Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

PDMS-coated hypercrosslinked porous organic polymers modified via double postsynthetic acidifications for ammonia capture

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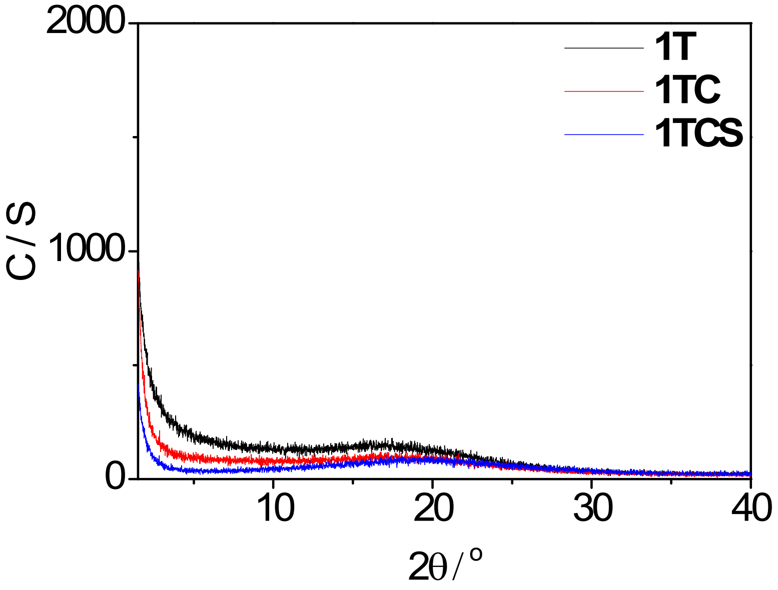
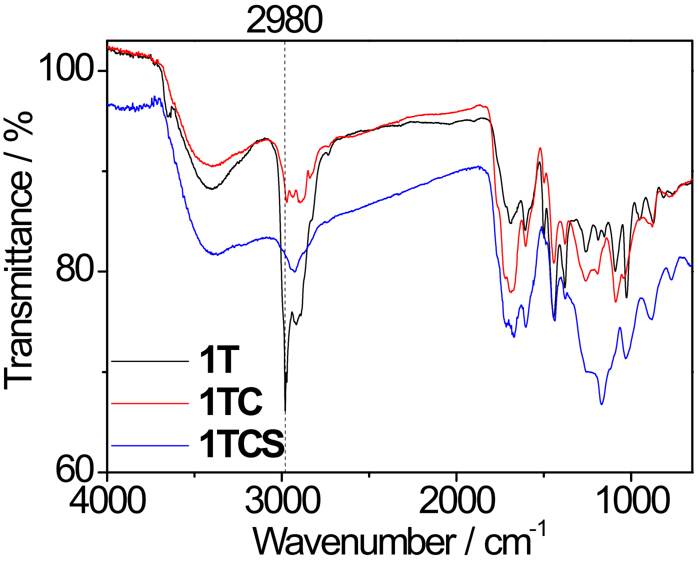


Fig. S1. Powder X-ray diffraction patterns of **1T**, **1TC**, and **1TCS**.



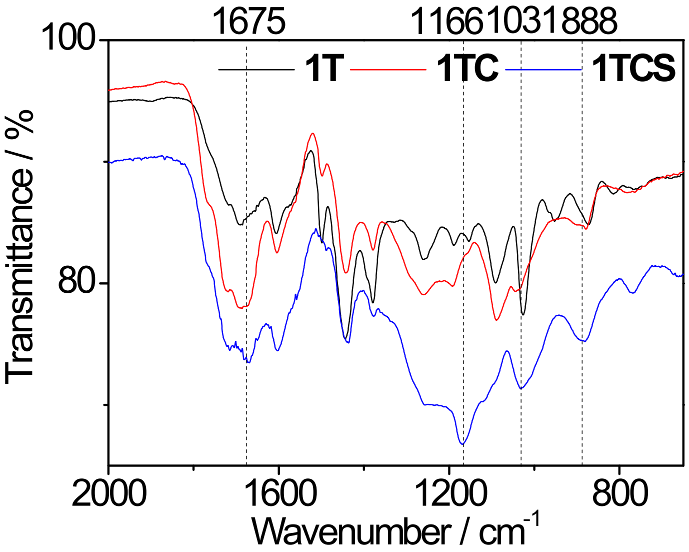
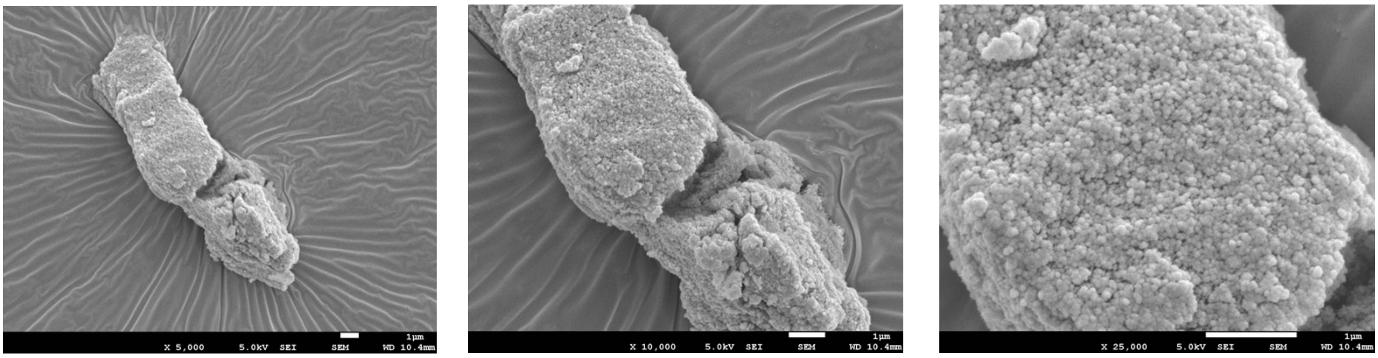


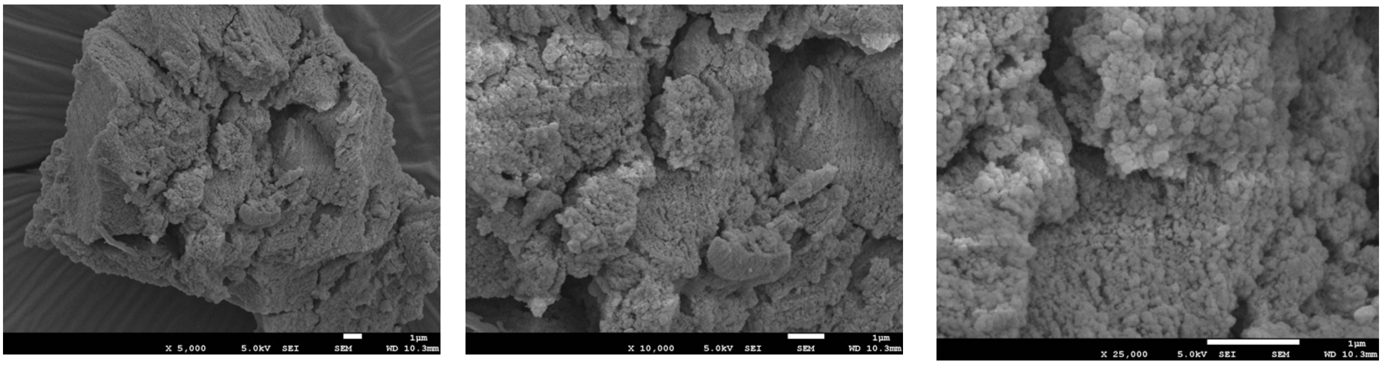
Fig. S2. IR spectra of **1T**, **1TC**, and **1TCS**. (top: 4000 cm^{-1} – 650 cm^{-1}, bottom: 2000 cm^{-1} -650 cm^{-1})

Table S1. Elemental analysis data about all compounds.

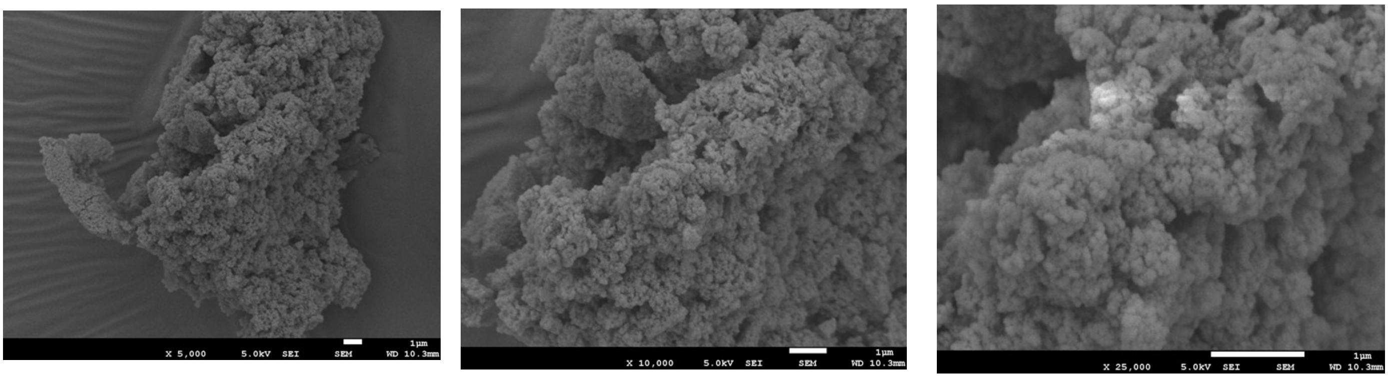
Compounds	C(%) Expt. / Calc.	H(%) Expt. / Calc.	S(%) Expt. / Calc.
1T $[(C_{26.76}H_{20.2936}O_{0.9}Cl_{0.02})(2.25H_2O)]$	81.1012 / 80.86	5.9093 / 6.29	0
1TC $[(C_{26.76}H_{17.4936}O_{3.7}Cl_{0.02})(2.5H_2O)]$	72.6117 / 72.39	5.2372 / 5.11	0
1TCS $[(C_{26.76}H_{17.4936}O_{6.55}Cl_{0.02}S_{0.95})(3.4H_2O)]$	60.3078 / 59.94	4.2670 / 4.57	5.5541 / 5.68



1T

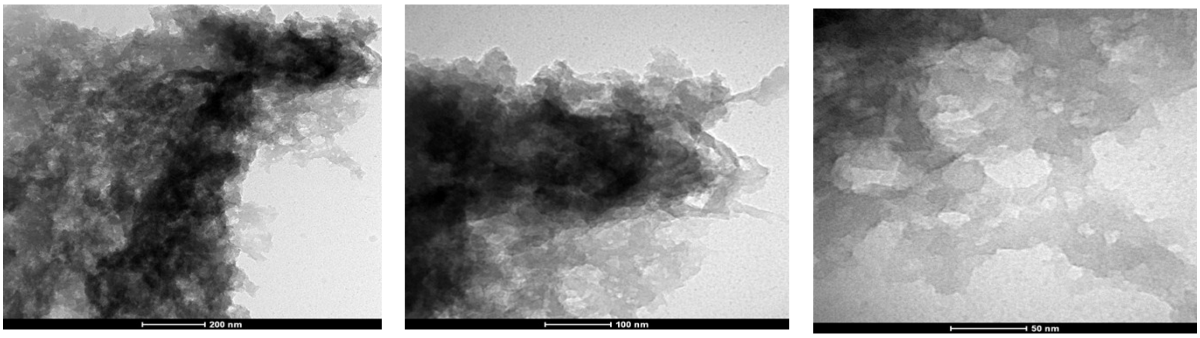


1TC

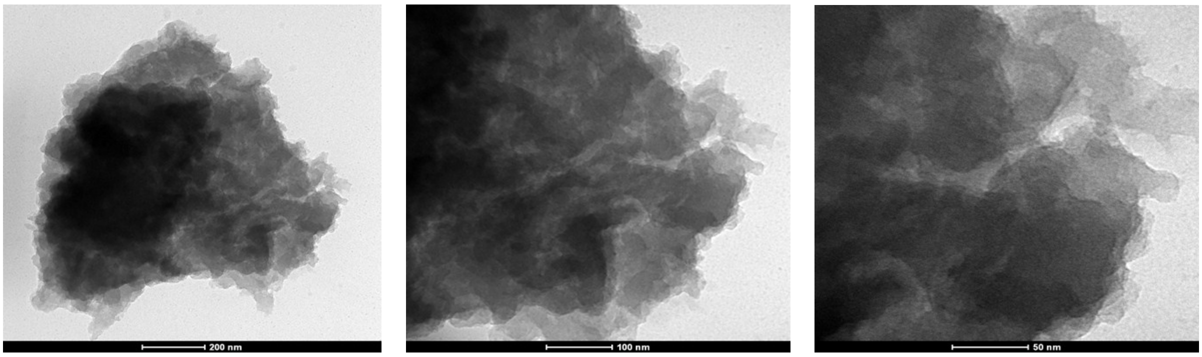


1TCS

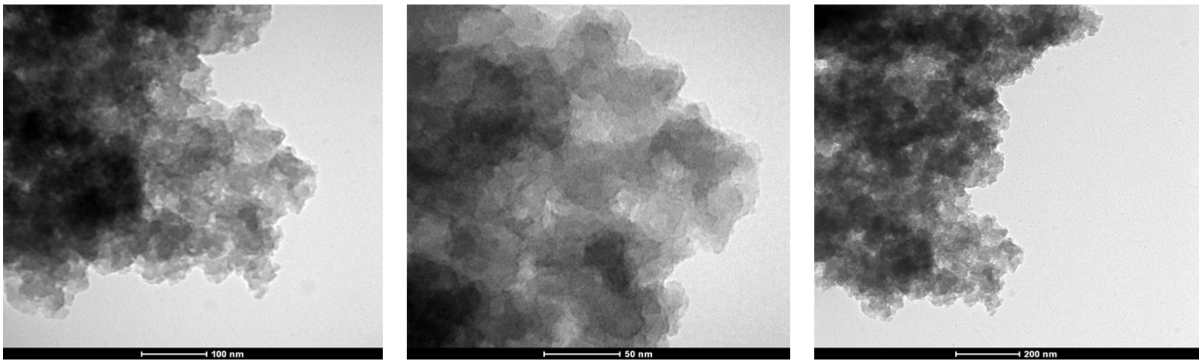
Fig. S3. SEM images for the samples. (left: x 5,000, middle: x 10,000, right: x 25,000)



1T

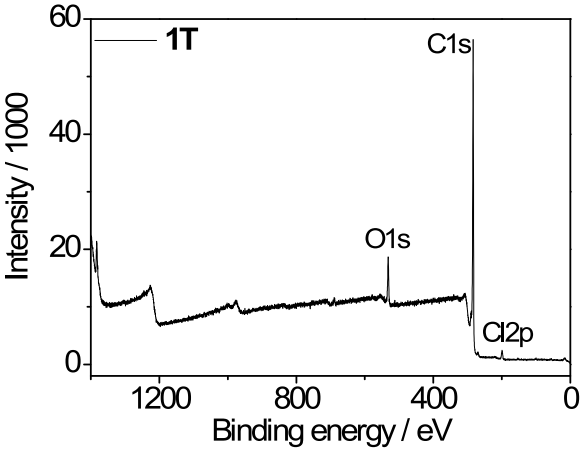


1TC

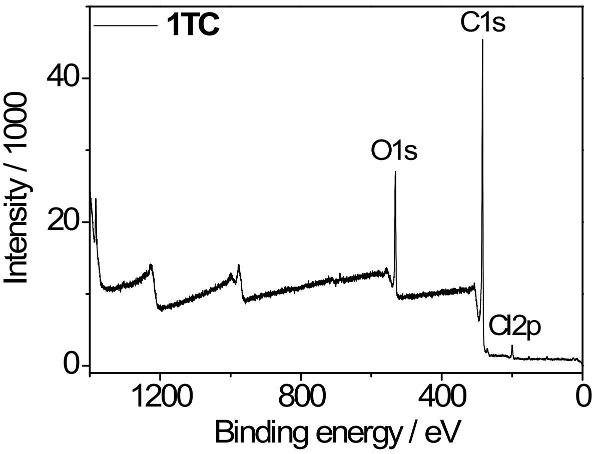


1TCS

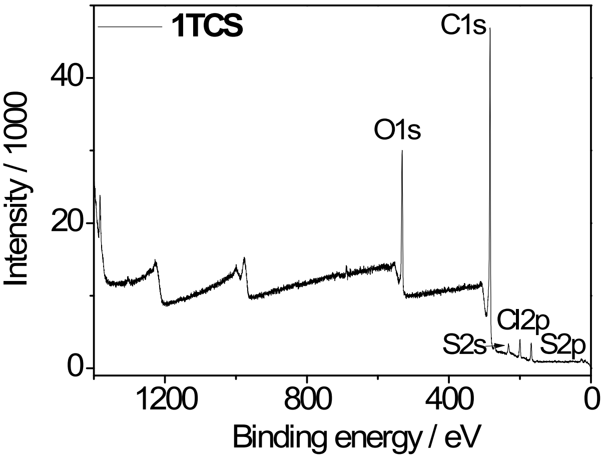
Fig. S4. TEM images for the samples. (left: x 5,000, middle: x 10,000, right: x 25,000)



(a)



(b)



(c)

Fig. S5. Survey scan of XPS data for (a) **1T**, (b) **1TC** and, (c) **1TCS**. S2s and S2p orbital related peaks were only observed in **1TCS**.

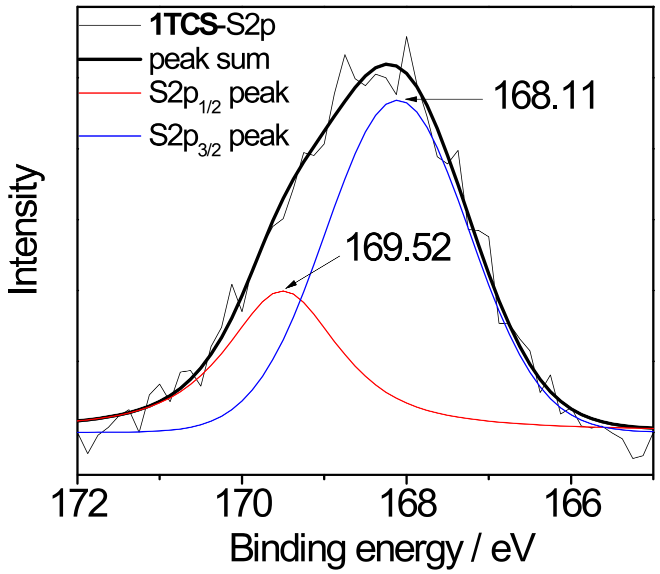
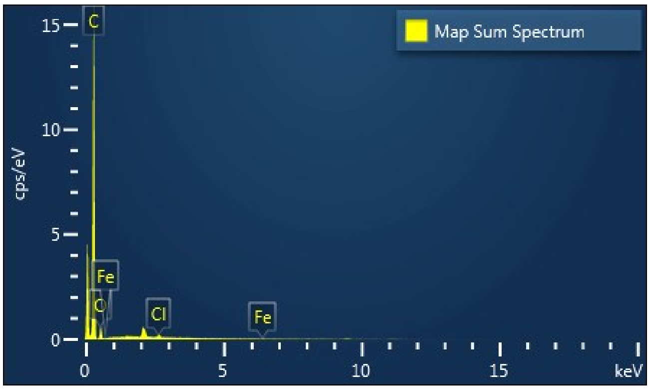
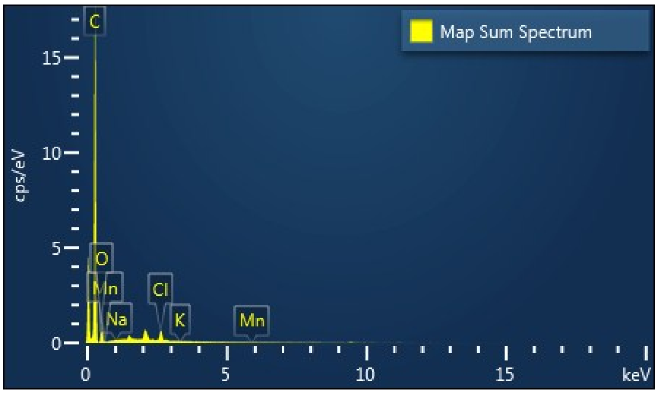


Fig. S6. Narrow scan of S2p that can be splited two states (S2p$_{1/2}$ and S2p$_{3/2}$) XPS data for **1TCS**.



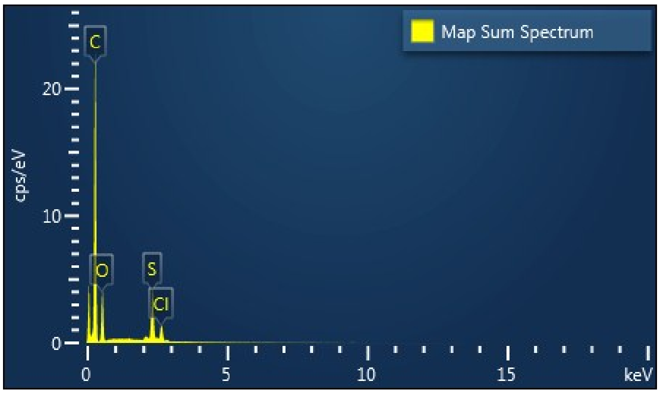
Element	Atomic %
C	93.22
O	6.63
Cl	0.11
Fe	0.04
Total:	100.00

(a)



Element	Atomic %
C	91.60
O	8.08
Na	0.00
Cl	0.31
K	0.00
Mn	0.01
Total:	100.00

(b)



Element	Atomic %
C	84.04
O	14.25
S	1.28
Cl	0.43
Total:	100.00

(c)

Fig. S7 . Energy dispersive X-ray SEM data for (a) **1T**, (b) **1TC**, and (c) **1TCS**.

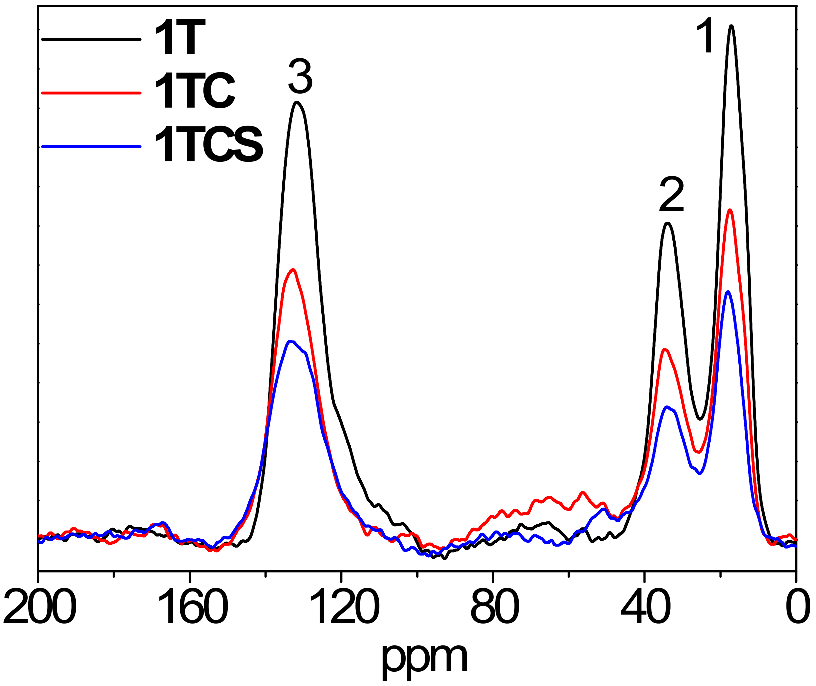


Fig. S8. Solid-state ^{13}C NMR spectra for all samples.

Table S2. Peak assignments about Fig. S8.

ppm (number)	Assignment
17 (1)	methyl carbons
34 (2)	methylene linker
128 - 140 (3)	aromatic carbons

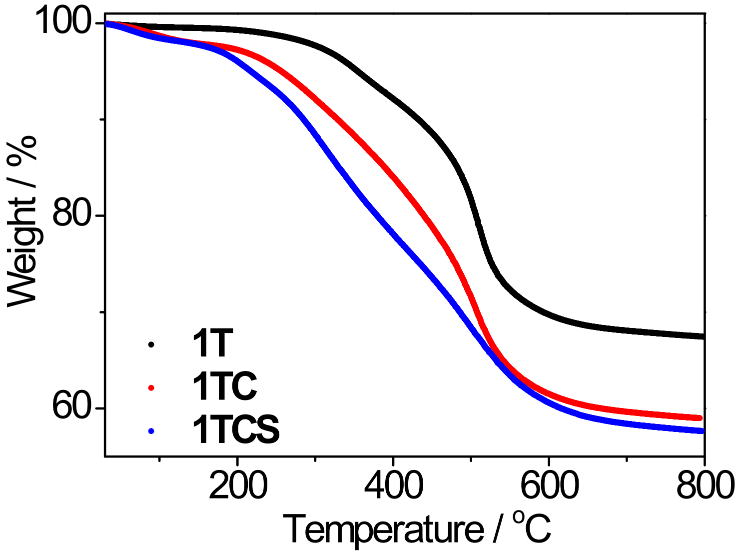


Fig. S9. TGA curves for all compounds.

Table S3. Elemental analysis data of **1TC** and **1TCS** before and after regeneration at 120 °C.

	1TC (before)	**1TC** (after)	**1TCS** (before)	**1TCS** (after)
C (%)	72.6117	72.5567	60.3078	60.3121
H (%)	5.2372	5.1725	4.2670	4.2430
S (%)	0	0	5.5541	5.5621

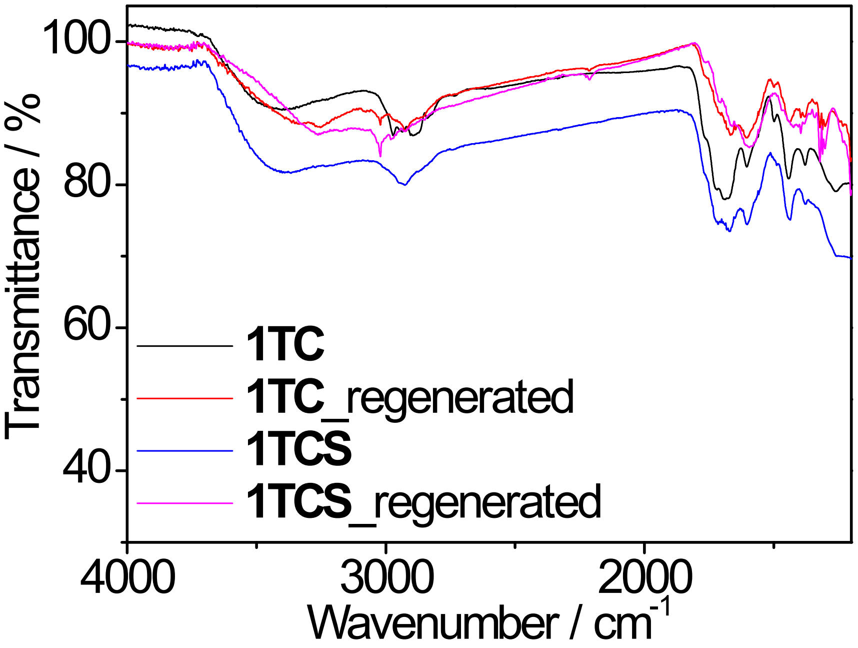
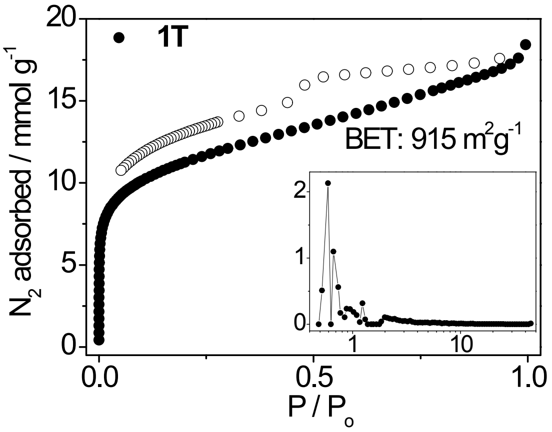
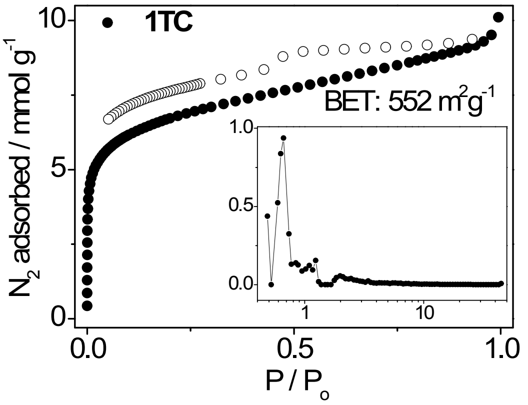


Fig. S10. IR data of **1TC** and **1TCS** before and after regeneration at 120 °C.

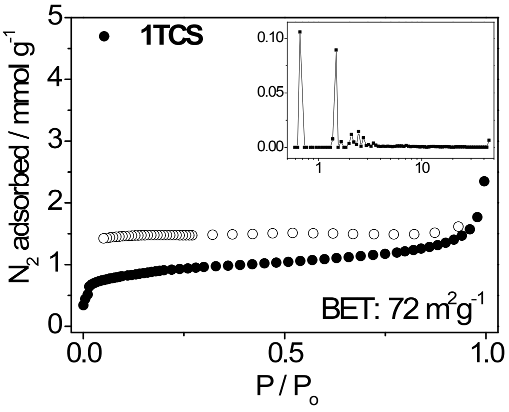
The elemental contents in **1TC** and **1TCS** remained invariant, together with almost no variation in IR spectra. These results indicate that there is no decay of the functional groups during regeneration process. Hence, the mass loss is due to the solvent removal upon heating. We added the additional EA and IR data in S14.



(a)



(b)



(c)

Fig. S11. N_2 isotherms at 77 K and pore size distributions of **1T**, **1TC**, and **1TCS**. The x-axis of inset indicates the pore width (nm) and the y-axis of inset shows the differential pore volume (cm^3 g^{-1}).

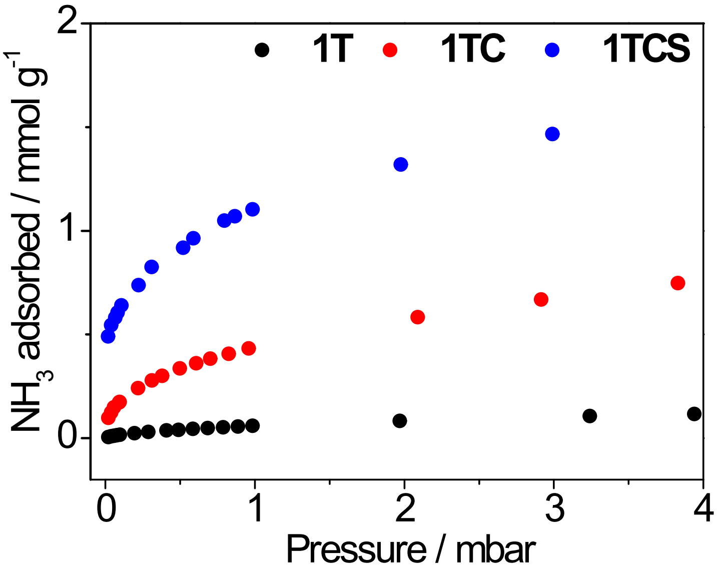


Fig. S12. Ammonia isotherms of the three samples at 298 K and very low pressures (< 4 mbar).

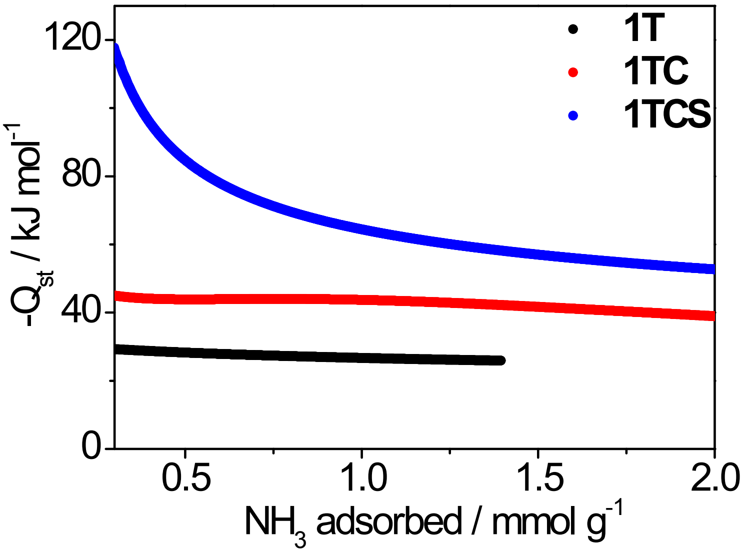


Fig. S13. Calculated isosteric heat of ammonia adsorption from isotherms for **1T**, **1TC**, and **1TCS**. Each isotherm was fitted using dual site or triple site Langmuir-Freundlich equation and the enthapy was calculated by Clausius-Clapeyron formula.

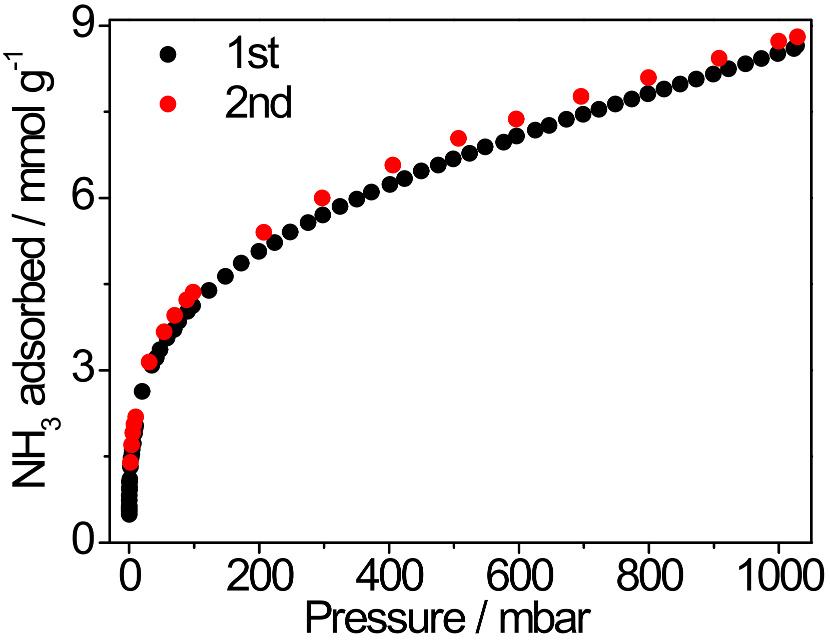


Fig. S14. Ammonia isotherms cycle of **1TCS** at 298 K.

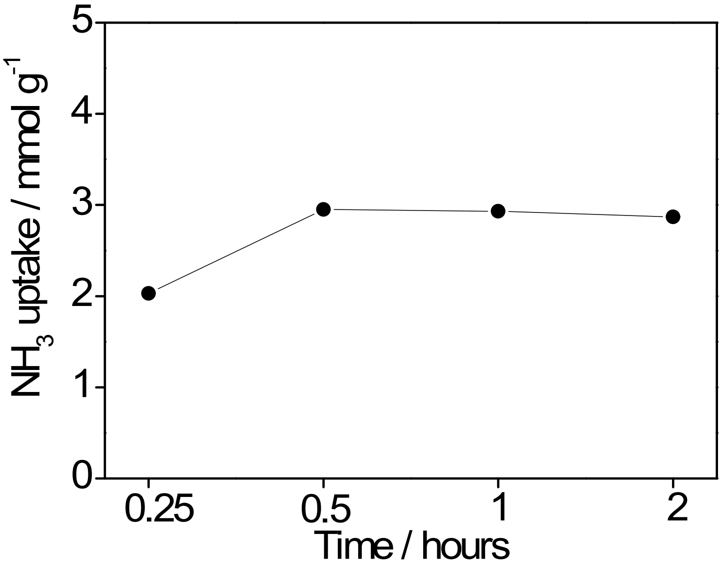


Fig. S15. Time-dependent ammonia uptake of **1TCS** in humid conditions. The uptake values were calculated from the titration experiments.

Experimental process of ammonia adsorption amount after co-adsorption.

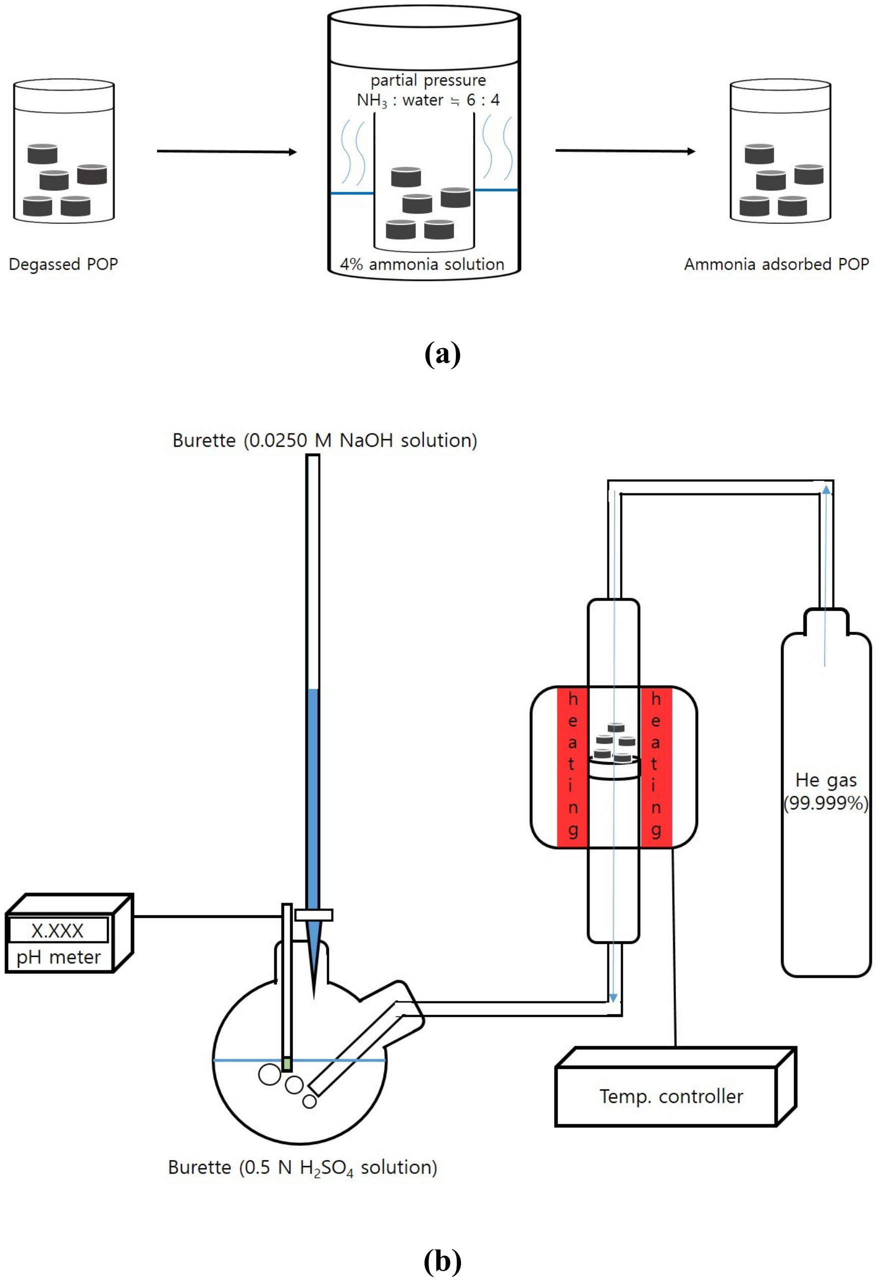


Fig. S16. Schematic diagram of an apparatus for NH_3 capture.[1, 2]

To evaluate adsorbed NH_3 amounts of pelletized **1TCS** and **1TCS@PDMS10** in humid conditions, the adsorption experiments was carried out as shown in Fig. S14a. After samples in 20 mL vial were activated at 120 °C (**1TCS**) or 160 °C (**1TCS@PDMS10**), the vial was transferred to a 70 mL vial containing 4% NH_3 solution and waited at 25 °C for 30 min. The pellets were removed in the vial. The NH_3-adsorbed pelletized samples were located in a column and the heating mantle was heated by temperature controller to 120 °C (**1TCS**) or 160 °C (**1TCS@PDMS10**) for 12 h under He gas (Fig. S14b). The removal NH_3 gases were absorbed by H_2SO_4 solution (0.5 mL 0.5 N H_2SO_4 + 30 mL distilled water). The solution was titrated by 0.0250 M NaOH using a pH meter.

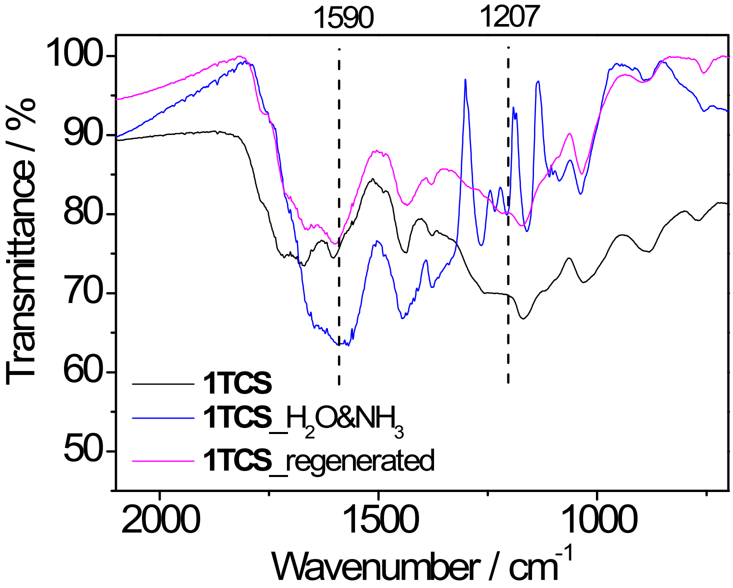


Fig. S17. IR spectra of **1TCS** after exposed or regenerated.

Table S4. List of reported ammonia adsortive porous materials, and their NH_3 capacity per surface area at low pressures.

Compounds	BET surface	NH_3 capacity (mmol g^{-1})	Adsorption Conditions	NH_3 capacity per surface area

	(m^{2}g^{-1})			(mmol m^{-2})
1T$^{\text{this work}}$	915	0.04	0.49 mbar 298 K	**4.372 x 10^{-5}**
1TC$^{\text{this work}}$	552	0.34	0.50 mbar 298 K	**6.159 x 10^{-4}**
1TCS$^{\text{this work}}$	72	0.92	0.52 mbar 298 K	**1.278 x 10^{-2}**
Fe-MIL-101-SO$_3$H[3]	1900	3.52	510 ppm 298 K	1.853 x 10^{-3}
UiO-66-NH$_3$Cl[3]	730	2.64	663 ppm 298 K	3.616 x 10^{-3}
UiO-66-NH$_2$[3]	900	0.93	488 ppm 298 K	1.033 x 10^{-3}
BPP-2[3]	965	0.97	636 ppm 298 K	1.005 x 10^{-3}
PPN-6-SO$_3$H[3]	1200	1.54	919 ppm 298 K	1.283 x 10^{-3}
BPP-5[3]	700	5.3(desorption)	203 ppm 298 K	7.571 x 10^{-3}
BPP-7[3]	705	4.5(desorption)	204 ppm 298 K	6.383 x 10^{-3}
P1-NH$_3$Cl[4]	975	0.37	0.5 mbar 298 K	3.795 x 10^{-4}
P1-SO$_3$H[4]	1220	1.35 0.01	0.5 mbar 298 K 50 ppm 298 K	1.107 x 10^{-3} 8.197 x 10^{-6}
P1-PO$_3$H$_2$[4]	835	3.3 2.03	0.5 mbar 298 K 50 ppm 298 K	3.952 x 10^{-3} 2.431 x 10^{-3}
P2-NH$_3$Cl[4]	980	0.27	0.5 mbar 298 K	2.755 x 10^{-4}
P2-SO$_3$H[4]	400	2.25 1.79	0.5 mbar 298 K 50 ppm 298 K	5.625 x 10^{-3} 4.475 x 10^{-3}
P2-CO$_2$H[4]	715	3.15 1.62	0.5 mbar 298 K 50 ppm	4.406 x 10^{-3} 2.266 x 10^{-3}
PAA[5]	365	1.6	1 mbar 298 K	4.384 x 10^{-3}
PI[5]	725	0.4	1 mbar 298 K	5.517 x 10^{-4}

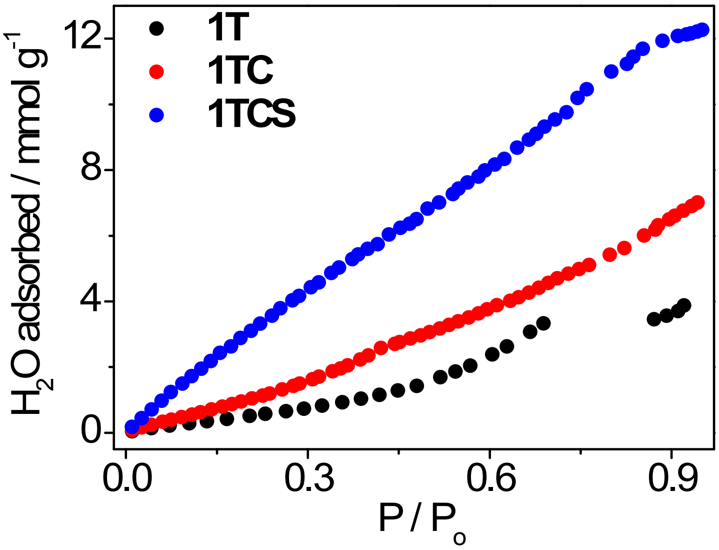


Fig. S18. Water vapor sorption isotherms of the samples at 298 K.

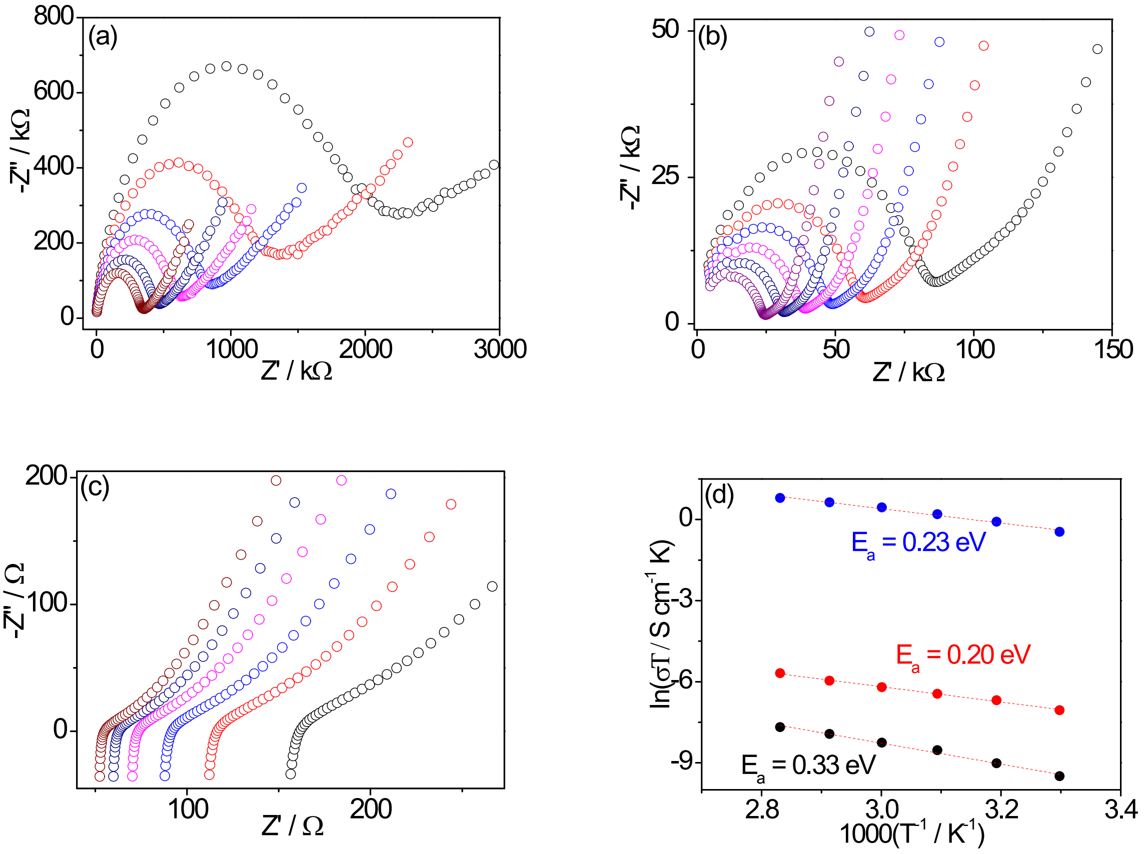
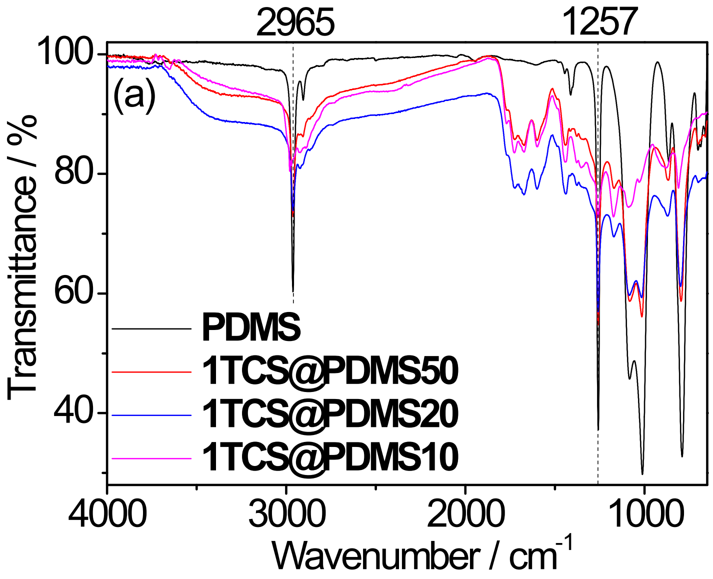


Fig. S19. Temperature-dependent impedance spectra for (a) **1T**, (b) **1TC** and, (c) **1TCS** at 90% RH. (d) Arrhenius plots for three samples.



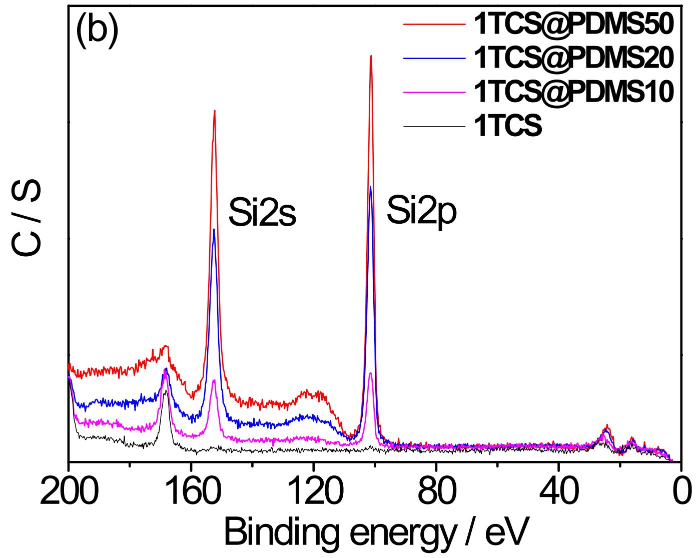
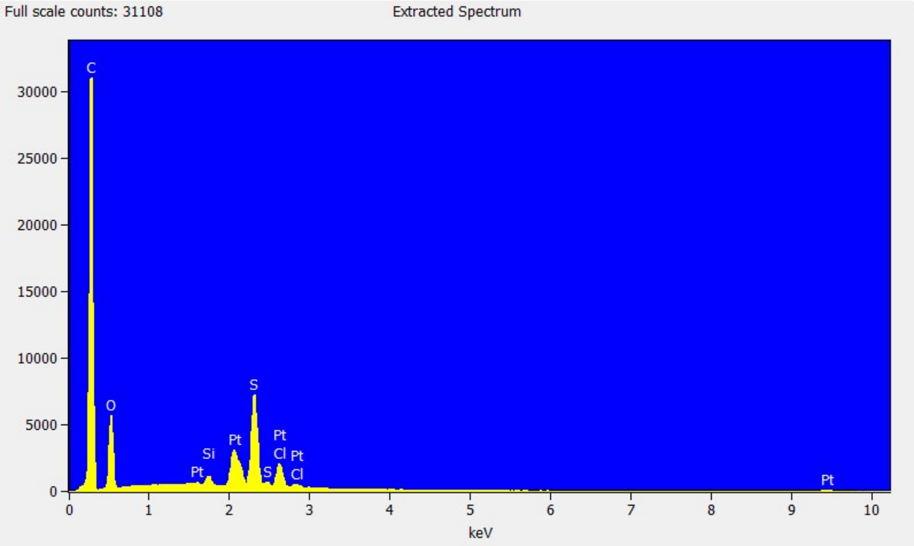


Fig. S20. (a) IR and (b) XPS data for PDMS-coated samples.



Element Line	***Weight %***	***Weight % Error***	***Atom %***	***Atom % Error***
C K	53.73	± 0.29	70.55	± 0.38
O K	22.47	± 0.20	22.15	± 0.20
Si K	0.68	± 0.03	0.38	± 0.02
S K	9.83	± 0.09	4.83	± 0.05
Cl K	2.78	± 0.06	1.24	± 0.03
Pt M	10.50	± 0.20	0.85	± 0.02
Total	100.00		100.00	

Fig. S21. EDS-SEM data for **1TCS@PDMS10** sample.

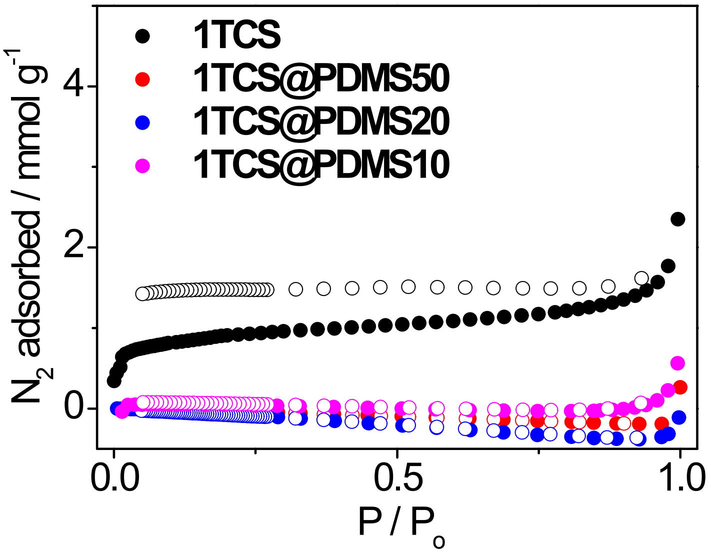


Fig. S22. N_2 isotherms of samples at 77 K.

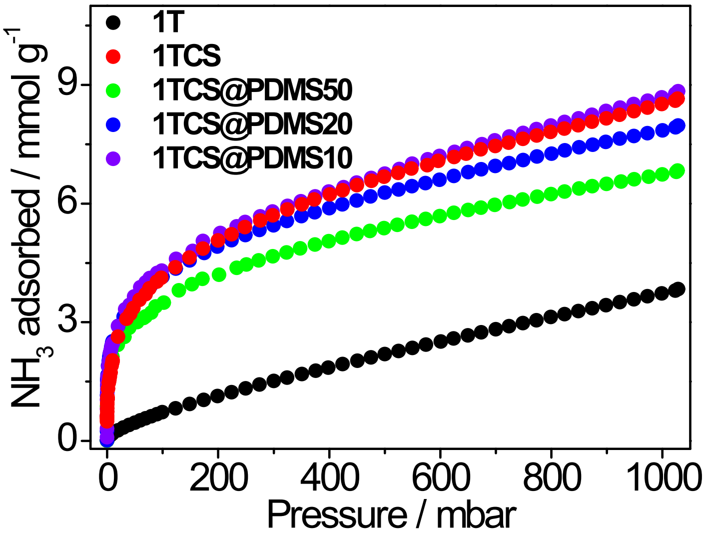


Fig. S23. NH_3 isotherms of samples at 298 K.

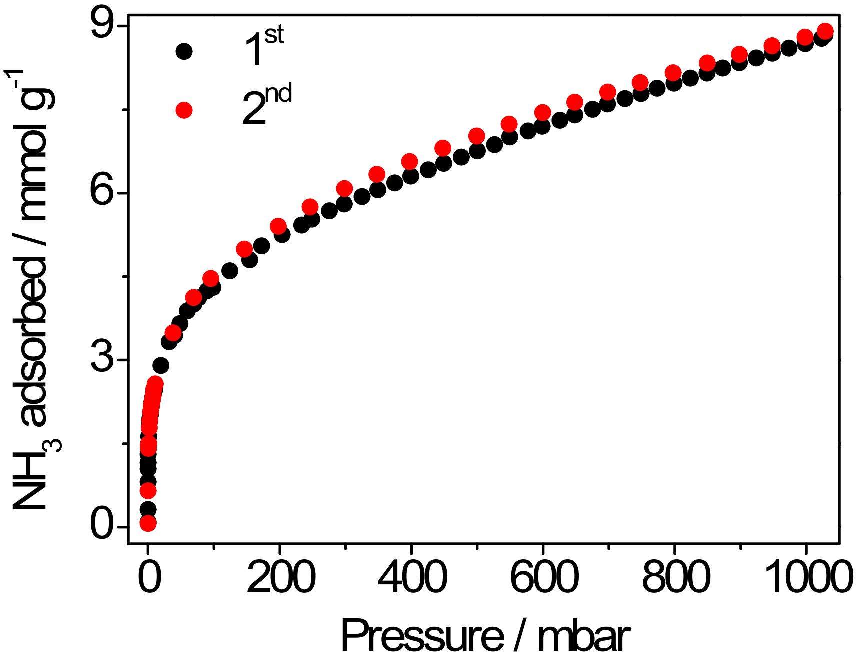
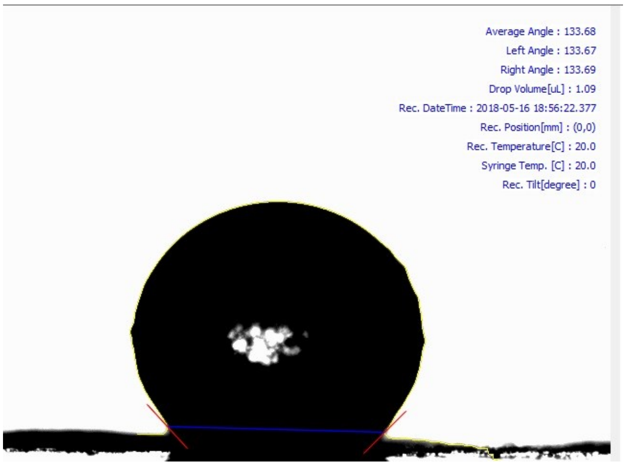


Fig. S24. Ammonia isotherms cycle of **1TCS@PDMS10** at 298 K.



```
Average Angle : 133.68
Left Angle : 133.67
Right Angle : 133.69
Drop Volume[uL] : 1.09
Rec. DateTime : 2018-05-16 18:56:22.377
Rec. Position[mm] : (0,0)
Rec. Temperature[C] : 20.0
Syringe Temp. [C] : 20.0
Rec. Tilt[degree] : 0
```

Average angle	133.68
Left angle	133.67
Right angle	133.69

1TCS@PDMS20

```
Average Angle : 134.06
Left Angle : 133.95
Right Angle : 134.16
Drop Volume[uL] : 1.18
Rec. DateTime : 2018-05-16 19:07:18.921
Rec. Position[mm] : (0,0)
Rec. Temperature[C] : 20.0
Syringe Temp. [C] : 20.0
Rec. Tilt[degree] : 0
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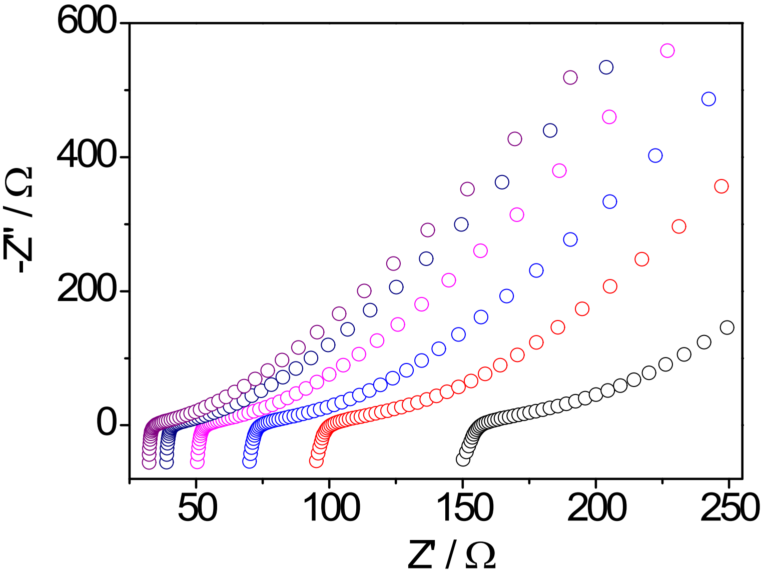
Average angle	134.06
Left angle	133.95
Right angle	134.16

1TCS@PDMS50

Fig. S25. Water droplet test for two samples.



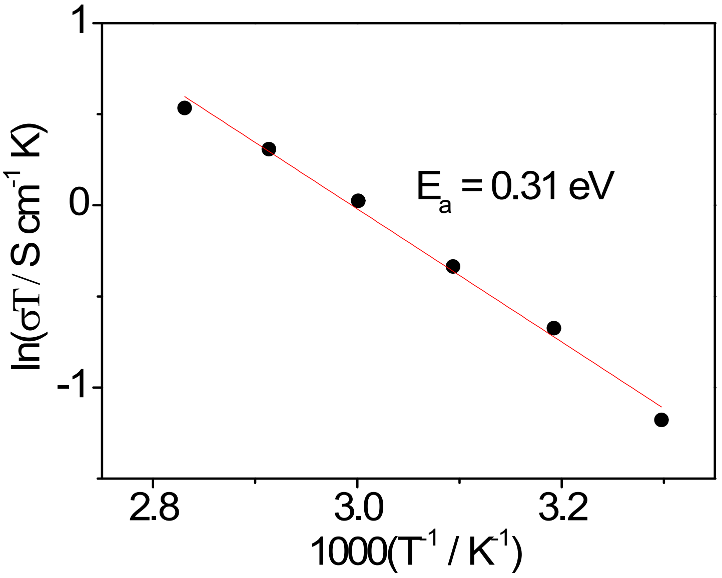


Fig. S26. Temperature-dependent impedance spectra (up) and Arrhenius plot (down) for **1TCS@PDMS10**.

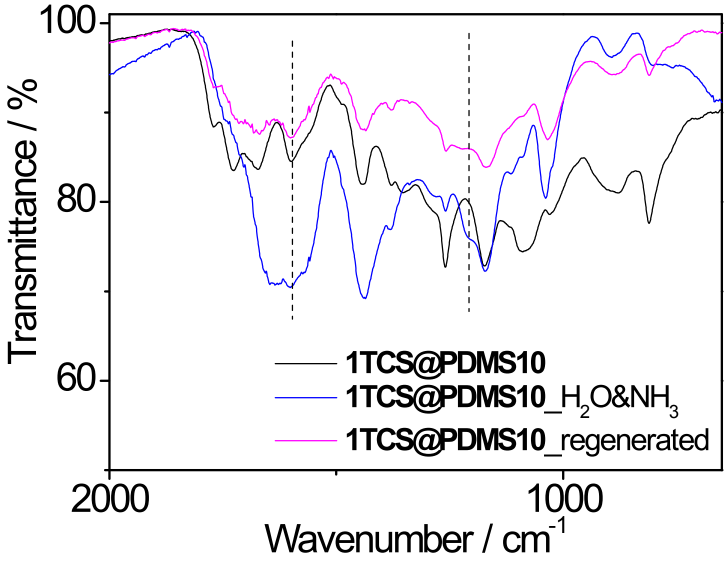


Fig. S27. IR spectrum of **1TCS@PDMS10** after exposed or regenerated.

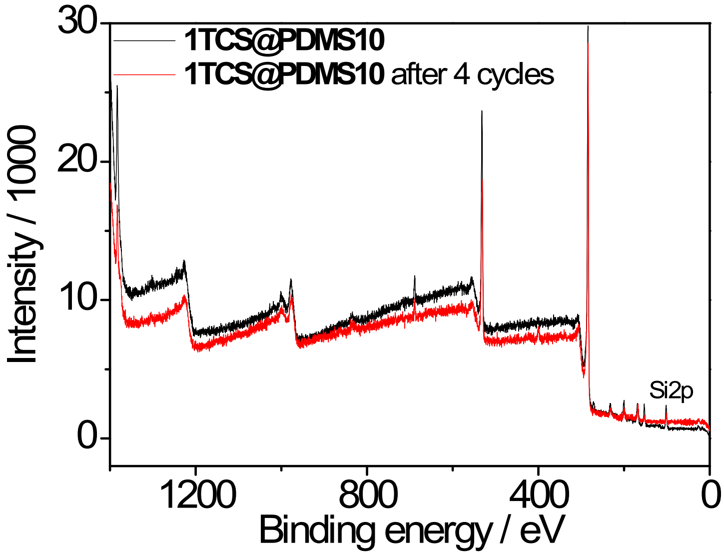


Fig. S28. XPS data of **1TCS@PDMS10** after regeneration.

References

1. Y. Chen, C. Yang, X. Wang, J. Yang, K. Ouyang and J. Li, *J. Mater. Chem. A*, 2016, **4**, 10345-10351.
2. Y. Chen, Y. Wang, C. Yang, S. Wang, J. Yang and J. Li, *ACS Sustainable Chem. Eng.*, 2017, **5**, 5082-5089.
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4. G. Barin, W. G. Peterson, V. Crocell`a, J. Xu, A. K. Colwell, A. Nandy, A. J. Reimer, S. Bordiga and R. J. Long, *Chem. Sci.*, 2017, **8**, 4399-4409.
5. J. W. Lee, G. Barin, G. W. Peterson, J. Xu, K. A. Colwell and J. R. Long, *ACS Appl. Mater. Interfaces*, 2017, **9**, 33504-33510.