Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
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Journal of Materials Chemistry A Accepted Manuscript

Enhanced recognition of nitrogen-containing organic compound by adjusting acidity of porous organic frameworks base (JUC-Z2)

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Nitrogen-containing organic compounds are very useful in industry while at last they often act as organic pollutants and very difficult to selectively recover. Normal porous adsorbents such as porous organic frameworks show almost no selectivity to them due to the insensitivity between pore size and the pollutants' molecular size. So a method of in adjusting acidity was applied to modify the porous organic frameworks to enhance the selectivity to nitrogen-containing organic compounds. In this work, a sulfonate grafted JUC-Z2, JUC-
10 Z2-SO$_3$H was prepared and exhibits high chemical stability (weight loss of 5% at 333 ^{o}C), and shows type-I nitrogen gas adsorption/desorption isotherm. The Brunauer–Emmett–Teller (BET) surface area for this network has been evaluated to be 1027 m^2 g^{-1}. The pore size of the JUC-Z2-SO$_3$H calculated by appropriate fitting of the quenched solid density functional theory (QSDFT) model to the isotherm yields a value of 1.0 nm. JUC-Z2-SO$_3$H can effectively arrest the amines than JUC-Z2 which in turn can be selectively recovered and reused. Furthermore, solvents with different polarities, such as, carbon tetrachloride (CCl$_4$), ethanol and methanol, were
15 chosen to conduct amine binding measurements with JUC-Z2 and JUC-Z2-SO$_3$H. The formation constant K$_f$ for JUC-Z2 and JUC-Z2-SO$_3$H in CCl$_4$, ethanol, and methanol drastically decreased with increasing in polarity, thus illustrating the solvent effect in amine binding. Other nitrogen-containing organic compounds such as aniline, DMF, and NMP cannot be adsorbed in both JUC-Z2 and JUC-Z2-SO$_3$H.

Introduction

20 Amines are essential raw materials in industry for manifold applications ranging from development of drugs, dyes and cosmetics,[1] to adsorption of environmentally baneful green house gases[2-3] and heavy metal ions.[4] These compounds are 25 already in the production stage but their manufacture poses potential threat in future of generating harmful by-products and wastes, deleterious to the water-bodies.[5-7] The balance of eco-system is dependent on the cycle of release of arrested amines and their recovery. However most of these amines are toxic and 30 some can even be easily absorbed by the skin of organisms which when released can be extremely detrimental to the eco-system. Thus an immediate challenge in the present scenario is to arrest organic amines. There are many techniques to adsorb amines. Chemical and catalytic oxidation methods can be employed for 35 this purpose but these methods are not industrially viable due to high energy and reagent consumption, and their usefulness is diminished by their limited applications.[8] In this article we address this issue by adjusting acidity by sulfonate grafted of organic porous materials JUC-Z2-SO$_3$H, so that it can effectively 40 arrest the amines and these arrested amines can be selectively recovered.

Starting material of JUC-Z2 (Scheme 1) is a porous organic framework (POF) base.[9-15] which has good absorption capacity, high porosity and surface area. It possesses high physical and 45 chemical stability owing to covalent bonding constituting its mesh structure. The overall structure has amorphous domains.

JUC-Z2 was synthesized from *para*-tribromotribenzylaniline monomer via Yamamoto type Ullmann cross-coupling reaction, in which the lamellar organic frameworks comprising of the 50 stacked sheets with an *hcb* topology were successively formed via self-assembly. It was found to have a well-defined uniform micropore distribution (1.18 nm), high surface area (S$_{BET}$ =2081 m^2 g^{-1}) and high physicochemical stability (> 430 ^{o}C) and open pore volume (total pore volume = 1.45 cm^3 g^{-1}, micropore volume 55 = 0.40 cm^3 g^{-1}). The effective low molecular weight binding sites of N atom led to relatively high interactions of the framework with guest molecules. To find an effective solution towards selective adsorption of amines based on their basicity, we modified the starting framework of JUC-Z2 with sulfonic acid 60 groups,[16] exploiting the fact that these functional groups have strong interactions with organic amines making their incorporation into the framework suitable for selective adsorption of amines. Herein, we provide the detailed study of basicity dependent selective adsorption of amines and nitrogen-containing 65 organic compounds as well as effect of polarity of solvents on their uptake and release.

Experimental section

Material synthesis

The starting materials and dehydrated solvents were purchased 70 from Aldrich Chemicals. JUC-Z2[17] were prepared as described in our previous work.

Synthesis of JUC-Z2-SO$_3$H 100 mg JUC-Z2 was slowly added to 10 mL dichloromethane, while being vigorously stirred on

ice/salt water bath (~ 10°C). When the suspension was formed 1mL chlorosulfonic acid was slowly added and stirred for three days at room temperature. Then the mixture was washed with cold water (100 mL×3) and subsequently dried at 100 °C under
5 vacuum for 12 h, to yield a pea green solid (137 mg) (Scheme 1).
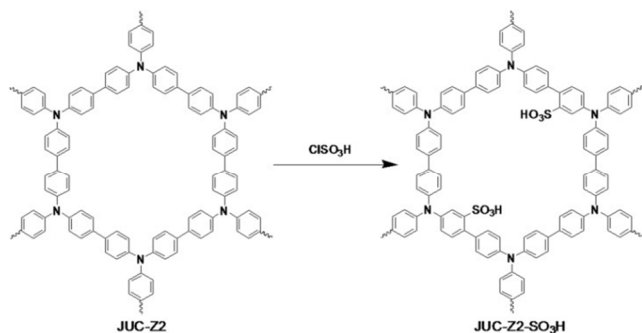
Scheme 1 Synthesis of grafting JUC-Z2-SO$_3$H

Material characterization The formation of JUC-Z2-SO$_3$H was confirmed by N$_2$ adsorption measurements, thermogravimetric
10 analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, and temperature programmed desorption experiments (TPD).

Thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) experiments The TGA was
15 performed using a SHIMADZU DTG-60 thermal analyzer at the heating rate of 10 °C min^{-1} in dry air atmosphere. The FTIR spectra (KBr) were measured using a SHIMADZU IR Affinity-1 Fourier transform infrared spectrometer.

20 **Low-pressure N$_2$ adsorption measurements** N$_2$ sorption isotherm measurements were performed on a Quantachrome Autosorb iQ2 surface area and pore size analyzer. After the removal of volatile entities by decantation, the sample was activated under a dynamic vacuum at 200 °C over night. Before
25 the measurement, the sample was degassed by using the ''degas'' function of the surface area analyzer at 200 °C for 12 h. A sample of 50 mg and UHP-grade nitrogen (99.999%) gas source were used in the nitrogen sorption measurements at 77 K maintained by liquid nitrogen throughout the whole measurement. Oil-free
30 vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

Temperature programmed desorption experiments. The
35 temperature programmed desorption of ammonia (NH$_3$-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorptions analysis unit with a thermal conductivity detector (TCD) under helium flow. Typically, 50 mg of powder samples was pre-treated in flowing helium flow at 500
40 °C for 2 h and saturated with an NH$_3$/He (1: 9) flow at 120 °C. Then, the sample was purged by a He flow for 2 h to remove the physically adsorbed NH$_3$ on the sample. Finally desorption of NH$_3$ was carried out from 150 to 600 °C with a heating rate at 10 °C min^{-1}.

45

Gas chromatographic (GC) experiments GC experiments were conducted using a SHIMADAZU GC-2014C, which was fitted with a 30 m × 0.25 mm × 0.25 μm cross-linked poly (ethylene glycol) capillary column and interfaced with a GC Light Real
50 Time Analysis. A flame ionization detector was used.
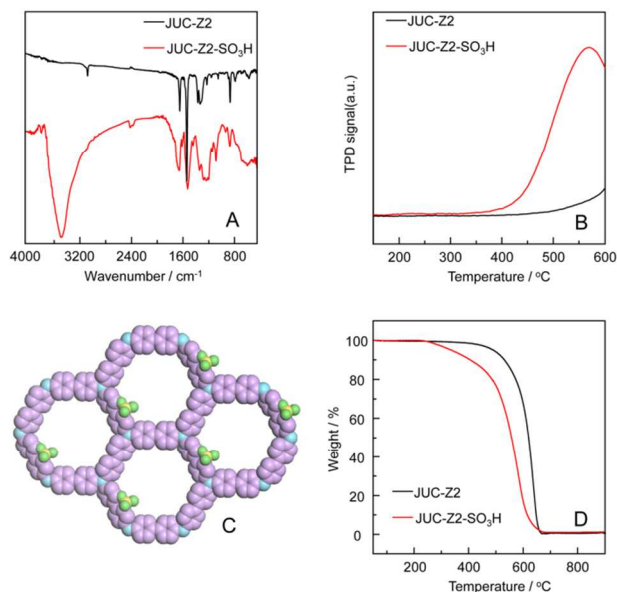
Results and Discussion

Structure of JUC-Z2-SO$_3$H

Fig. 1 (A) FTIR spectra of JUC-Z2 (black), JUC-Z2-SO$_3$H (red) from 400
55 - 4000 cm^{-1}; (B) TPD spectrum of JUC-Z2 (black), JUC-Z2-SO$_3$H (red) from 150 °C to 600 °C; (C) Proposed structure of JUC-Z2-SO$_3$H in top view (C, purpl; N, blue; O, green; S, yellow); (D) TGA of JUC-Z2 (black) and JUC-Z2-SO$_3$H (red) under dry air from 50 to 900 °C at the heating rate of 10 °C min^{-1}.

60 The reaction procedure was monitored by Fourier transform infrared (Fig. 1A). The FTIR spectrum of JUC-Z2-SO$_3$H showed at 1190 cm^{-1}, 1070 cm^{-1}, 620 cm^{-1} and 530 cm^{-1}, which was characteristic of -SO$_3$H group, and 3580 cm^{-1} peak may attribute to the OH$^-$ in the -SO$_3$H. This indicated that -SO$_3$H group was
65 successfully grafted onto the porous polymer network. We employed acid-base titration method with phenolphthalein as indicator to determine the degree of sulfonation which was found to be 3.21 mmol g^{-1} (Table S1-S3). The result suggests that 1 sulfonic acid group was grafted onto approximately 3 (3.05 in
70 calculation) benzene units. To characterize the grafting of Lewis acid sites, we investigated the binding of NH$_3$ with sample through temperature-programmed desorption (TPD). As shown in Fig. 1B, the desorption spectrum with an obvious desorption band at 565 °C indicates that Lewis-acid sites are available in the JUC-
75 Z2-SO$_3$H compared with JUC-Z2.

The proposed framework was constructed and optimized by using the Forcite Plus module in Material Studio 2 (Fig. 1C). Thermogravimetric analysis (Fig.1D) was used to evaluate the thermal stability of JUC-Z2-SO$_3$H. The solid was heated at 100
80 °C under vacuum for 10 h to remove volatile guest adsorbed in the pore of JUC-Z2-SO$_3$H. The 5 wt% weight loss of purified JUC-Z2-SO$_3$H is 333 °C under dry air, which suggests that the JUC-Z2-SO$_3$H still maintain the high thermo stability.
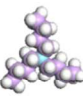
85 **Porosity of the JUC-SO$_3$H**
Nitrogen gas adsorption/desorption isotherm of the networks

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Table 1 Inclusion of host solids JUC-Z2-SO$_3$H and JUC-Z2 with organic amines/nitrogen-containing compounds in different system.

Amines	Structure	Radius / nm	pKb	Solvent	JUC-Z2-SO$_3$H			JUC-Z2		
					K_f / M^{-1}	$\Delta_r G_m(T)^a$ / kJ mol^{-1}	[BS]$_o$/ω / mmol g^{-1}	K_f / M^{-1}	$\Delta_r G_m(T)^a$ / kJ mol^{-1}	[BS]$_o$/ω / mmol g^{-1}
Ethylenediamine		0.26	4.10	CCl$_4$	13.6	-6.5	18.1	1.9	-1.6	13.3
				Ethanol	9.4	-5.6	14.3	0.9	0.1	9.6
				Methanol	2.2	-1.9	3.2	0.5	1.6	4.2
Butylamine		0.32	3.37	CCl$_4$	4.2	-3.6	16.4	1.2	-0.4	14.9
				Ethanol	1.2	-0.5	12.3	0.8	0.5	9.7
				Methanol	0.9	0.3	6.8	0.3	2.9	3.6
Dipropylamine		0.40	3.00	CCl$_4$	3.2	-2.9	18.8	1.2	-0.6	5.6
				Ethanol	1.0	0.05	10.7	0.4	2.6	1.1
				Methanol	0	0	0	0	0	0
Tributylamine		0.55	3.13	CCl$_4$	1.6	-1.1	13.1	0.7	0.7	2.7
				Ethanol	0.4	2.1	5.3	0	0	0
				Methanol	0	0	0	0	0	0
Aniline		0.32	9.41	CCl$_4$	0	0	0	0	0	0
				Ethanol	0	0	0	0	0	0
				Methanol	0	0	0	0	0	0
N, N-Dimethylformamide		0.24	12.52	CCl$_4$	0	0	0	0	0	0
				Ethanol	0	0	0	0	0	0
				Methanol	0	0	0	0	0	0
N-methyl-2-pyrrolidone		0.26	12.54	CCl$_4$	0	0	0	0	0	0
				Ethanol	0	0	0	0	0	0
				Methanol	0	0	0	0	0	0

^{a}$\Delta_r G_m(T)$ is calculated with equation 4
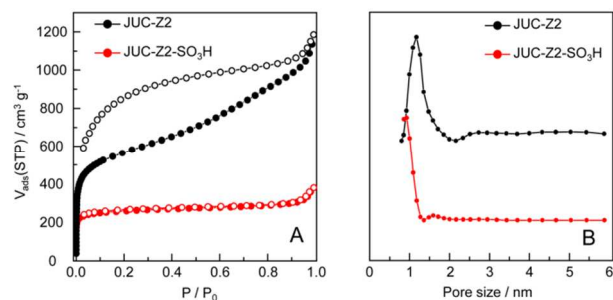
Fig. 2 (A) N$_2$ sorption isotherms of JUC-Z2 (black) and JUC-Z2-SO$_3$H (red) (solid symbols, adsorption; open symbols, desorption) and (B) the pore size distribution for JUC-Z2-SO$_3$H and JUC-Z2 derived from N$_2$ adsorption calculated by QSDFT method using slit pore model.

were recorded at 77K. Notably, JUC-Z2 exhibited targeted two-dimensional (2D) sheet structure of *hcb* topology and the

Brunauer–Emmett–Teller (BET) surface area was evaluated to be 2081 m^2 g^{-1} (Figure 2). The pore size of the JUC-Z2 was calculated by appropriate fitting of the quench solid density functional theory (QSDFT) model to the isotherm yielding a value of 1.18 nm, and open pore volume (total pore volume = 1.45 cm^3 g^{-1}, micropore volume = 0.40 cm^3 g^{-1}). JUC-Z2-SO$_3$H showed ideal type-I isotherm. The BET surface area and pore size obtained from the experimental data were found to be 1027 m^2 g^{-1} and 1 nm, respectively. The total pore volume of JUC-Z2-SO$_3$H is 0.535 cm^3 g^{-1} and micropore volume is 0.40 cm^3 g^{-1}, suggesting grafted –SO$_3$H group only provide a chemical binding site and does not decrease the micropore volume and pore size more compared with original JUC-Z2.

Binding of JUC-Z2 and JUC-Z2-SO$_3$H with nitrogen containing compounds

The formation constant (K_f) for the host-guest complex formed

between a binding site (BS) of an insoluble host and a guest molecule (G) was defined as k_{ad}/k_{de} in Equation (1) by analogy with the Langmuir isotherm for adsorption of gas molecules on solid surfaces.

$$BS + G \frac{k_{ad}}{k_{de}} BS \cdot G$$

5 $$K_f = \frac{k_{ad}}{k_{de}} = \frac{[BS \cdot G]}{[BS][G]} \quad (1)$$

If θ is defined as fractional coverage,

$$\theta = \frac{[BS \cdot G]}{[BS]_0} = \frac{[G]}{([G] + 1/K_f)} \quad (2)$$

Then

$$[BS \cdot G]/\omega = \frac{([BS]_0/\omega)[G]}{([G] + 1/K_f)} \quad (3)$$

10 ω is the amount of host solid per unit volume of the solution (mg mL^{-1}). Change in guest concentration was measured by GC, and the data were fitted to Equation (3). The concentration of G bound to BS ([BS•G]) against [G] was plotted (Fig. 3 & 5). The K_f and $[BS]_0$ values were estimated by analyzing data according 15 to Equation (3). [18] The $\Delta_r G_m(T)$ were calculated by equation (4).

$$\Delta_r G_m = -RT \ln K \quad (4)$$

As-synthesized JUC-Z2 and JUC-Z2-SO$_3$H samples were first degassed at 423 K under vacuum for 12 h. About 5 mg of each solid sample was immersed in anhydrous organic solvent 20 solutions containing guests and keep the total volume of 5 mL for 4 h at 302 K. The initial concentrations of guest molecules ([G]$_0$) were varied from 5.119 × 10^{-2} to 6.296 × 10^{-1} M and recorded in Table 2.

Table 2 Initial guest concentrations ([G]$_0$)

Guests	Initial guests concentration ([G]$_0$,M)
Ethylenediamine	0.5990-5.990× 10^{-1}
Butylamine	0.6614-6.614× 10^{-1}
Dipropylamine	0.5119-5.119× 10^{-1}
Tributylamine	0.6296-6.296× 10^{-1}
Aniline	0.5477-5.477× 10^{-1}
N,N-dimethylformamide	0.5131-5.131× 10^{-1}
N-methyl-2-pyrrolidone	0.5185-5.185× 10^{-1}

25

Adsorption and Recognition of amine

The absorbance of ethylenediamine in CCl$_4$ increased with increasing in concentration. The interactions of ethylenediamine with JUC-Z2 and with JUC-Z2-SO$_3$H were plotted using [BS•G] 30 (the concentration of G bound to BS) against [G]. The data were then fitted to Equation (3) to obtain the formation constant (K_f) and the maximum amount (mole) of ethylenediamine ([BS]$_0$/ω). The analysis of the data in CCl$_4$ system exhibited a value of K_f = 13.6 M^{-1} and [BS]$_0$/ω = 18.1 mmol g^{-1} for JUC-Z2-SO$_3$H (Fig. 3), 35 and K_f= 1.9 M^{-1} and [BS]$_0$/ω = 13.3 mmol g^{-1} for JUC-Z2 at 302

K, respectively (Fig. 3). These values of [BS]$_0$/ω indicated that the host solids, JUC-Z2-SO$_3$H and JUC-Z2, had 18.1 and 13.3 binding sites respectively, for the ethylenediamine molecule per formula of the solid. Moreover, JUC-Z2-SO$_3$H showed higher 40 binding constant and higher binding energy than that of JUC-Z2 due to the introduction of sulfonate group.

The degassed host JUC-Z2-SO$_3$H binds ethylenediamine, butylamine, dipropylamine and tributylamine in CCl$_4$, exhibiting Langmuir isotherm curves. The amount of the guests bound to the 45 host solid was measured by GC; the formation constant (K_f) and the number of binding sites for guest molecules (mol) per g of the host ([BS]$_0$/ω) were also estimated. The host differentiates organic guests with the K_f values in the order of ethylenediamine > butylamine > dipropylamine > tributylamine > aniline = N, N- 50 dimethylformamid (DMF) = N-methyl-2-pyrrolidone (NMP) = 0 (Table 1). This indicates that the JUC-Z2-SO$_3$H can recognize amine from other nitrogen containing compound and do not adsorb aniline, DMF, and NMP at all. The recognition sequence to amine of JUC-Z2-SO$_3$H is in agreement with molecular radius 55 when pKb is around 3-4.1.
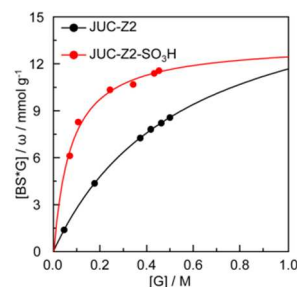

Fig. 3 Binding of host solid JUC-Z2-SO$_3$H and JUC-Z2 with ethylenediamine in CCl$_4$.
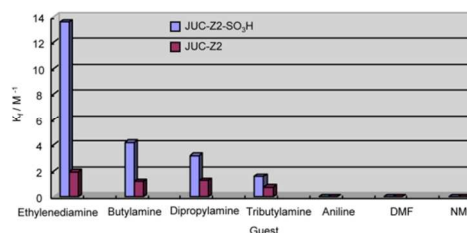

60 **Fig. 4** K_f of JUC-Z2-SO$_3$H and JUC-Z2 in CCl$_4$.

In this work, we found that the basicity is weak or weaker than aniline (pKb is 9.4), there is no any adsorption in JUC-Z2-SO$_3$H even though molecular radius of DMF is as small as 0.24 nm. As a parallel experiment, we used the same method to test the 65 binding constants with JUC-Z2. K_f value of ethylenediamine with JUC-Z2-SO$_3$H as host was 13.6 M^{-1}, while with JUC-Z2 is 1.9 M^{-1}, showing a significant seven-fold increase. JUC-Z2 has similar K_f with ethylenediamin, butylamine, dipropylamine, and tributylamine ranging from 1.9 M^{-1} to 0.7 M^{-1} and no adsorption 70 to aniline, DMF, and NMP, indicating weak recognition ability to these amine and nitrogen-containing organic compounds. Generally to say, physical recognition such as pore size recognition is often used for selective adsorption of pore materials. But in our case, we proved that in a porous organic 75 base as JUC-Z2, pore size showed almost no selectivity or very

weak selectivity. After introduction sulfonic group onto the aromatic framework, the obviously seven-fold increase of selectivity to amine was observed. It was evident that the sulfonated host favours the organic amines that were able to form

[5] acid-base interactions with the exposed sulfonic acid groups while pore size/guest molecular size was not key point for recognition (Fig. 4). Pores mainly contribute the void for adsorption amine molecules while the sulfonic acid group endow enhanced recognition property to the organic framework.

[10] In case of aniline, DMF and NMP adsorption uptake, there was a direct correlation of basicity of amines with the binding constant (K_f). For instance in the case of both the host frameworks, JUC-Z2 and its sulfonated analogue, there was a pKb (around 9.4) value below which no amine was taken up

[15] (Table 1).

Solvent effect of Guest Binding of JUC-Z2 and JUC-Z2-SO₃H

Fig. 5 Binding of host solid JUC-Z2-SO$_3$H with organic guests A (ethylenediamine), B (butylamine), C (dipropylamine), D (tributylamine)

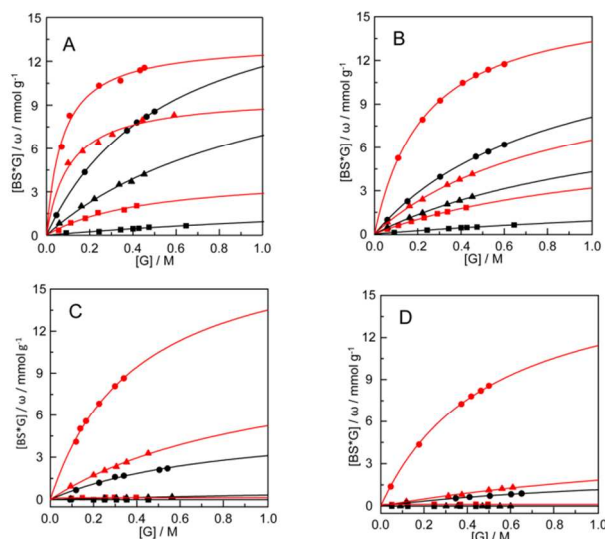[20] in different solvent. CCl$_4$ (●), ethanol (▲), methanol (■), and Binding of host solid JUC-Z2 with organic guests A (ethylenediamine), B (butylamine), C (dipropylamine), D (tributylamine) in different solvent. CCl$_4$ (●), ethanol (▲), methanol (■)

To explore how the solvent polarity affect the recognition ability

[25] of porous organic frameworks, we chose CCl$_4$, ethanol, and methanol as solvents because their polarities cover a range from 1.6 (CCl$_4$) to 6.6 (methanol). Using the same experimental procedure, we also studied the binding of JUC-Z2 and JUC-Z2-SO$_3$H, with ethylenediamine in ethanol and methanol solutions.

[30] When the host materials were immersed in ethylenediamine organic solvent for 4 h at room temperature, the concentration ethylenediamine, measured by GC was observed to decrease sharply in CCl$_4$, to a moderate extent in ethanol where as a slight decrease was observed in case of methanol (Table 1). Using the

[35] same method, we compute formation constant, K_f for other organic guests in different solvent systems. For example, the K_f of JUC-Z2-SO$_3$H binding ethylenediamine decreased from 13.6 M^{-1} in CCl$_4$ to 9.4 M^{-1} in ethanol and 2.2 M^{-1} in methanol (table 1). Interestingly, in the case of adsorption of dipropylamine and

[40] tributylamine by JUC-Z2-SO$_3$H, it shows high adsorption uptake in CCl$_4$ (3.2 M^{-1} and 1.6 M^{-1}, respectively) while no adsorption in

methanol. Such a correlation of solvent polarity and amine uptake is more the matter of uptake by the guest framework, which is explained as we find a decrease in binding constant with an

[45] increase in polarity of the solvent. Moreover, solvent effect results provide a method of selective adsorption and effectively release amine by simply adjust polarity of solvent. We also studied the amine recovery by using different solvents. First, JUC-Z2-SO$_3$H (5 mg) and tributlamine was immersed in

[50] anhydrous CCl$_4$ solutions in 10 mL volumetric flask to keep the initial concentration of tributylamine is 440.7 mmol L^{-1}. After 4 h at 302 K, the concentration of tributylamine changed to 417.2 mmol L^{-1}. Then, the solvent were evaporated and the resulting solid mixture was immersed in CH$_3$OH. The concentration of

[55] tributylamine become to 439.9 mol L^{-1}, suggesting that the arrested amine was recovered from host material. It demonstrated that JUC-Z2-SO$_3$H can efficient arrest and recover amine by using different solvent.

Conclusions

[60] To conclude, in this paper we addressed the issue of nitrogen-containing organic compounds uptake by organic porous materials JUC-Z2 and, its sulfonate derivate, JUC-Z2-SO$_3$H. In fact sulfonation was carried out to enhance the efficacy of amine uptake. It demonstrated that weaker basicity nitrogen containing

[65] compounds could not be adsorbed in JUC-Z2-SO$_3$H. We demonstrated that it was possible to vary the extent of uptake of amines by varying solvent polarity. This was possible due to the recognition of the solvent by the host binding sites which led to a competition between the binding amines and the solvent

[70] molecules. As the solvent polarity increased the solvent molecules win the competition releasing amines from the host-framework. Such a competition was also well substantiated from the dependence of binding energy of the guest amines on solvent polarity. This work would lead to greener pathways for arresting

[75] amines and recovering them in a facile fashion after use by employing JUC-Z2 type porous materials as reported here.

Notes and references

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