System, Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Luoyu Road No. 1037, Wuhan, 430074, China.

^e State Key Laboratory of Applied Organic Chemistry, Lanzhou University, College of Chemistry and Chemical Engineering, Lanzhou 730000, China

^d Department of Chemistry, SBA School of Science & Engineering (SSE), Lahore University of Management Sciences (LUMS), DHA, Lahore Cantt – 54792, Lahore, Pakistan

[†]Buyi Li and Zhenhong Guan contributed equally.

Solid NMR



Figure S1 ¹³C (CP/MAS) NMR of SMPs-1. The ¹³C CP/MAS NMR of SMPs-1 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Asterisks denote spinning sidebands.



Figure S2 ¹³C (CP/MAS) NMR of SMPs-2. The ¹³C CP/MAS NMR of SMPs-2 shows resonance peaks near 139 and 130 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Because naphthalene is π -conjugate compound, the chemical shifts of the non-coupling aromatic carbons are very close and form a broad peak at 130 ppm. The π -conjugate system also affects the chemical shift of coupling aromatic carbon changing it to 139 ppm. Asterisks denote spinning sidebands.



Figure S3 ¹³C (CP/MAS) NMR of SMPs-3. The ¹³C CP/MAS NMR of SMPs-3 shows broad resonance peaks at 126 ppm. Compared to naphthalene, pyrene possessed larger π -conjugate system, the chemical shifts of all aromatic carbons are very close and form a broad peak at 126 ppm. The chemical shift of coupling aromatic carbons expected at lower filed (higher ppm) is covered by the broad peak. Asterisks denote spinning sidebands.



ppm (t1)

Figure S4 ¹³C (CP/MAS) NMR of SMPs-4. The ¹³C CP/MAS NMR of SMPs-4 shows resonance peaks at 111 ppm, 128 ppm, 139 ppm and 155ppm which are consistent with the chemical shift of meso-tetraphenylporphyrin. The broad peaks at 128 ppm and 139 ppm is due to large π -conjugate system. Asterisks denote spinning sidebands.



Figure S5 ¹³C (CP/MAS) NMR of SMPs-5. The ¹³C CP/MAS NMR of SMPs-5 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Resonance peak at 54 ppm is due to the carbon of - CH₂-NH₂. Asterisks denote spinning sidebands.



ppm (t1)

Figure S6¹³C (CP/MAS) NMR of SMPs-6a. The ¹³C CP/MAS NMR of SMPs-6a shows resonance peak at 149 ppm due to the carbon of –COOH. The peak at 140 ppm is due to coupling aromatic carbon. The peak at 127 ppm is for non-coupling aromatic carbon on the sym-PhPh₃ monomer. The peak at 125 ppm was for non-coupling aromatic carbon on the benzoic acid. Asterisks denote spinning sidebands. Asterisks denote spinning sidebands.



Figure S7 ¹³C (CP/MAS) NMR of SMPs-7. The ¹³C CP/MAS NMR of SMPs-7 shows resonance peaks at 141 and 127 ppm due to coupling aromatic carbons and non-coupling aromatic carbons respectively. Resonance peak at 108 ppm is due to the non-coupling carbons of pyrrole ring. Asterisks denote spinning sidebands.



Figure S8¹³C (CP/MAS) NMR of SMPs-8a. The ¹³C CP/MAS NMR of SMPs-8 shows resonance peaks at 140 and 128 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Asterisks denote spinning sidebands.



Figure S9 ³¹P HPDEC/MAS NMR of SMPs-8a and SMPs-8b. Comparing to SMPs-8a, the ³¹P HPDEC/MAS NMR resonance peaks of SMPs-8b became slightly broader and shifted from 21 ppm to 27 ppm, which indicate the successful coordination of Pd^{II} with the phosphorous atom. Asterisks denote spinning sidebands.



Figure S10 ¹³C (CP/MAS) NMR of SMPs-9a. The ¹³C CP/MAS NMR of SMPs-9a shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Resonance peak at 155 ppm is due to the carbon near N in pyridine ring. Asterisks denote spinning sidebands.



Figure S11 ¹³C (CP/MAS) NMR of SMPs-10. The ¹³C CP/MAS NMR of SMPs-10 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons (including thiophene carbon) and non-coupling aromatic carbons (including thiophene carbon) respectively. Asterisks denote spinning sidebands.



Figure S12 ¹³C (CP/MAS) NMR of SMPs-11. The ¹³C CP/MAS NMR of SMPs-11 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons (including furan carbon) and non-coupling aromatic carbons respectively. Resonance peak at 111 ppm is due to the non-coupling furan carbon. Asterisks denote spinning sidebands.



Figure S13 ¹³C (CP/MAS) NMR of SMPs-12. The ¹³C CP/MAS NMR of SMPs-12 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Resonance peak at 55 ppm is due to the carbon of – OCH₃. Resonance peaks at 160 ppm is due to the aromatic carbon linking with –OCH₃. Asterisks denote spinning sidebands.



ppm (t1)

Figure S14 ¹³C (CP/MAS) NMR of SMPs-13. The ¹³C CP/MAS NMR of SMPs-13 shows resonance peaks at 140 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Resonance peaks at 145 ppm is due to the aromatic carbon linking with –OH. Asterisks denote spinning sidebands.



Figure S15 ¹³C (CP/MAS) NMR of SMPs-14. The ¹³C CP/MAS NMR of SMPs-14 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Asterisks denote spinning sidebands.



Figure S16 ¹³C (CP/MAS) NMR of SMPs-15. The ¹³C CP/MAS NMR of SMPs-15 shows resonance peaks at 141 and 127 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Resonance peak at 146 ppm is due to the carbon near N in 1,10-phenanthroline. Asterisks denote spinning sidebands.



Figure S17 ¹³C (CP/MAS) NMR of SMPs-16. The ¹³C CP/MAS NMR of SMPs-16 shows resonance peaks at 140 and 126 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Asterisks denote spinning sidebands.



Figure S18 ¹³C (CP/MAS) NMR of SMPs-17. The ¹³C CP/MAS NMR of SMPs-17 shows resonance peaks at 140 and 126 ppm due to the coupling of aromatic carbons and non-coupling aromatic carbons respectively. Resonance peak at 28 ppm is due to the carbon of – CH_2 -. Resonance peaks at 119 ppm is due to the carbon of -CN. Asterisks denote spinning sidebands.

FT-IR

In the FTIR spectrum of all samples (**Fig. S19-S35**), weak peaks near 3000 cm⁻¹ are attributed to C-H stretching in aromatic ring; peaks near 1600 cm⁻¹, 1500 cm⁻¹ and 1450 cm⁻¹ are attributed to aromatic ring skeleton vibrations; and peaks near 1000 cm⁻¹ are attributed to C-H bending in aromatic ring, which are consistent with the structure of monomers.



Figure S19 FT-IR spectrum of SMPs-1.







Figure S21 FT-IR spectrum of SMPs-3.



Figure S22 FT-IR spectrum of SMPs-4.









(b) Figure S24 FT-IR spectrum of SMPs-6a (a) and SMPs-6b (b).



Figure S25 FT-IR spectrum of SMPs-7.



Figure S26 FT-IR spectrum of SMPs-8a.



Figure S27 FT-IR spectrum of SMPs-9a.



Figure S29 FT-IR spectrum of SMPs-11.



Figure S30 FT-IR spectrum of SMPs-12.



Figure S31 FT-IR spectrum of SMPs-13.











Figure S34 FT-IR spectrum of SMPs-16.



Figure S35 FT-IR spectrum of SMPs-17.



Figure S36 SEM image of SMPs-1





Figure S38 SEM image of SMPs-3







Figure S41 SEM image of SMPs-6a









Spot Magn Det WD 30 20000x SE 53 HUST 1 µm Figure S44 SEM image of SMPs-9a



Figure S45 SEM image of SMPs-10











Figure S50 SEM image of SMPs-15









Figure S53 Volumetric H_2 adsorption and desorption isotherms up to 1.13 bar at 77.3 K



Figure S54 volumetric CO_2 adsorption and desorption isotherms up to 1.13 bar at 273.15 K (a) and 298.15 K (b) of SMPs.



Figure S55 Nitrogen adsorption (solid) and desorption (open) isotherms of SMPs-8a (a) and SMPs-8b (b); Pore size distributions calculated using DFT methods (slit pore models, differential pore volumes. pore width) of SMPs-8a (c) and SMPs-8b (d).



Figure S56 Nitrogen adsorption (solid) and desorption (open) isotherms of SMPs-9a (a) and SMPs-9b (b); Pore size distributions calculated using DFT methods (slit pore models, differential pore volumes. pore width) of SMPs-9a (c) and SMPs-9b (d).



Figure S57 Selective oxidation of alcohols catalyzed by SMPs-9b.



Figure S58 Solid-state UV-vis spectrum of SMPs-1.



Figure S59 Solid-state UV-vis spectrum of SMPs-3.



Figure S60 Solid-state UV-vis spectrum of SMPs-5.



Figure S61 Solid-state UV-vis spectrum of SMPs-6a.



Figure S62 Solid-state UV-vis spectrum of SMPs-9a.



Figure S63 Solid-state UV-vis spectrum of SMPs-14.



Figure S64 Solid-state UV-vis spectrum of SMPs-15.



Figure S65 Solid-state UV-vis spectrum of SMPs-16.



Figure S66 Solid-state UV-vis spectrum of SMPs-17.



Figure S67 Fluorescence spectra of SMPs-1. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 490 nm.



Figure S68 Fluorescence spectra of SMPs-3. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 415 nm.



Figure S69 Fluorescence spectra of SMPs-5. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 524 nm.



Figure S70 Fluorescence spectra of SMPs-6a. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 497 nm.



Figure S71 Fluorescence spectra of SMPs-9a. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 490 nm.



Figure S72 Fluorescence spectra of SMPs-14. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 325 nm.



Figure S73 Fluorescence spectra of SMPs-15. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 300 nm.



Figure S74 Fluorescence spectra of SMPs-16. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 365 nm.



Figure S75 Fluorescence spectra of SMPs-17. Excitation spectrum is black line and emission spectrum is red line. Excitation wavelength is 445 nm.

compla	Monomora	$\mathbf{S}_{\text{BET}}{}^{a}$	$S_L{}^b$	PV ^c	MPV ^d	CO_2^e
sample	ne wonomers		(m^2/g)	(cm^{3}/g)	(cm^{3}/g)	(wt. %)
SMPs-1	sym-PhPh ₃	1254	1667	0.66	0.51	10.4
SMPs-5	sym-PhPh ₃ & benzyl amine	856	1139	0.53	0.35	11.2
SMPs-6a	sym-PhPh ₃ & benzoic acid	879	1178	0.47	0.35	8.2
SMPs-6b	sym-PhPh ₃ & potassium benzoic acid	838	1113	0.43	0.34	10.1
SMPs-7	sym-PhPh ₃ & pyrrole	1421	1424	0.83	0.58	11.5
SMPs-10	sym-PhPh ₃ & thiophene	1109	1506	0.61	0.45	8.8
SMPs-11	sym-PhPh ₃ & furan	1111	1421	0.58	0.45	10.2
SMPs-12	sym-PhPh ₃ & anisole	766	981	0.42	0.30	7.6
SMPs-13	sym-PhPh ₃ & phenol	798	1080	0.44	0.32	8.0
SMPs-14	sym-PhPh ₃ &phenylene diamines	914	1229	0.57	0.38	9.4

Table S1 Composition surface area, pore structure and CO_2 adsorption properties of SMPs with various functional groups

^a Surface area calculated from nitrogen adsorption isotherms at 77.3 K using BET equation. ^b Surface area calculated from nitrogen adsorption isotherms at 77.3 K using Langmuir equation. ^c Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.995$, 77.3 K. ^d Micropore volume calculated from the nitrogen isotherm at $P/P_0 = 0.050$. ^e CO₂ uptake determined volumetrically using a Micromeritics ASAP 2020 M analyzer at 1.00 bar and 298.15 K.

Samplas	Monomors	$\mathbf{S}_{\text{BET}}{}^a$	$\mathbf{S}_{\mathrm{L}}{}^{\mathrm{b}}$	PV ^c	MPV ^d
Samples	Wohomers	(m^2/g)	(m^2/g)	(cm ³ /g)	(cm^3/g)
SMPs-8a	sym-PhPh ₃ & PPh ₃	680	915	0.73	0.26
SMPs-8b	sym-PhPh ₃ & PPh ₃ -Pd	651	868	0.61	0.25
SMPs-9a	sym-PhPh ₃ & 2,2'-bipyridine	750	993	0.51	0.31
SMPs-9b	sym-PhPh ₃ & 2,2'-bipyridine-Cu	719	956	0.45	0.30

Table S2 Composition, surface area and porosity of the samples for heterogenous catalysis.

^a Surface area calculated from nitrogen adsorption isotherms at 77.3 K using BET equation. ^b Surface area calculated from nitrogen adsorption isotherms at 77.3 K using Langmuir equation. ^c Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.995$, 77.3 K. ^d Micropore volume calculated from the nitrogen isotherm at $P/P_0 = 0.050$.

 N	Management	$S_{BET}{}^a$	$S_L{}^b$	PVc	MPV ^d
NO.	Monomers	(m ² /g)	(m ² /g)	(cm ³ /g)	(cm ³ /g)
SMPs-1	sym-PhPh ₃	1254	1667	0.66	0.51
SMPs-3	pyrene	636	844	0.32	0.26
SMPs 5	sym-PhPh ₃ & benzyl amine	856	1139	0.53	0.35
SMPs-6	sym-PhPh ₃ & benzoic acid	879	1178	0.47	0.35
SMPs-9a	sym-PhPh ₃ & 2,2'-bipyridine	750	993	0.51	0.31
SMPs-14	sym-PhPh ₃ & phenylene diamines	914	1229	0.57	0.38
SMPs-15	sym-PhPh ₃ & 1,10-phenanthroline	422	560	0.30	0.17
SMPs-16	sym-PhPh ₃ & pyrene	542	728	0.30	0.22
SMPs-17	sym-PhPh ₃ & phenyl cyanide	445	594	0.25	0.17

Table S3 Composition, surface area and pore structure of fluorescent SMPs.

^a Surface area calculated from nitrogen adsorption isotherms at 77.3 K using BET equation. ^b Surface area calculated from nitrogen adsorption isotherms at 77.3 K using Langmuir equation. ^c Pore volume calculated from nitrogen isotherm at $P/P_0 = 0.995$, 77.3 K. ^d Micropore volume calculated from the nitrogen isotherm at $P/P_0 = 0.050$.

sample	Monomer	С	Н	0	N	S
		(%)	(%)	(%)	(%)	(%)
SMPs-1	sym-PhPh ₃	77.90	4.52	_	0.00	_
SMPs-2	naphthalene	77.43	4.96	_	0.00	_
SMPs-3	pyrene	75.06	4.75	_	0.00	_
SMPs-4	meso-tetraphenylporphyrin	75.06	5.13	_	4.38	_
SMPs-5	sym-PhPh ₃ & benzyl amine	68.81	4.05	_	2.87	_
SMPs-6a	sym-PhPh ₃ & benzoic acid	58.67	5.03	10.96	0.00	_
SMPs-6b	sym-PhPh ₃ & potassium benzoate		4.63	9.51	0.00	_
SMPs-7	sym-PhPh ₃ & pyrrole	58.59	3.96	_	2.78	_
SMPs-8a	sym-PhPh ₃ & PPh ₃	72.76	5.23	_	0.00	_
SMPs-9a	sym-PhPh ₃ & 2,2'-bipyridine	70.10	5.27	_	0.34	_
SMPs-10	sym-PhPh ₃ & thiophene	63.67	4.41	_	0.00	7.56
SMPs-11	sym-PhPh ₃ & furan	66.47	4.34	4.16	0.00	_
SMPs-12	sym-PhPh ₃ & anisole	66.95	4.95	4.01	0.00	_
SMPs-13	sym-PhPh ₃ & phenol	66.75	4.71	4.27	0.00	_
SMPs-14	sym-PhPh ₃ &phenylene diamines	68.57	5.04	_	2.82	_
SMPs-15	sym-PhPh ₃ & 1,10- phenanthroline	67.19	5.09	_	0.79	_
SMPs-16	sym-PhPh ₃ & pyrene	79.45	5.03	_	0.00	_
SMPs-17	sym-PhPh ₃ & phenyl cyanide	62.27	4.35	_	1.56	_

Table 54 C, H, O, N, 5 contents of SMPS 1-	Table S4	C, H	, O	, N,	S	contents of SMPs	1-17
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Table S5 Al contents of SMPs 1-8.

sample	Monomer	Al contents (%)
SMPs-1	sym-PhPh ₃	0.030
SMPs-2	naphthalene	0.034
SMPs-3	pyrene	0.020
SMPs-4	meso-tetraphenylporphyrin	0.027
SMPs-5	sym-PhPh3 & benzyl amine	0.048
SMPs-6a	sym-PhPh ₃ & benzoic acid	0.042
SMPs-7	sym-PhPh ₃ & pyrrole	0.045
SMPs-8a	sym-PhPh ₃ & PPh ₃	0.044

Table S6 Comparison of conductance (resistance)^a

samples	Conductance	resistance	literature
	(S)	(ohm)	
TP-COF	~8×10 ⁻⁸	$\sim 1.25 \times 10^{7}$	Angew. Chem. Int. Ed. 2009, 48, 3207
TP-COF+I ₂	~2×10-8	\sim 5×10 ⁷	Angew. Chem. Int. Ed. 2009, 48, 3207
NiPc COF	~1.7×10-8	~6×107	Angew. Chem. Int. Ed. 2011, 50, 1289
ZnP-COF	~3×10 ⁻⁸	$\sim 3 \times 10^7$	Angew. Chem. Int. Ed. 2012, 51, 2618
SMPs-7	1.1×10-6	8.8×10^5	This work
SMPs-7+ I ₂	1.2×10-5	8.7×10^{4}	This work
SMPs-7+HCl	1.3×10-4	7.6×10 ³	This work

^a Some data is calculated by figures in literatures (as the specific thickness and area of samples are not mentioned in literatures, the conductance and resistance are compared here).

¹H NMR

Biphenyl



¹H NMR (400 MHz, CDCl₃,): δ 7.59 (d, J = 7.2 Hz, 4H), 7.44 (t, J = 8.0 Hz, 4H,), 7.34 (tt, J_a = 1.2 Hz, J_b = 7.6 Hz, 2H).

2-Methyl-biphenyl



¹H NMR (400 MHz, CDCl₃,): δ 7.45 (d, J = 11.2 Hz, 2H), 7.37-7.40 (m, 3H), 7.29-7.33 (m, 4H), 2.34 (s, 3H).

4-Nitro-biphenyl



¹H NMR (400 MHz, CDCl₃,): δ 8.30 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.62-7.64 (m, 2H), 7.43-7.52 (m, 3H).

4-Methoxy-biphenyl

¹H NMR (400 MHz, CDCl₃,): δ 7.51-7.56 (m, 4H), 7.39-7.43 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H)

4-Trifluoromethyl-biphenyl



¹H NMR (400 MHz, CDCl₃): δ 7.67 (s, 4H), 7.57 (d, J = 8.0 Hz, 2H), 7.47-7.37 (m, 3H).





