Electronic Supplementary Material (ESI) for Chemical Communications

Polyanionic and polyzwitterionic azobenzene ionic liquid-functionalized silica materials and their chromatographic applications

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Characterizations:

From the elemental analysis results, sulfonic azobenzene moieties grafted onto the silica is 0.87 μmol m^{-2} for Sil-PAzO. After cation-exchange, the bonding density is 0.92 μmol m^{-2} for Sil-PAzO-ImC_{18} calculated from the content of nitrogen. For Sil-P(AzO-ImC_{18}), the bonding density of the monomer couple is 0.84 μmol m^{-2}, which is very near to that of previous two materials. As pointed out by the reviewer, 1 μmol m^{-2} is equivalent to 0.6 molecule or ion pair *per* nm^2, so these quantities are about 0.5 groups *per* nm^2. That means 1 ion pair exist in 2 nm^2 on the silica surface.

In the DRIFT spectrum for the Sil-PAzO surface, obvious characteristic signals at 1601 and 1504 cm^{-1} are attributed to the stretching vibration of phenyl bond of sulfonic azobenzene. Additional peaks at 2926 and 2855 cm^{-1} assigned to the C–H stretching of the tetrahedral carbon were appeared for Sil-PAzO-ImC_{18} and Sil-P(AzO-ImC_{18}) (Fig. S3, ESI).

From the solid ^{13}C NMR, we can see that the spectra of these two IL-grafted silica materials are very similar, especially the ratio of the height between *trans* and *gauche* peaks (Fig. S4, ESI).

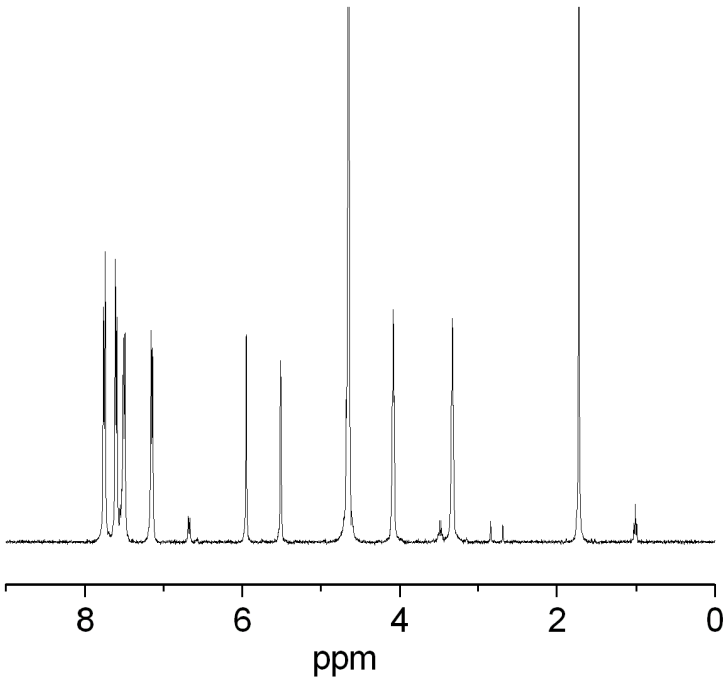

Fig. S1 ^{1}H NMR spectrum of MA-AzO.

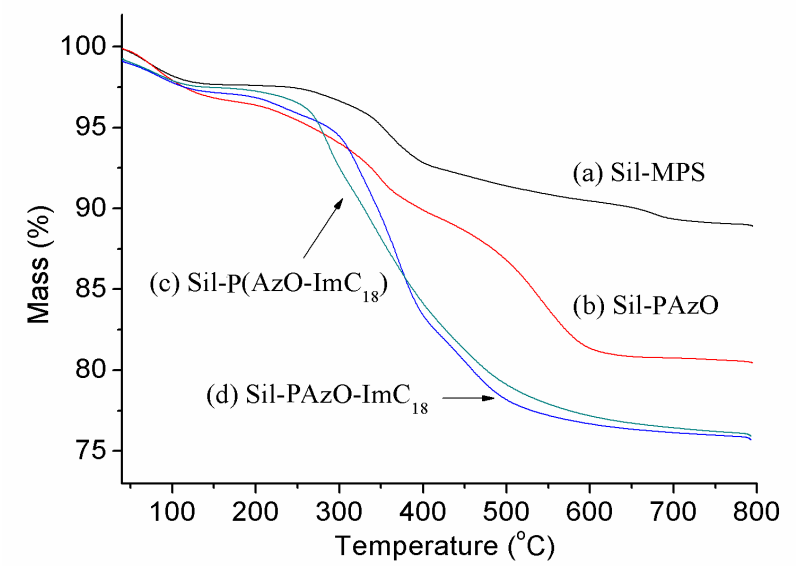

Fig. S2 Thermogravimetric curves of Sil-MPS (a), Sil-PAzO (b), Sil-PAzO-ImC_{18} (c), and Sil-P(AzO-ImC_{18}) (d).

Table S1. Elemental analysis of Sil-MPS, Sil-PAzO, Sil-PAzO-ImC_{18}, and Sil-P(AzO-ImC_{18}).

Sample	%C	H%	N%	C/N(det.)[a]	C/N(cal.)[b]	Coverage ($\mu mol/m^2$)
Sil-MPS	4.42	1.27	-	-	-	4.34 (C)[c]
Sil-PAzO	9.40	1.76	1.28	4.19	4.07	0.87 (N)[d]
Sil-PAzO-ImC_{18}	14.26	2.38	1.90	5.61	5.85	0.92 (N)[d]
Sil-P(AzO-ImC_{18})	14.22	2.41	1.73	6.13	6.00	0.84 (N)[d]

In Sil-PAzO, C/N = [9.40%-4.42%×(1-9.40%-1.76%-1.28%)]/1.28%=4.19

In Sil-PAzO, coverage ($\mu mol/m^2$)=1.28%/14/4/(1-9.40%-1.76%-1.28%)/300=0.87

In Sil-PAzO-ImC_{18}, C/N = [14.26%-4.42%×(1-14.26%-2.38%-1.90%)]/1.90%=5.61

In Sil-PAzO-ImC_{18}, coverage ($\mu mol/m^2$)=1.90%/14/6/(1-14.26%-2.38%-1.90%)/300=0.92

In Sil-P(AzO-ImC_{18}), C/N = [14.22%-4.42%×(1-14.22%-2.41%-1.73%)]/1.73%=6.13

In Sil-P(AzO-ImC_{18}), coverage ($\mu mol/m^2$)=1.73%/14/6/(1-14.22%-2.41%-1.73%)/300=0.84

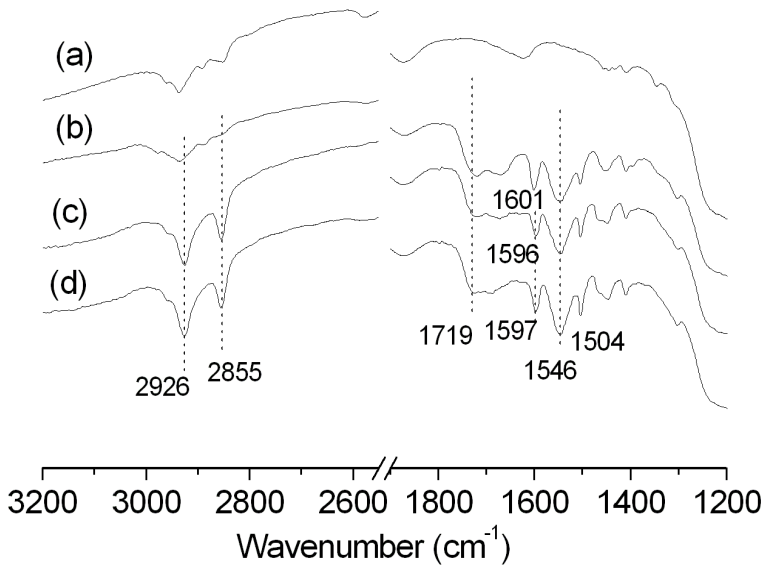

Fig. S3 DRIFT Spectra of Sil-MPS (a), Sil-PAzO (b), Sil-PAzO-ImC_{18} (c), and Sil-P(AzO-ImC_{18}) (d).

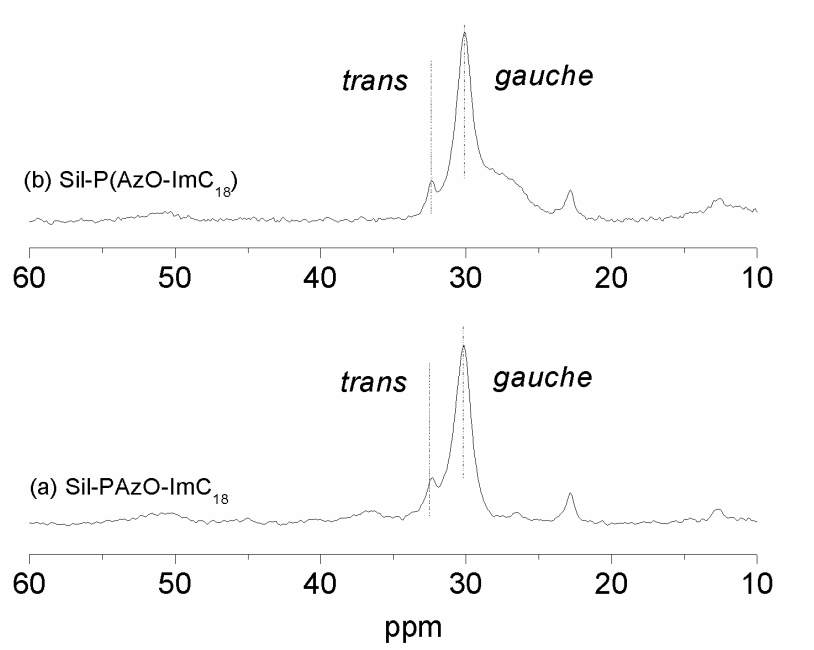

Fig. S4. Solid ^{13}C NMR of Sil-PAzO-ImC_{18} (a) and Sil-(PAzO-ImC_{18}) (b) materials.

Table S2. Retention factors (*k*) and separation factors (α) of *o*-, *m*-, *p*-terphenyls and triphenylene on Sil-PAzO, Sil-PAzO-ImC_{18}, Sil-(PAzO-ImC_{18}) and ODS columns. The chromatographic conditions were the same as in Fig. 2.

	Sil-PAzO		Sil-PAzO-ImC_{18}		Sil-P(AzO-ImC_{18})		ODS	
Analytes	*k*	α	*k*	α	*k*	α	*k*	α
o-Terphenyl	1.71	-	0.64	-	0.67	-	3.04	-
m-Terphenyl	2.80	1.64	1.24	1.95	1.25	1.87	4.45	1.46
p-Terphenyl	2.97	1.06	1.52	1.23	1.52	1.22	4.55	1.02
Triphenylene	4.17	1.40	2.54	1.67	2.50	1.65	4.78	1.05

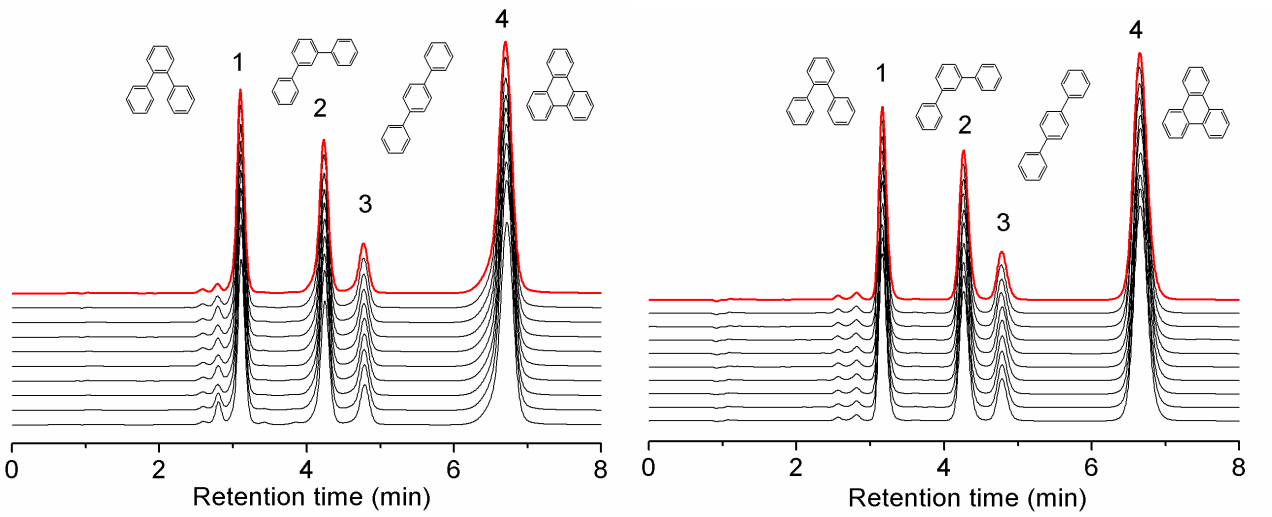

Fig. S5 The overlapped chromatograms at the separation of *o*-terphenyl, *m*-terphenyl, *p*-terphenyl, triphenylene for (a) Sil-PAzO-ImC_{18} and (b) Sil-P(AzO-ImC_{18}) columns using 90% methanol as mobile phase at 10 °C. The mixture was injected 10 times continuously. The RSD values (n = 10) of the retention factors of the analytes were 0.18-0.39% for (a) and 0.24-0.35% for (b).