Ship-in-a-bottle synthesis of amine-functionalized ionic liquids in NaY zeolite for CO2 capture

Yinghao Yu1, Jingzhang Mai1, Lefu Wang1, Xuehui Li1, Zheng Jiang2 & Furong Wang1

1School of Chemistry and Chemical Engineering, Pulp & Paper Engineering State Key Laboratory of China, South China University of Technology, Guangzhou 510640, P. R. China, 2Faculty of Engineering and the Environment, University of Southampton, Highfield, Southampton SO17 1BJ, UK.

CO2 capture on solid materials possesses significant advantages on the operation cost, process for large-scale CO2 capture and storage (CCS) that stimulates great interest in exploring high-performance solid CO2 adsorbents. A ship-in-a-bottle strategy was successfully developed to prepare the [APMIM]Br@NaY host–guest system in which an amine-functionalized ionic liquid (IL), 1-aminopropyl-3-methylimidazolium bromide ([APMIM]Br), was in-situ encapsulated in the NaY supercages. The genuine host-guest systems were thoroughly characterized and tested in CO2 capture from simulated flue gas. It was evidenced the encapsulated ILs are more stable than the bulk ILs. These host–guest systems exhibited superb overall CO2 capture capacity up to 4.94 mmol g⁻¹ and the chemically adsorbed CO2 achieved 1.85 mmol g⁻¹ depending on the [APMIM]Br loading amount. The chemisorbed CO2 can be desorbed rapidly by flushing with N2 gas at 50°C. The optimized [APMIM]Br@NaY system remains its original CO2 capture capacity in multiple cycling tests under prolonged harsh adsorption-desorption conditions. The excellent physicochemical properties and the CO2 capture performance of the host-guest systems offer them great promise for the future practice in the industrial CO2 capture.

The human society is facing unprecedented threat of climate change due to the continuously increasing air CO2 level induced by the roaring energy demand that will still have to be supplied by fossil fuels in the next decades1,2. It was reported the emission of the anthropogenic CO2 will reach 43 gigatons in 2035, rising 50% from that in 20093. In combating climate change, CO2 capture and storage (CCS) using various CO2 absorbents represents the sole effective solution to reduce such a huge scale of CO24. Currently, organic amines, ionic liquids (ILs) or alkaline scrubbers have been explored as effective absorbents in CCS though they are either corrosive or costly that challenges the process engineering and transportation. Porous solid adsorbents have recently been emerged for CO2 capture and attracted intensive interest since the materials are less corrosive, cost-effective and easy to transport5.

To date, various adsorbent materials have been explored for CO2 capture, including “molecular basket” sorbents (MBS), metal–organic frameworks (MOFs) and alkanolamine modified zeolites6. Song and co-workers have done pioneering and systematic research on CO2 capture with the “molecular basket” sorbents (MBS) and reach the CO2 adsorption capacity above 3 mmol/g at 75°C and a CO2 partial pressure of 15 kPa. The MBS materials are featured with the amine polymer (polyethyleneimine, PEI) immobilized onto porous supports (MCM-417, SBA-158, carbon materials10, bentonite11, and silica-gel12). MOFs have been widely used in gas adsorption due to their unique structural properties, such as robustness, good thermal stabilities and ultrahigh specific surface area13–16 and they can achieve high CO2 adsorption capacity up to 54 mmol/g under room temperature and high pressure (50 bar)13. However, the CO2 storage capacity of MOFs becomes lower than zeolites at low pressures (<10 bar), not mention that the partial pressure of CO2 in flue gas is only 0.15 bar17. Moreover, MOFs materials suffer from long-term stability issues because the acidic or polar impurities (e.g. H2S, SO2, and NOx, etc) in the flue gas would markedly reduce their CO2 storage capacity or even damage the structure of MOFs1. Commercialized zeolites are more plausible for gas adsorption due to their advantages in large gas uptake at low pressure, high chemical and thermal stability, easier regeneration and moderate cost18–20. However, adsorption capacities of zeolites decline rapidly once the temperature is higher than 30°C and even become negligible above 200°C1. In addition, their selectivity to CO2 in the existence of other gases (N2, CH4, H2O, etc.) is not ideal. Hence, the zeolites should be modified for CO2 capture from flue gas2,21. Alkanolamines, such as...
Table 1 | Elemental analysis of NaY, [APMIM]Br@NaY-X and [BMIM]Br@NaY

| Samples      | C (wt %) | H (wt %) | N (wt %) | IL loading (wt %) | IL/supercage |
|--------------|----------|----------|----------|-------------------|--------------|
| NaY          | 0.02     | 2.95     | 0.25     | --                | --           |
| [APMIM]Br@NaY0.5 | 2.55     | 2.67     | 1.45     | 6.64              | 0.49         |
| [APMIM]Br@NaY1  | 4.35     | 2.80     | 2.34     | 11.36             | 0.89         |
| [APMIM]Br@NaY2  | 6.77     | 2.74     | 3.55     | 17.68             | 1.49         |
| [APMIM]Br@NaY4  | 7.43     | 2.87     | 3.73     | 19.42             | 1.67         |
| [APMIM]Br@NaY8  | 7.62     | 2.70     | 4.02     | 19.92             | 1.73         |
| [APMIM]Br@NaY10 | 8.06     | 2.69     | 4.13     | 21.06*            | 1.85         |
| [APMIM]Br@NaY2  | 6.77     | 2.80     | 3.73     | 19.42             | 1.67         |
| [APMIM]Br@NaY4  | 7.43     | 2.87     | 3.73     | 19.42             | 1.67         |
| [APMIM]Br@NaY8  | 7.62     | 2.70     | 4.02     | 19.92             | 1.73         |
| [APMIM]Br@NaY10 | 8.06     | 2.69     | 4.13     | 21.06*            | 1.85         |
| [APMIM]Br@NaY2  | 6.77     | 2.80     | 3.73     | 19.42             | 1.67         |
| [APMIM]Br@NaY4  | 7.43     | 2.87     | 3.73     | 19.42             | 1.67         |
| [APMIM]Br@NaY8  | 7.62     | 2.70     | 4.02     | 19.92             | 1.73         |
| [APMIM]Br@NaY10 | 8.06     | 2.69     | 4.13     | 21.06*            | 1.85         |

*a*In accordance with the results of TGA.

Results

Physicochemical characteristics of the IL@NaY host-guest systems. The detailed preparation process of all the host-guest systems and the corresponding abbreviations of all the samples were presented in the Methods section. During the synthesis process, all the un-reacted reagents and non-encapsulated ILs were removed from the host-guest systems via careful Soxhlet extraction, while the encapsulated IL guests are too large to escape from the zeolite aperture windows yet kept inside the supercages. The results are in agreement with the observation for (C₆H₅)₃CCl@HY zeolite systems, in which (C₆H₅)₃CCl remained in the HY zeolite supercages, while small precursors of CCl₄ and benzene were removed completely by Soxhlet extraction. Elemental analysis was conducted to determine the molar ratio of encapsulated ILs to supercages (IL/supercage) of NaY zeolite and the results were listed in Table 1. The IL/supercage ratio of [APMIM]Br@NaY-0.5 is 0.49, suggesting that 98% (0.49/0.5 = 0.98) of [APMIM]Br IL was encapsulated in NaY. The IL/supercage ratio is increased from 0.49 to 1.67 as X increasing from 0.5 to 4, whereas the ratio remains less than 2.0 even when X got to 10. The nonlinear change of the IL/supercage value reveals there is a balance between the guest ILs and supercages. Such ratio can’t reach 2.0 because the number of perfect supercages is smaller than the theoretical value (0.67 mmol supercages per gram of NaY) due to the structural defects existing in the NaY zeolite.

The influence of IL loading on the morphology of NaY zeolite was investigated via TEM characterization. The collected TEM images of NaY, [BMIM]Br@NaY, and [APMIM]Br@NaY-X (shown in Fig. S1-8) are almost the same, suggesting the encapsulated ILs won’t affect the rigid framework of the NaY zeolite and thus its morphology remains unchanged.

TGA was conducted to study the thermal stability of NaY zeolite, ILs and the host-guest systems. Typical TGA profiles of NaY, [BMIM]Br@NaY, and [APMIM]Br@NaY-X are comparatively shown in Figure 1. Remarkable weight losses of the bulk ILs of [BMIM]Br and [APMIM]Br appear at 260 and 235°C, respectively, suggesting the thermal decomposition of these ILs initiated at such temperature. However, the onset decomposition temperatures (T_d) are enhanced to 369 and 323°C for the encapsulated [BMIM]Br and [APMIM]Br ILs, respectively, revealing the NaY encapsulated ILs are much more stable than their bulk analogues. The enhanced thermal stability of the ILs in the porous host–guest systems can be attributed to the encapsulation effect of zeolite supercages. When heating up to
in Figure 2A. The N2 sorption isotherms of all the samples display the surface area of these host-guest systems and the results are shown SCIENTIFIC analysis.

confined into the pores of the NaY zeolite as discussed in the element Table 1) on the NaY zeolite. The results verify the ILs have been ILs (18.50% of [BMIM]Br and 21.06% of [APMIM]Br as shown in [APMIM]Br@NaY-10 are 18.39 and 20.80%, respectively, which are well consistent with the loading percentages of the corresponding BET specific surface area (SBET) of the host-guest materials dropped from 456 to 149 m2 g

Figure 2 presents the XRD patterns of NaY and its derived host-guest samples. The characteristic Raman shifts of bulk ILs were difficult to wash out and necessitated exhaustive Soxhlet extraction. The characteristic Raman shifts of bulk ILs ([BMIM]Br and [APMIM]Br) and their corresponding host-guest systems ([BMIM]Br@NaY-BE, [BMIM]Br@NaY, [APMIM]Br@NaY-10-BE, and [APMIM]Br@NaY-10) and NaY display the same sharp and characteristic absorption bands around 500 cm

600°C, the total weight losses of the [BMIM]Br@NaY and [APMIM]Br@NaY-10 are 18.39 and 20.80%, respectively, which are well consistent with the loading percentages of the corresponding ILs (18.50% of [BMIM]Br and 21.06% of [APMIM]Br as shown in Table 1) on the NaY zeolite. The results verify the ILs have been confined into the pores of the NaY zeolite as discussed in the element analysis.

N2 sorption experiments at −196°C were performed to investigate the surface area of these host-guest systems and the results are shown in Figure 2A. The N2 sorption isotherms of all the samples display typical type-I hysteresis loops along with sharp uptakes in the low relative pressure regions, revealing the characteristic microporous structure of NaY zeolite was not damaged during the fabrication of the host-guest systems. However, the pore volume of the host-guest systems went down nonlinearly as increase of the IL loading, in particular more significant drop when X is smaller than 4. The specific surface areas of the materials were determined using the Brunauer–Emmett–Teller (BET) method to analyze the adsorption branches of the isotherms. As increase the [APMIM]Br loading, the BET specific surface area (SBET) of the host-guest materials dropped down from 456 to 149 m2 g

Figure 2B presents the XRD patterns of NaY and its derived host-guest samples. It can be found that all the samples displayed the similar NaY diffraction patterns, revealing the IL encapsulation process, N-methylimidazole was initially diffused into the supercages of NaY zeolite following with rapid reaction to generate [APMIM]Br once 3-bromopropylamine was added. The as-generated [APMIM]Br would occupy the supercages and thus inhibit further inward diffusion of unreacted 3-bromopropylamine. Hence, unreacted 3-bromopropylamine would be easily removed in the subsequent washing and filtration. In contrast, the pre-entrapped N-methylimidazole molecules were difficult to wash out and necessitated exhaustive Soxhlet extraction. The characteristic Raman vibration bands due to N–C, the total weight losses of the [BMIM]Br@NaY and [APMIM]Br@NaY-10 even after intensive Soxhlet extraction, clearly revealing that the large-sized [BMIM]Br and [APMIM]Br ILs were encapsulated firmly or sterically confined within the NaY supercages. More importantly, there are no obvious chemical shifts observed between bulk ILs ([BMIM]Br and [APMIM]Br) and their corresponding host-guest systems ([BMIM]Br@NaY and [APMIM]Br@NaY-10 host-guest systems after Soxhlet extraction. The results strongly evidence ILs have been filled into the NaY supercages, in very good accordance with the discussions in TEM, XRD and N2 isotherm sections. The characteristic stretching vibration at 558 cm

Figure 3 shows the FT–Raman spectra of typical samples and Table 2 lists the assignments of the characteristic Raman vibration bands. As shown in Figure 3A, all the host–guest systems ([BMIM]Br@NaY-BE, [BMIM]Br@NaY, [APMIM]Br@NaY-10-BE, and [APMIM]Br@NaY-10) and NaY display the same sharp and characteristic absorption bands around 500 cm

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Br@NaY, and [APMIM]Br@NaY-10), indicating there is no covalent bond existing between the immobilized ILs and NaY. The confinement of ILs in the NaY supercages should be mainly attributed to the steric effects and electrostatic forces.

Detailed FT–Raman spectra of [APMIM]Br@NaY-X are shown in Figure 3B. Characteristic bands of ILs at 1023, 1332, and 1416 cm\(^{-1}\) can hardly be discerned in the spectrum of [APMIM]Br@NaY-0.5. While the intensities of these bands increase rapidly as the X value increased from 1 to 4. The intensity of the characteristic Raman bands increase slower upon further increasing X value from 8 to 10, suggesting there is an equilibrium for the encapsulation of ILs into the NaY supercages, which also accords well with previous discussions in elemental analysis and XRD sections. In addition, the Raman shifts at 2926 cm\(^{-1}\) (CH\(_2\) stretching in the side chain) is clearly visible at lower X values but disappears or is merged into the band at 2968 cm\(^{-1}\) (CH\(_3\) symmetrical stretching) for the high-loading [APMIM]Br@NaY-8 and [APMIM]Br@NaY-10. This can be attributed to unusual changes in the symmetry and coordination geometry of the [APMIM]Br molecules as confined in the NaY supercages\(^{19,38}\).

**CO\(_2\)** adsorption performance. The CO\(_2\) capture capacity of these host-guest systems was evaluated through measurements of their CO\(_2\) adsorption isotherms at 0°C from 0 to 1 atm and the results are shown in Figure 4. It can be seen that CO\(_2\) adsorption capacity of NaY is 5.89 mmol g\(^{-1}\), and the capacity of [APMIM]Br@NaY-X is decreased from 4.94 to 3.79 mmol g\(^{-1}\) with X increasing from 0.5 to 2, and the capacity can still reach up to 3.22 mmol g\(^{-1}\) for [APMIM]Br@NaY-10.

The value of the CO\(_2\) adsorption comprises of both the chemical and physical adsorption of CO\(_2\). As a new class of CO\(_2\) adsorbents, it is necessary to investigate the chemisorption performance of the novel host-guest materials since the chemisorbed CO\(_2\) is pivotal for CCS. CO\(_2\)-TPD measurements were carried out to determine the chemisorption amount of CO\(_2\) in the host–guest systems (Figure 5). As shown in Figure 5, all desorption curves were fitted into four characteristic peaks, corresponding to CO\(_2\) adsorption on the intrinsic basic sites of NaY (peaks \(a\) and \(b\) at 180 and 240°C), imidazolium cations (peak \(c\) at 136°C) and \(-\text{NH}_2\) groups (peak \(d\) at 108°C), which will benefit the analysis of CO\(_2\) chemisorption mechanism on both the NaY zeolite and derived host–guest systems. On the NaY zeolite (Figure 5A(a) and 5A(d)), CO\(_2\) chemisorbed on the intrinsic Lewis basic sites associated with the lattice oxygen in the NaY framework. In contrast, on the [BMIM]Br@NaY systems (Figure 5A(b) and 5A(e)), CO\(_2\) can be chemically adsorbed on both the intrinsic basic sites in NaY and imidazolium cations of the encapsulated ILs. Indeed, the CO\(_2\) can reversibly react with imidazolium cations\(^{44}\) (or imidazolium-like cations\(^{45}\)) and generate 1,3-dialkyliimidazolium-2-carboxylate compound at relatively low temperature. Such a chemisorption was also confirmed by the isosteric heat of CO\(_2\) adsorption on [BMIM]Br@NaY (seen in Figure S9-11), where the high adsorption isosteric heat was due to the chemisorption\(^{46,47}\) on carbene centres in the imidazolium cations. In addition to the two types of chemisorption associated with the lattice oxygen and carbene centres, [APMIM]Br@NaY materials also possess –NH\(_2\) group (Figure 5A(c) and 5A(g)) as an extra chemisorption centre. In principle, the active –NH\(_2\) groups can react quantitatively with CO\(_2\) at the molar ratio of 2:1\(^{26,27}\). In brief, as compared in Figure 5A, CO\(_2\) chemically adsorbed on the intrinsic Lewis basic sites of NaY is more difficult to be desorbed than the chemisorbed CO\(_2\) on the host–guest systems. The phenomenon can be attributed to the stronger basicity of intrinsic basic sites in NaY than that of imidazolium cations or of –NH\(_2\) groups\(^{25,48}\). As for the [APMIM]Br@NaY host–guest systems, they possess three types of adsorption centers due to the Lewis basic site of NaY, carbene centers and free –NH\(_2\) groups. It can be seen from Figure 5A that the CO\(_2\) desorption peaks shift to lower temperature along with the increase of ILs loading, suggesting the contribution of Lewis basic centers decreased significantly yet the contribution of carbene and free –NH\(_2\) groups improved. The reduced contribution of Lewis basic sites may be arisen from the

![Figure 3](https://www.nature.com/scientificreports/4:5997/doi:10.1038/srep05997)

**Figure 3** | (A): FT–Raman spectra of N-methylimidazole, 3-bromopropylamine, NaY, [APMIM]Br, [BMIM]Br, [APMIM]Br@NaY-10, [BMIM]Br@NaY, and host–guest systems before Soxhlet extraction ([BMIM]Br@NaY-BE and [APMIM]Br@NaY-10-BE); (B): FT–Raman spectra of [APMIM]Br@NaY-X (X = 0.5, 1, 2, 4, 8, 10).
ILs coverage on inner walls of NaY pores and the strong interaction between ILs and NaY. The comparison of desorption amount of CO₂ adsorbed at 35 and 50°C shows more CO₂ was released from the sample adsorbed CO₂ at higher temperature, which reveals the ILs functional groups determined the chemisorption of CO₂ on the host-guest system. More detailed mechanism of CO₂ chemisorption on [APMIM]Br@NaY was proposed in the Supplementary information. From the practical application point of view, the host-guest systems will be easier to regenerate than NaY zeolite as well as more energy-effective for the large scale CO₂ adsorption-desorption cycling.

In order to quantitatively investigate the influence of adsorption temperature on the CO₂ chemisorption behavior on host-guest materials, their CO₂ chemisorption capacities were calculated and listed in Table S1. The area of peak δ in the CO₂-TPD profile of [APMIM]Br@NaY-10 is doubled when the adsorption temperature increases from 35 (A = 713, Table S1, run c) to 50°C (A = 1413, Table S1, run g), while the corresponding CO₂ chemisorption capacity increases from 1.38 to 1.85 mmol g⁻¹. The results suggest that the chemisorption induced by –NH₂ of the ILs dominated the CO₂ chemisorption at relatively high temperature and the interaction between CO₂ and –NH₂ could be activated by mild heating. More importantly, as shown in Figure 5A(f), upon flushing with N₂ at 50°C the peak δ disappears and the amount of the desorbed CO₂ decreases from 1.85 mmol g⁻¹ (Table S1, run g) to 0.89 mmol/g (Table S1, run f), revealing that CO₂ chemisorbed by –NH₂ groups can be easily released and this host–guest system of [APMIM]Br@NaY-10 can be regenerated at medium temperature. Low temperature regeneration is highly plausible for practical CCS due to reduced energy penalty.

Figure 5B presents the CO₂ desorption profiles on a series of [APMIM]Br@NaY-X and the corresponding desorption areas were calculated (Table S2). CO₂ chemisorption capacities of [APMIM]Br@NaY-X increase gradually from 0.98 to 1.85 mmol g⁻¹ when X increases from 0.5 to 10. With increasing the IL loading in the host-guest materials, the areas of γ and δ desorption peaks increase sharply (from 335 to 897 and from 0 to 1418, respectively), whereas those of z and β peaks decrease gradually. These changes reveal that the quantities of imidazolium cations (peak γ) and –NH₂ groups (peak δ) in the host–guest systems are increased while the number of free Lewis basic sites in the NaY zeolite framework are reduced.

**Table 2 | Characteristic Raman bands and their corresponding assignments**

| Band (cm⁻¹) | Assignments |
|-------------|--------------|
| 500         | Framework Si–O and Al–O vibration in the zeolite⁹⁹ |
| 558         | Stretching vibration of C–Br bond in 3-bromopropylamine⁶⁹ |
| 660         | N–CH₃ stretching and ring bending (in-plane)⁶⁹ |
| 1023        | CH₃ bending and ring bending (in-plane)⁴¹,⁴² |
| 1332        | Ring stretching and CH₃ bending⁴¹,⁴² |
| 1416        | CH₃ symmetrical bending⁴¹,⁴² |
| 1453        | CH₂ deformation in the side chain⁴³ |
| 2926        | CH₂ stretching in the side chain⁴³ |
| 2968        | CH₃ symmetrical stretching in the side chain⁴³ |

**Discussion**

Both zeolites and ILs possess their own remarkable advantages and disadvantages in CO₂ capture, while the IL@zeolite host-guest systems would synergistically combine the advantages of individual constituents as well as minimise their disadvantages. Zeolites are featured with high chemical and thermal stability and a moderate cost, but themselves aren’t ideal for CO₂ capture because of their low adsorption capacity at high temperature and poor selectivity to CO₂ over other gases. Indeed, the CO₂ adsorption isotherms and TPD results reveal that the CO₂ adsorption on NaY is too strong to recover and considerably sensitive to both reaction temperature and pressure. ILs may have high CO₂ storage capacity yet is not stable at high temperature as well as necessitate remarkable energy for CO₂ capture and regeneration cycles⁶⁶. In the current work, the [APMIM]Br@NaY host-guest systems were successfully synthesised through a facile in-situ ship-in-a-bottle synthesis strategy that realised filling a ship (large-sized ILs) into a bottle (NaY microporous supercages). The obtained [APMIM]Br@NaY host-guest systems exhibited superior performance in CO₂ capture to the [APMIM]Br IL and NaY zeolite: first, the encapsulated ILs (Tₘ ≈ 323°C) are thermally more stable than the bulk analogues (Tₘ ≈ 236°C) due to the encapsulation effect as well as the strong interaction between the zeolite adsorption capacities of the regenerated to the fresh adsorbent was defined as adsorption index. Figure 6B shows the calculated adsorption indexes in 10 cycling tests of the [APMIM]Br@NaY-10. Clearly, after 10 adsorption-desorption cycling operations the adsorption index was only reduced from 100% to 94.5%, suggesting that most CO₂ molecules can be effectively desorbed and the [APMIM]Br@NaY samples are sufficiently stable for recycling applications in CCS process. The negligible decrease of the adsorption capacity can be attributed to the slight loss of accessible –NH₂ sites during the high-temperature (280°C) regeneration. As discussed in the CO₂ TPD section, CO₂ chemisorbed on the [APMIM]Br@NaY can be easily flushed off with N₂ at 50°C, hence, the stability of [APMIM]Br@NaY in the harsher prolonged cycling adsorption-desorption tests may promise the material using for the practical CCS.
supercages and ILs; second, at high temperature (50 °C), the host-guest system possess higher CO2 chemisorption capacity than NaY zeolite, which can be attributed to the introduction of imidazolium cations and functional –NH2 groups; third, as shown in CO2 TPD tests, CO2 adsorption on [APMIM]Br@NaY is mainly attributed to chemical adsorption that is rather stable during storage and transportation, more importantly, such chemisorbed CO2 can be easily desorbed by flushing with N2 at 50 °C and thus significantly reduce the energy penalty for the regeneration. The outstanding adsorption-desorption performance of the host-guest systems was verified through the 10 adsorption-regeneration cycling tests under even more stringent conditions. The CO2 chemisorption capacity of [APMIM]Br@NaY can also be tuned through changing the loading of [APMIM]Br or increasing the functional groups (carbene or –NH2 groups) within ILs. In all, the ship-in-a-bottle synthesis provides a facile strategy to design the IL@zeolite host-guest systems that offer great promise to capture CO2 from flue gas at large scale and reduced energy penalty.

**Methods**

**Preparation of the host-guest systems.** The host-guest systems were prepared by ship-in-a-bottle strategy. The principle of the ship-in-a-bottle synthesis of [APMIM]Br@NaY was presented in Supplementary information and depicted in Figure S13. As shown in Figure S13, N-methylimidazole and 3-bromopropylamine entered supercages of NaY in sequence following with fast reaction with each other to generate [APMIM]Br@NaY. For comparison, the non-alkaline functionalized IL, 1-butyl-3-methyl imidazolium bromide ([BMIM]Br), was also encapsulated in NaY by using the same strategy to obtain [BMIM]Br@NaY. The preparation procedures are detailed as follows.

A series of [APMIM]Br@NaY host–guest systems with varying [APMIM]Br loading amount were prepared by changing the molar ratio of N-methylimidazole to NaY supercages (the molar ratio is abbreviated as X, and the host-guest systems are denoted as [APMIM]Br@NaY-X, X = 0.5, 1, 2, 4, 8, 10). For example, to prepare [APMIM]Br@NaY-8, 3.00 g NaY (2.00 mmol of supercages33) and 1.31 g (16.00 mmol) of N-methylimidazole were added to a flask (50 mL) containing 10 mL of 3-bromopropylamine (17.60 mmol, dissolved in 10 mL of ethanol) was then added to the mixture and refluxed for another 24 h. The obtained mixture was washed and filtered with ethanol (3 × 20 mL) prior to Soxhlet extraction in ethanol for 24 h. The product was then dried at 80 °C in vacuum for 24 h to get a white solid.
CO2 adsorption experiments. CO2 adsorption isotherms under static conditions were recorded on ASAP 2010 (Micromeritics) at 0°C within a pressure range from 0 to 1 atm. Before the adsorption measurements, the samples were degassed at 100°C under vacuum for 6 h prior to adsorption. The Brunauer–Emmett–Teller (BET) theory was used to calculate the specific surface areas. XRD patterns between 5° and 45° were obtained on a Bruker D-8 Advance diffracto-meter equipped with a LynxEye position-sensitive detector and a Cu Kα X-ray source (40 kV, 40 mA) at a scanning step of 0.02°. FT-Raman spectroscopy was carried out using LabRamHRR (Horiba Jobin Yvon Inc.).

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**Author contributions**

All the study was designed and the article writing was supervised by X.L. and Z.J. The experiment of BET, TEM, XRD analysis, and prolonged use of the samples was carried out by Y.Y., who was also involved in all the data analyses and paper writing. The experiments of ship-in-a-bottle synthesis, elemental analysis, Raman, CO₂ adsorption was constructed by J.M, he also was a part of the drafting. TGA and the corresponding analysis were carried out by L.W. and F.W. All authors discussed the results and commented on the manuscript.

**Additional information**

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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