Supporting Information

New nitrogen-rich azo-bridged porphyrin conjugated microporous networks for high performance of gas capture and storage

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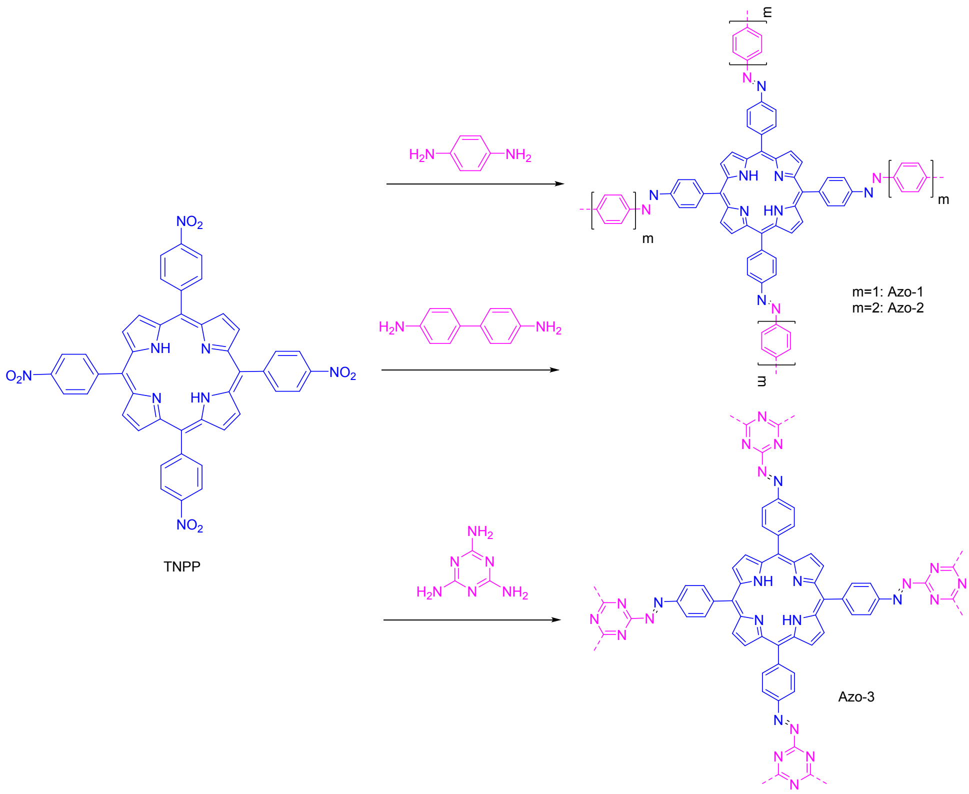
Synthesis of Azo-2, TNPP (0.3176 g, 0.4 mmol), benzidine (0.1474 g, 0.8 mmol) and KOH (0.22 g, 3.94 mmol) were dissolved in DMF (25 mL). The reaction mixture was heated to 150 °C and stirred for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, added with 150 mL of distilled water and stirred for 1 h. Black precipitate was filtered off and washed several times with distilled water, acetone and THF in order to remove any unreacted monomers and KOH. Subsequently, black precipitates were dried at 60 °C under vacuum overnight to yield Azo-2: 0.30g. The rate was 65% with elemental analysis of C, 74.82; H, 9.92; N, 14.01 (%).

Synthesis of Azo-3, TNPP (0.3176 g, 0.4 mmol), melamine (0.0673 g, 0.53 mmol) and KOH (0.22 g, 3.94 mmol) were dissolved in DMF (25 mL). The reaction mixture was heated to 150 °C and stirred for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, added with 150 mL of distilled water and stirred for 1 h. Black precipitate was filtered off and washed several times with distilled water, acetone and THF in order to remove any unreacted monomers and KOH. Subsequently, black precipitates were dried at 60 °C under vacuum overnight to yield Azo-3: 0.29g. Yield were was 75% with elemental analysis of C, 72.03; H, 4.40; N, 15.49 (%).



Scheme 1S. Synthesis of polymers Azo-1, Azo-2, and Azo-3 under the same condition: TNPP and amino-containing building blocks, KOH, DMF, 150 ^{o}C, 24 h.

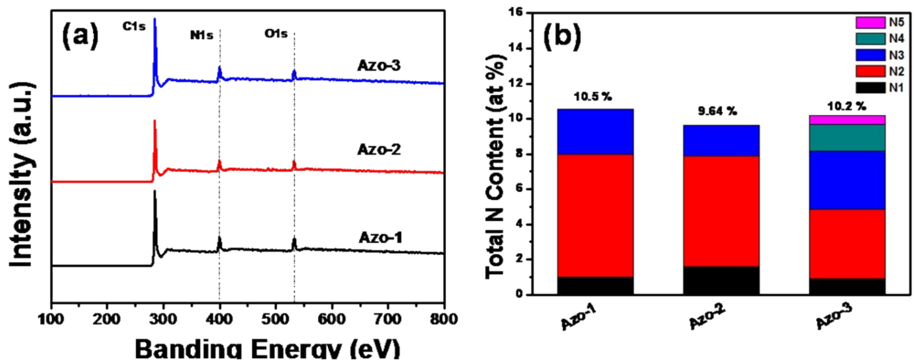


Fig.S1. (a) XPS survey spectra, (b) atomic percentages of different nitrogen species for Azos.

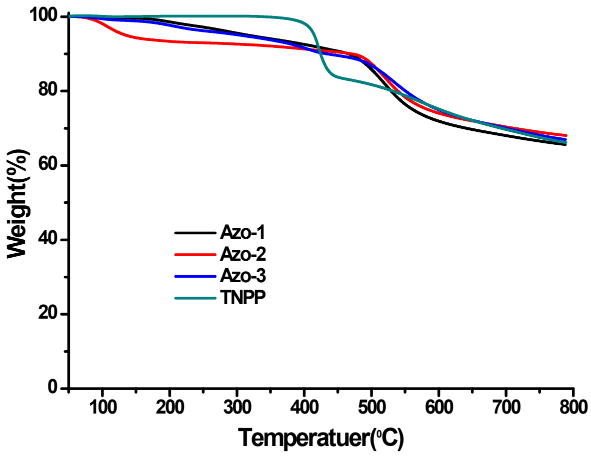


Fig.S2. TGA curves of Azo-1, Azo-2 and Azo-3 under N_2 atmosphere up to 800°C at a rate of 20°Cmin^{-1}.

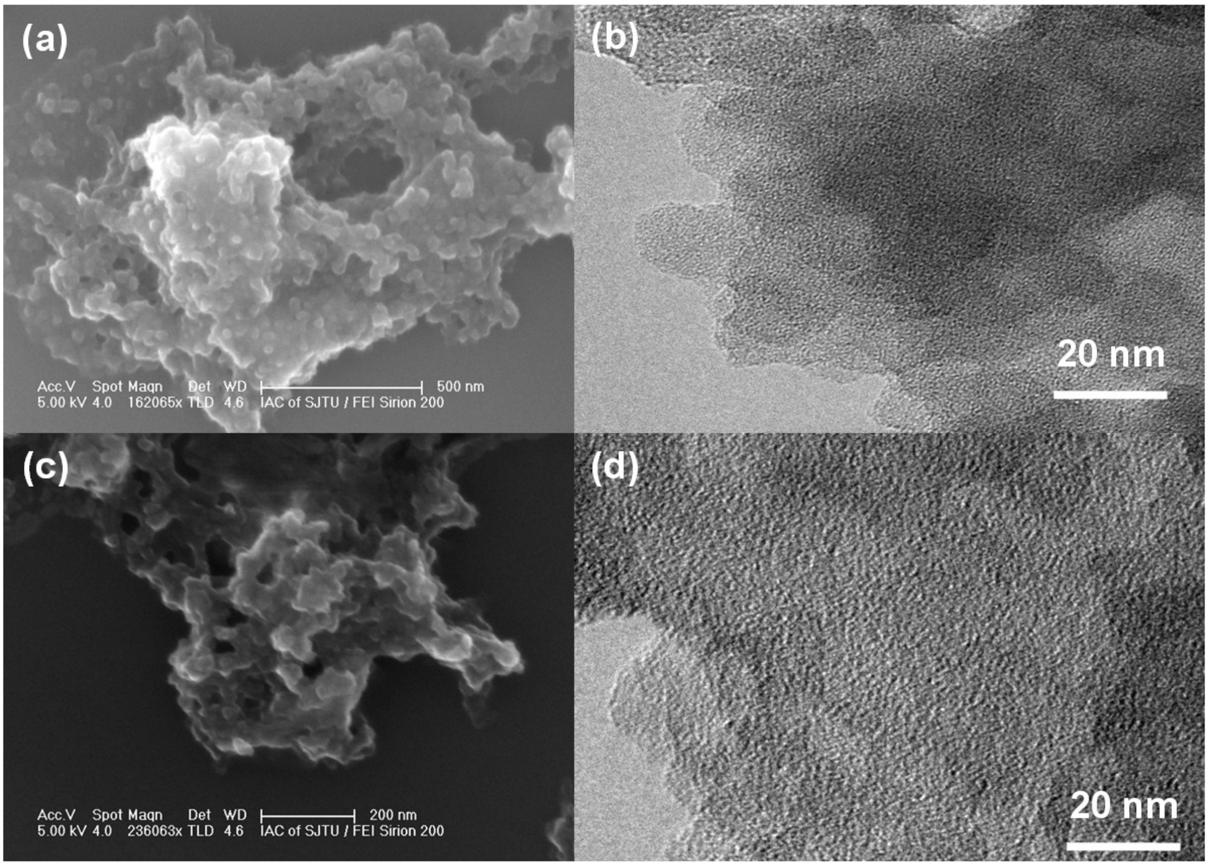


Fig.S3. Typical SEM images and TEM images of Azos. ((a) (b) is for Azo-2 and (c) (d) is for Azo-3).

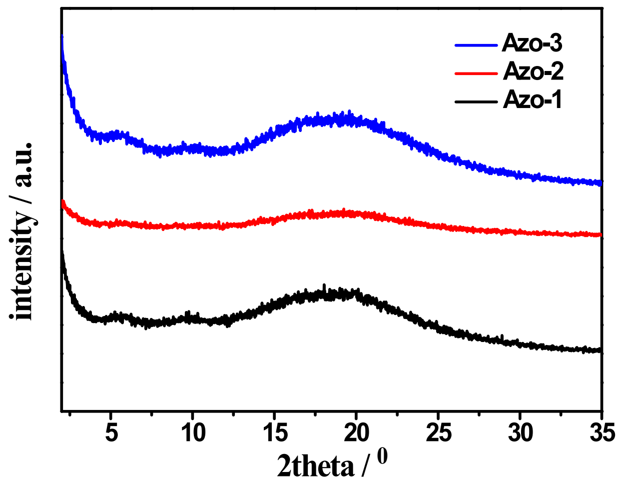


Fig.S4. XRD patterns of Azo-1, Azo-2, and Azo-3.

Table S1. Surface Properties and CO_2 Uptake for reported networks

Name	S_{BET} [m^2/g]	CO^2 uptake [mmolg^{-1}]^a (wt %)		References
		273K	298K	
CTF-0	687	1.53(6.30)	-	PhisanKatekomol[1]
CMP-1	837	1.56(6.86)	-	Robert Dawson[2]
CMP-1-$(CH_3)_2$	899	0.94(4.14)	-	Robert Dawson[2]
CMP-1-COOH	522	1.60(7.04)	-	Robert Dawson[2]
DmaTph	431	1.65(7.26)	-	SharathKandambeth[3]
PAF-1	5600	2.05(9.02)	1.09(4.80)	Teng Ben[4]
PAF-3	2932	3.48(15.3)	1.82(8.0)	Teng Ben[4]
PAF-4	2246	2.43(10.7)	1.16(5.1)	Teng Ben[4]
COF-1	750	2.32(10.21)	-	Hiroyasu Furukawa[5]
TPI-1	809	2.45(10.78)	-	Mario R. Liebl[6]
azo-CMP-1	-	2.45(10.76)	1.48(6.53)	Hasmukh A. Patel[7]
azo-CMP-2	-	2.55(11.24)	1.53(6.73)	Hasmukh A. Patel[7]
azo-CMP-3	-	1.93(8.51)	1.22(5.36)	Hasmukh A. Patel[7]
Nerwork-1	3160	-	1.48(6.54)	James R. Holst[8]
Nerwork-2	1102	-	0.91(4.01)	James R. Holst[8]
Nerwork-3	3180	-	1.72(7.56)	James R. Holst[8]
Nerwork-A	4077	2.65(11.66)	1.45(6.38)	Robert Dawson[9]
Nerwork-D	1213	2.42(10.65)	1.33(5.85)	Robert Dawson[9]
Nerwork-E	1470	2.95(12.98)	1.77(7.79)	Robert Dawson[9]
Nerwork-F	653	1.80(7.92)	1.08(4.75)	Robert Dawson[9]
Nerwork-G	1056	2.15(9.46)	1.25(5.5)	Robert Dawson[9]
N-heterocyclic carbenes	475	-	2.17 (9.55)	Coskun[10]

Porphyin1	1510	3.17 (13.9)	-	Liu, X.[11]
Porphyrin2	557	2.76 (12.1)	1.42 (7.9)	Neti[12]
Azo-POF1	712	2.97 (13.1)	1.88 (8.31)	Lu[13]
Azo-anline	412-801	4.46 (19.7)	2.94 (13.0)	Arab[14]
Azo-1	571	2.14(9.42)	1.62 (7.11)	Our work
Azo-2	675	3.98(17.52)	2.04(8.97)	Our work
Azo-3	520	2.87(12.63)	1.50(6.60)	Our work

[a] CO_2 uptake measured at 273 K , 298 K and 1 bar.

Table S2. Surface properties and H_2 uptake for reported networks

Name	S_{BET} [m^2/g]	H_2 uptake [wt %][a]	References
CMP-3B	325	0.53	Jia-Xing Jiang[15]
Network-5	1470	1.00	James R. Holst[8]
Network-1	682	0.81	Robert Dawson[16]
Azo-1	571	0.86	Our work
Azo-2	675	1.15	Our work
Azo-3	520	0.97	Our work

[a] H_2 uptake measured at 77 K and 1 bar.

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