*Supporting Information for the manuscript*:

# Amino Functionalized Zn/Cd- Metal−Organic Frameworks for Selective $CO_2$ Adsorption and Knoevenagel Condensation Reaction

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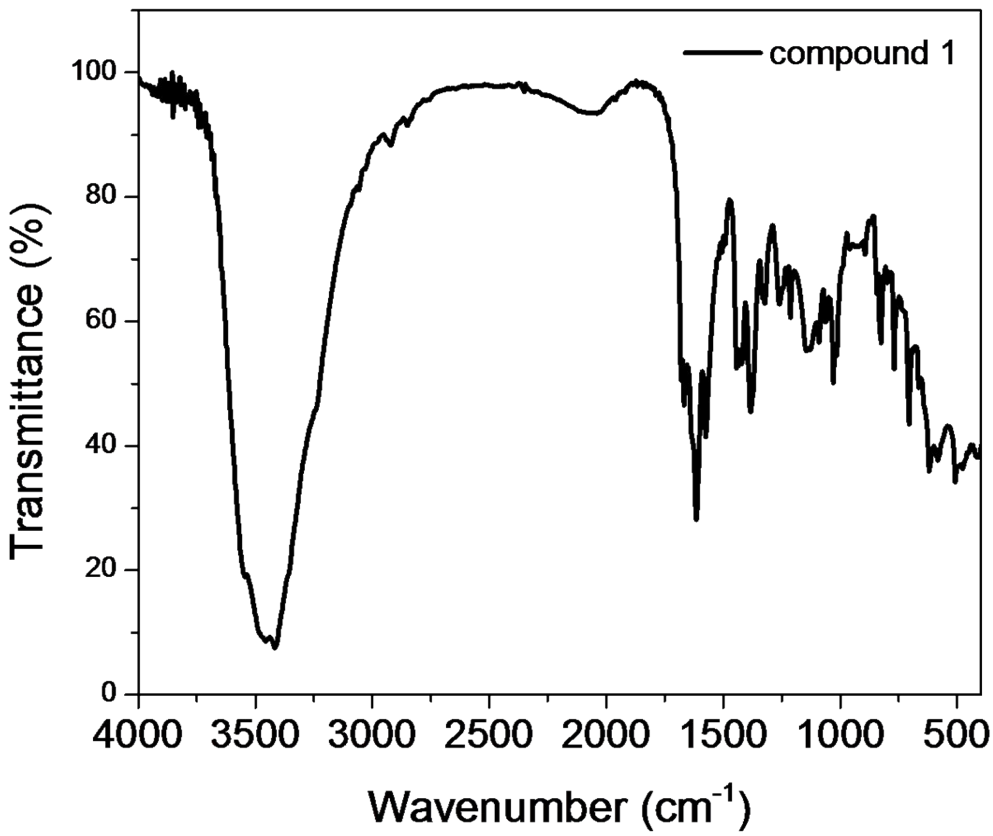



**Figure S1.** The IR spectra of **1**.

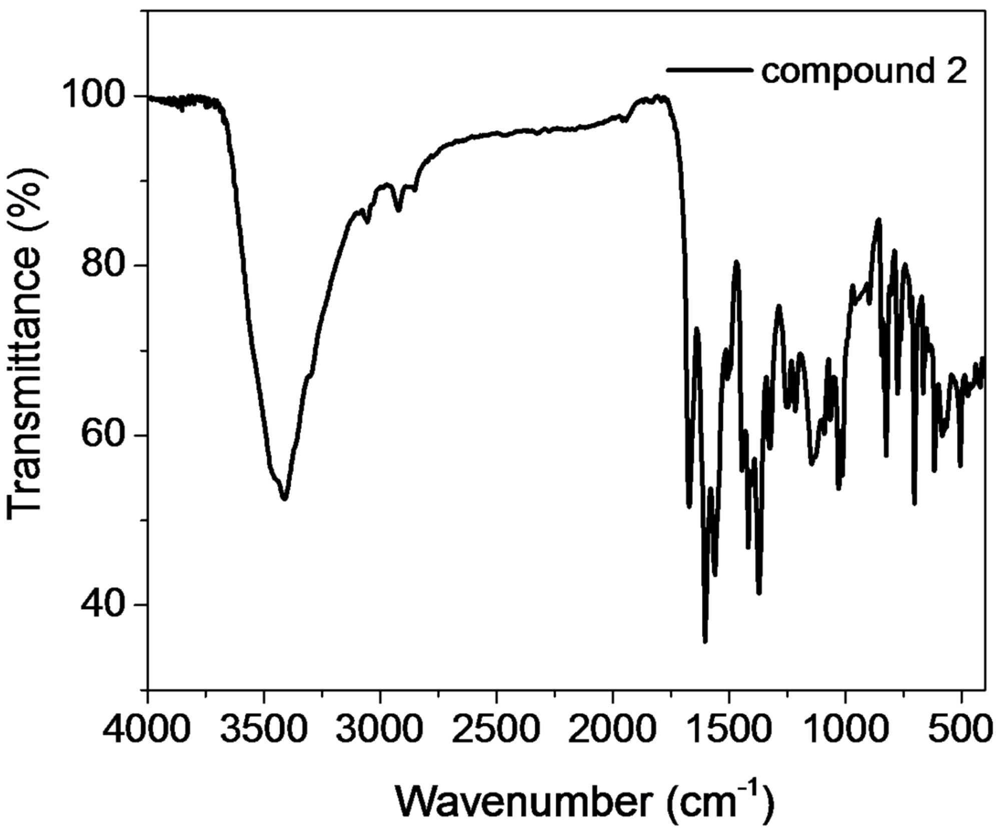



**Figure S2.** The IR spectra of **2**.

**Table S1** Crystallographic data for **1** and **2**

| Compounds | **1** | **2** |
|---|---|---|
| Formula | $ZnC_{25}H_{20}N_6O_5S_2$ | $CdC_{25}H_{21}N_6O_{5.5}S_2$ |
| Formula weight | 613.96 | 670.01 |
| Temperature (K) | 150 | 150 |
| Crystal system | orthorhombic | monoclinic |
| Space group | *Pccn* | $P2_1/n$ |
| $a$ (Å) | 18.5564(2) | 13.56520(10) |
| $b$ (Å) | 17.2237(2) | 14.40230(10) |
| $c$ (Å) | 16.5743(2) | 13.93520(10) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 90 | 100.8040(10) |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 5297.31(11) | 2674.26(3) |
| $Z$ | 8 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.540 | 1.664 |
| $F$(000) | 2512.0 | 1168.0 |
| Reflections Collected | 18616 | 14867 |
| Independent Reflections | 5234 | 5251 |
| observed data [$I > 2\sigma(I)$] | 4601 | 4722 |
| $R_{int}$ | 0.0311 | 0.0375 |
| GOF on $F^2$ | 1.043 | 1.097 |
| $R_1$ $^a$, $wR_2$ $^b$ [$I$>2$\sigma(I)$] | 0.0332, 0.0842 | 0.0397, 0.1120 |
| $R_1$, $wR_2$ (all data) | 0.0387, 0.0870 | 0.0428, 0.1140 |

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $^bwR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

**Table S2**. Selected bond lengths (Å) and angles (°) for **1** and **2**.

| | | | |
|---|---|---|---|
| **1** | | | |
| Zn(1)−O(1) | 2.0003(14) | Zn(1)−O(2)#2 | 2.0352(14) |
| Zn(1)−O(3)#1 | 2.0907(15) | Zn(1)−O(4)#1 | 2.3179(16) |
| Zn(1)−N(1) | 2.1512(17) | Zn(1)−N(2)#3 | 2.1893(18) |
| O(2)−Zn(1)#2 | 2.0351(14) | O(3)−Zn(1)#4 | 2.0906(15) |
| O(4)−Zn(1)#4 | 2.3179(16) | N(2)−Zn(1)#6 | 2.1893(18) |
| O(1)−Zn(1)−O(2)#1 | 120.73(6) | O(1)−Zn(1)−O(3)#2 | 151.72(6) |
| O(1)−Zn(1)−O(4)#2 | 92.31(6) | O(1)−Zn(1)−N(1) | 88.37(6) |
| O(1)−Zn(1)−N(2)#3 | 91.35(6) | O(2)#1−Zn(1)−O(3)#2 | 87.55(6) |
| O(2)#1−Zn(1)−O(4)#2 | 146.63(6) | O(2)#1−Zn(1)−N(1) | 87.88(6) |
| O(2)#1−Zn(1)−N(2)#3 | 92.37(6) | O(3)#2−Zn(1)−O(4)#2 | 59.46(6) |
| O(3)#2−Zn(1)−N(1) | 92.32(6) | O(3)#2−Zn(1)−N(2)#3 | 87.87(6) |
| N(1)−Zn(1)−O(4)#2 | 88.53(6) | N(1)−Zn(1)−N(2)#3 | 179.70(7) |
| N(2)#3−Zn(1)−O(4)#2 | 91.36(6) | | |
| **2** | | | |
| Cd(1)−O(1) | 2.242(2) | Cd(1)−O(2)#2 | 2.291(2) |
| Cd(1)−O(3)#1 | 2.339(2) | Cd(1)−O(4)#1 | 2.409(2) |
| Cd(1)−N(1) | 2.321(3) | Cd(1)−N(2)#3 | 2.340(3) |
| O(2)−Cd(1)#2 | 2.291(2) | O(3)−Cd(1)#4 | 2.339(2) |
| O(4)−Cd(1)#4 | 2.409(2) | N(2)−Cd(1)#5 | 2.339(3) |
| O(1)−Cd(1)−O(2)#2 | 123.34(8) | O(1)−Cd(1)−O(3)#1 | 149.18(8) |
| O(1)−Cd(1)−O(4)#1 | 96.73(8) | O(1)−Cd(1)−N(1) | 97.86(9) |
| O(1)−Cd(1)−N(2)#3 | 85.62(9) | O(2)#2−Cd(1)−O(3)#1 | 85.87(8) |
| O(2)#2−Cd(1)−O(4)#1 | 139.92(8) | O(2)#2−Cd(1)−N(1) | 86.03(9) |
| O(2)#2−Cd(1)−N(2)#3 | 84.31(9) | O(3)#1−Cd(1)−O(4)#1 | 54.93(8) |
| O(3)#1−Cd(1)−N(2)#3 | 88.15(11) | N(1)−Cd(1)−O(3)#1 | 93.40(11) |
| N(1)−Cd(1)−O(4)#1 | 88.13(10) | N(1)−Cd(1)−N(2)#3 | 170.09(11) |
| N(2)#3−Cd(1)−O(4)#1 | 100.73(10) | | |

Symmetry code for **1**: #1. 1/2 + *x*, - *y*, 1/2 - *z*; #2. 1 - *x*, - *y*, 1 - *z*; #3. + *x*, -1 + *y*, + *z*; #4. - 1/2 + *x*, - *y*, 1/2 - *z*; #5. 3/2 - *x*, 1/2 - *y*, + *z*; #6. + *x*, 1 + *y*, + *z*; #7. 1/2 - *x*, 1/2 - *y*, + *z*. Symmetry code for **2**: #2. 2 - *x*, 1 - *y*, 2 - *z*; #1. 1/2+ *x*, 3/2 - *y*, - 1/2 + *z*; #3. 1 + *x*, + *y*, 1 + *z*; #4. -1/2 + *x*, 3/2 - *y*, 1/2 + *z*; #5. - 1 + *x*, + *y*, -1 + *z*.

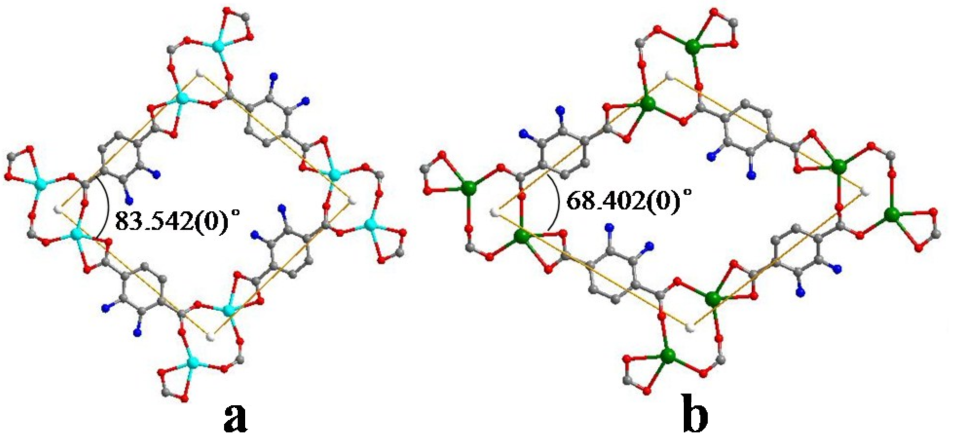



**Figure S3.** The rhombus-shaped grids in 2D sheet layers for **1** and **2**.

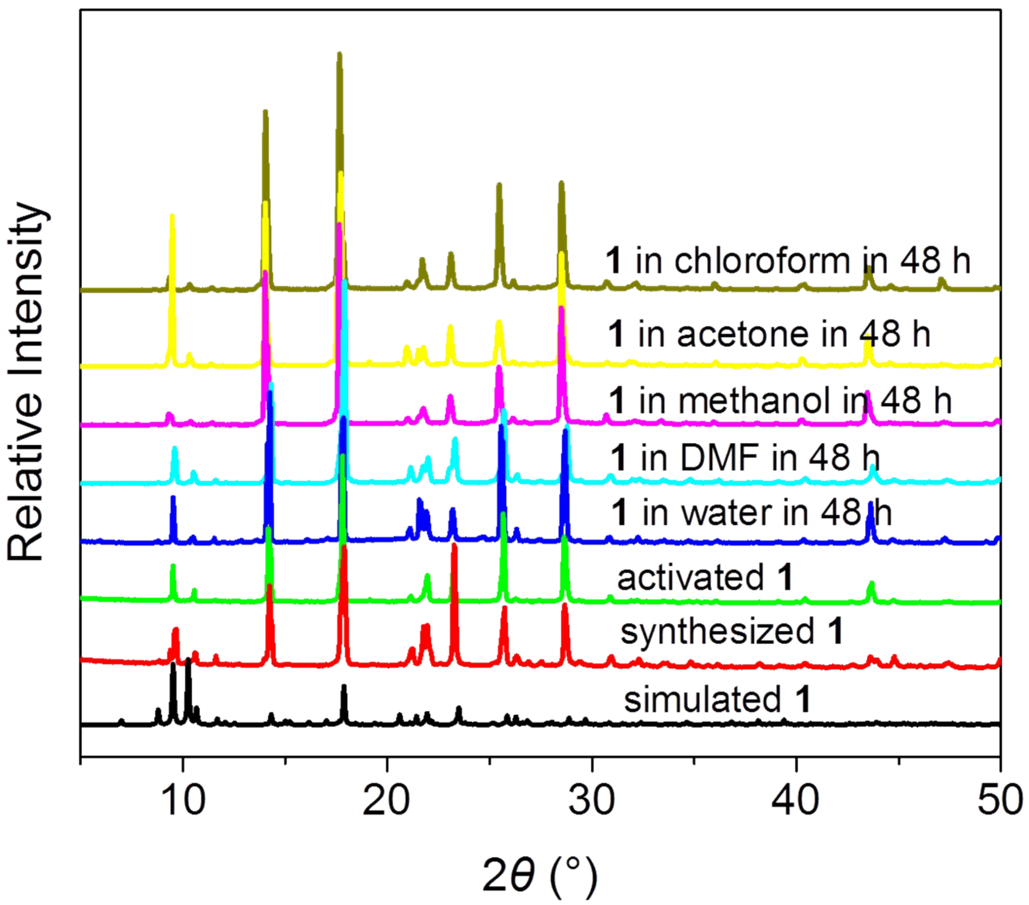



**Figure S4.** PXRD patterns of **1**.

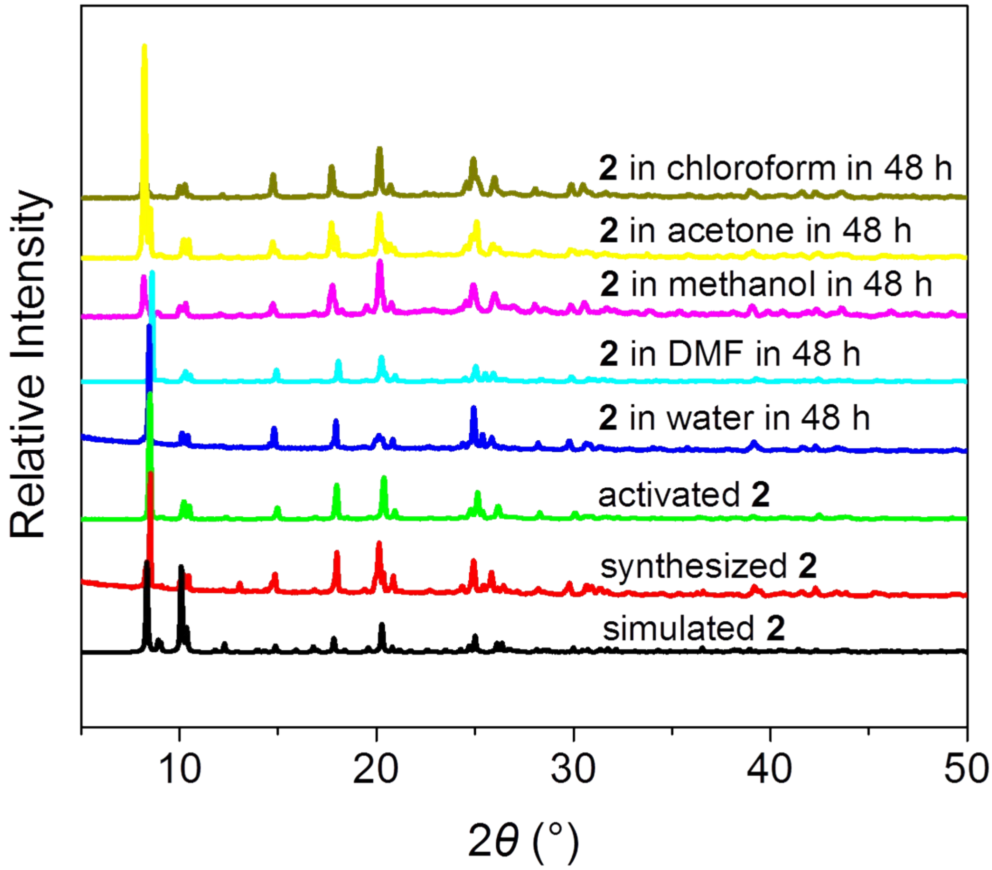



**Figure S5.** PXRD patterns of **2**.

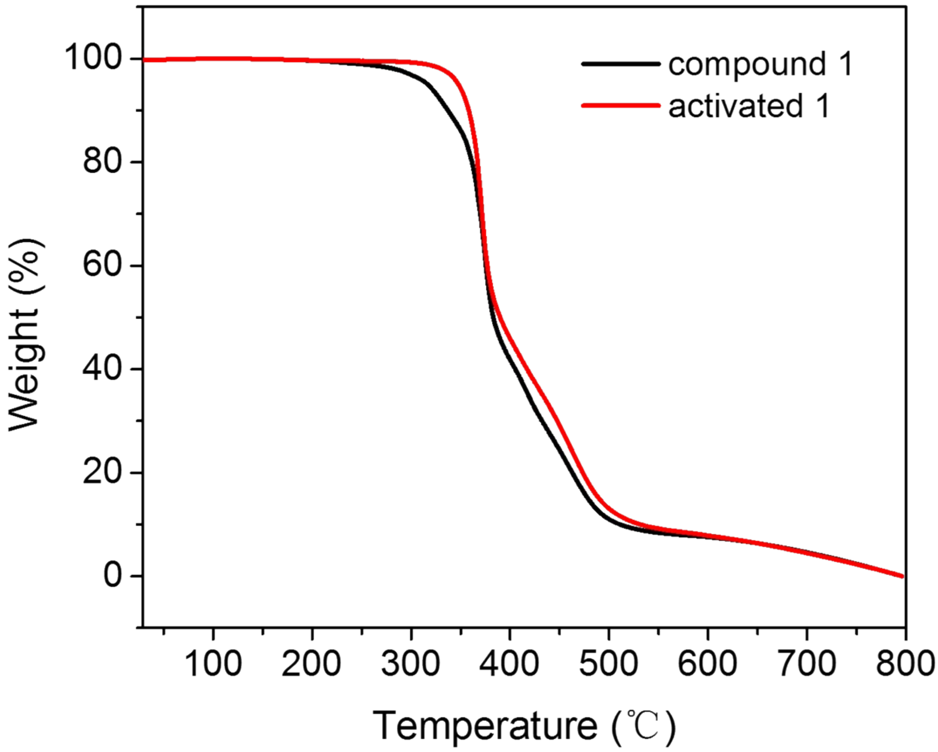



**Figure S6.** Thermogravimetric analyses plots of synthesized **1** and activated **1**.

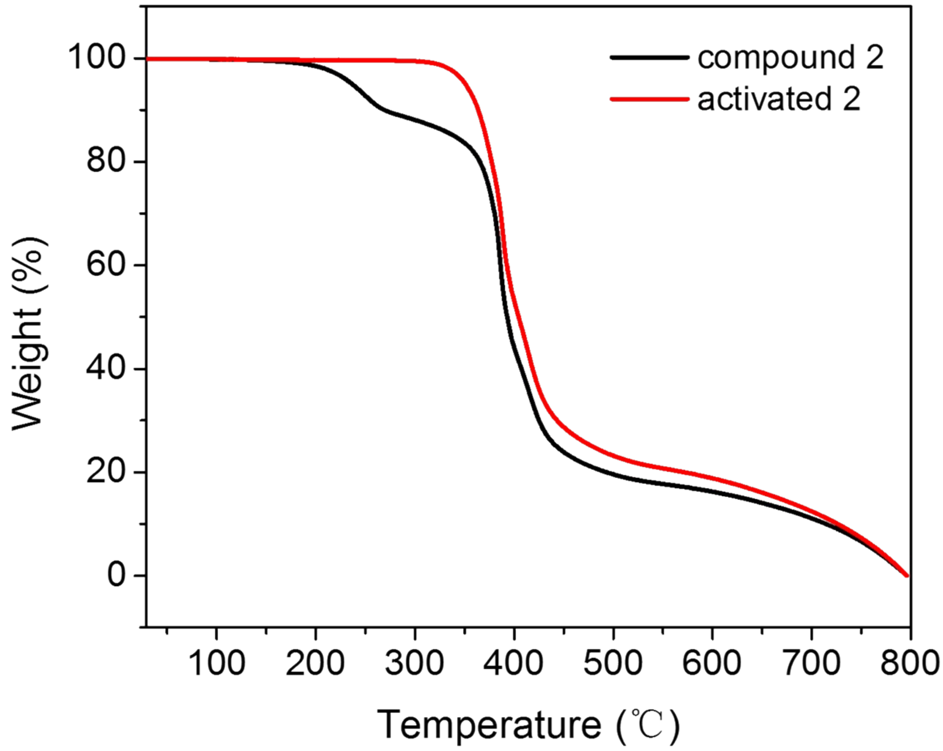



**Figure S7.** Thermogravimetric analyses plots of synthesized **2** and activated **2**.

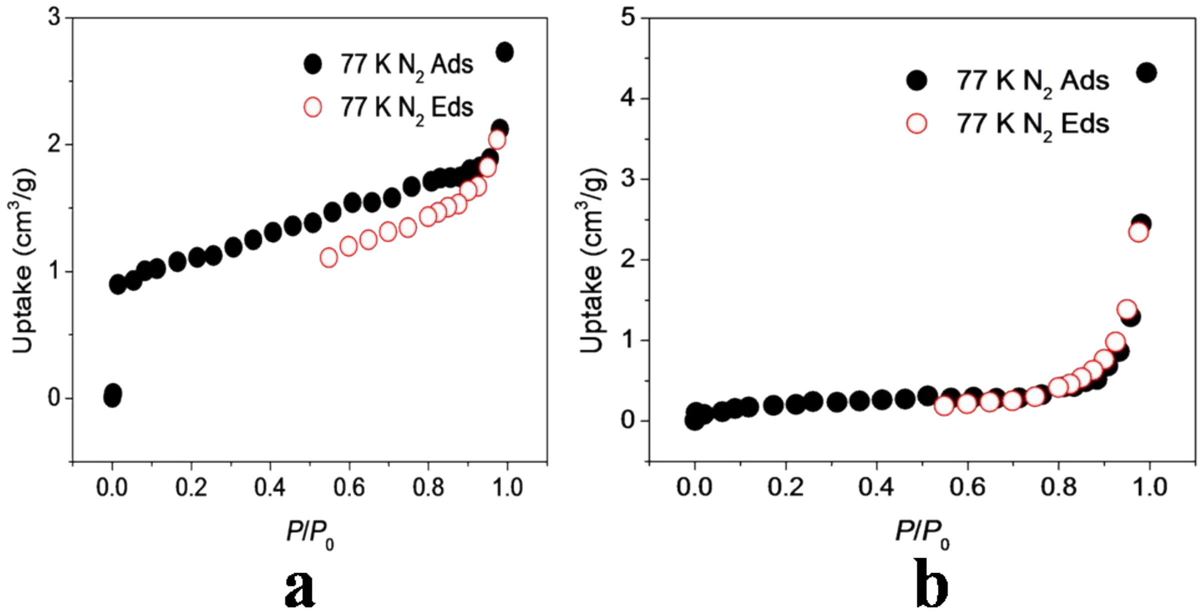



**Figure S8.** (a) $N_2$ adsorption isotherms at 77 K for **1**. (b) $N_2$ adsorption isotherms at 77 K for **2**. Filled and open symbols represent adsorption and desorption, respectively.

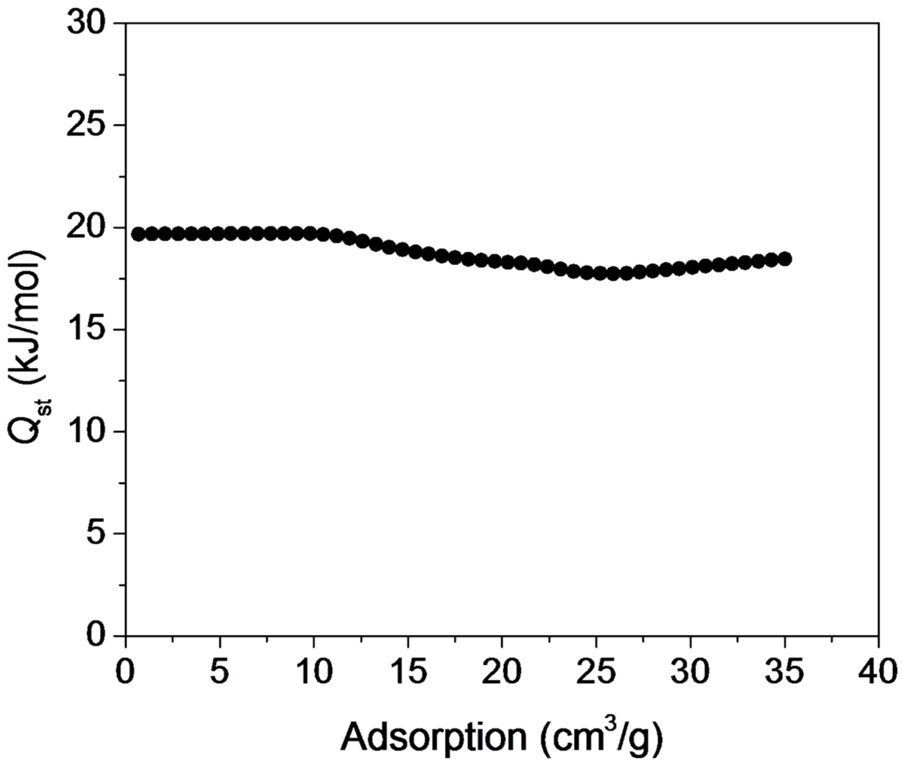



**Figure S9.** Isosteric heat of adsorption versus $CO_2$ loading for **2**.

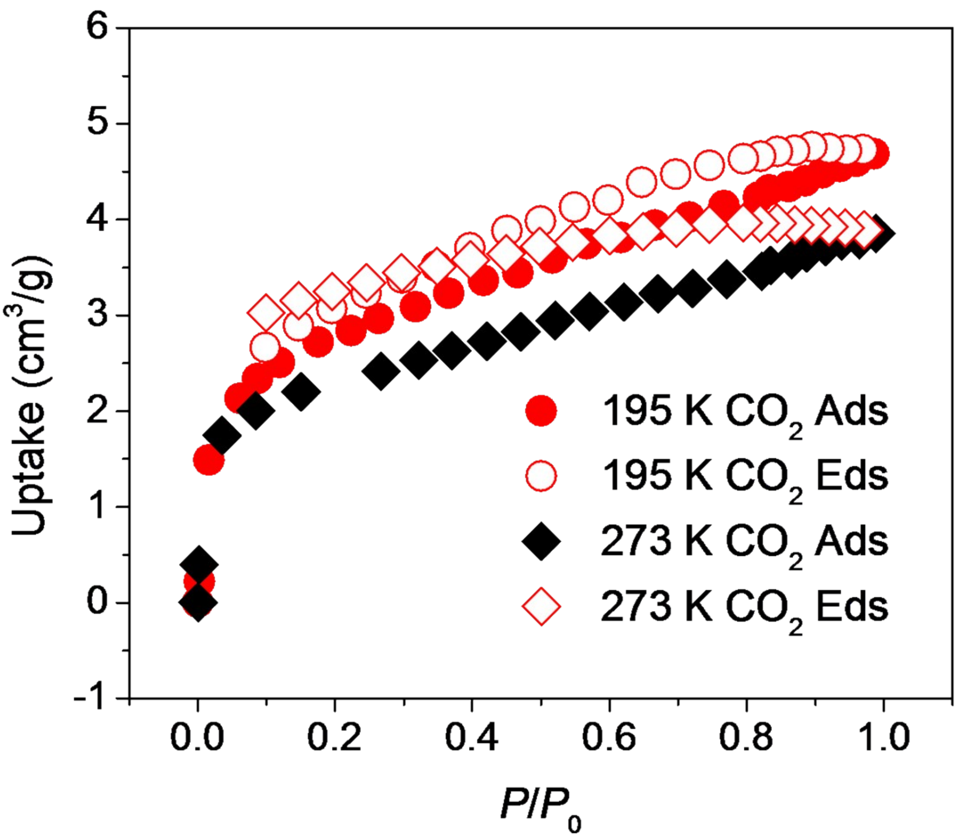



**Figure S10.** $CO_2$ adsorption isotherms at 195 K and 273 K for **1**. Filled and open symbols represent adsorption and desorption, respectively.

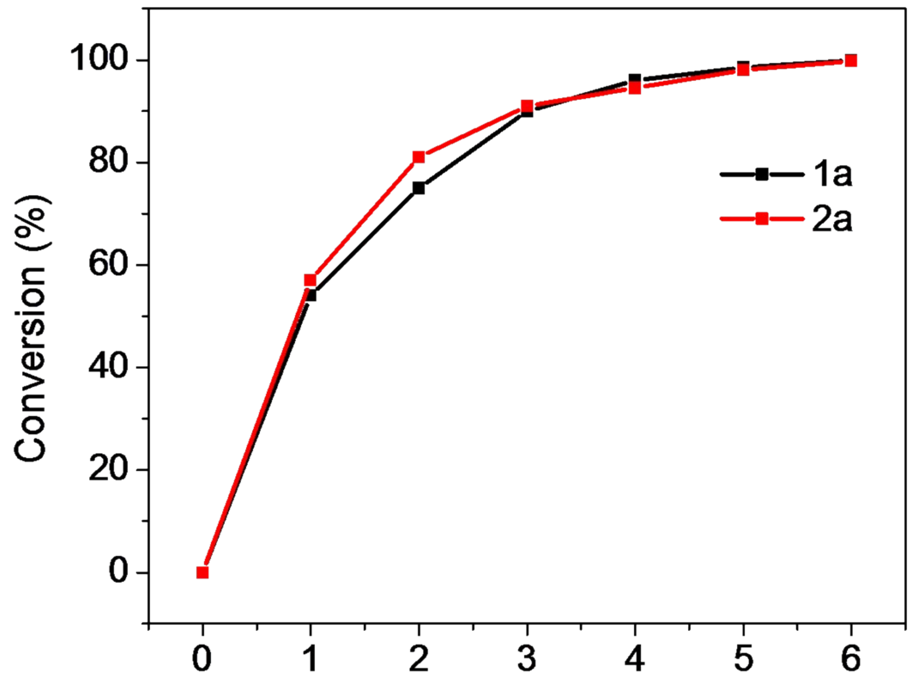
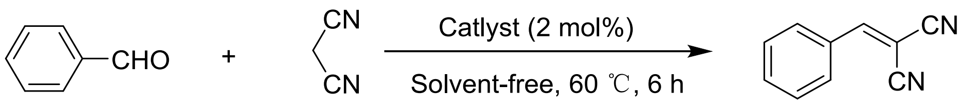



**Figure S11.** Reaction conversion versus reaction time for Knoevenagel condensation reaction of benzaldehyde and malononitrile with **1a** and **2a** as catalyst.

**Table S4.** Knoevenagel condensation reactions of benzaldehyde catalyzed by different catalysts.




| Entry | Catalyst | Yield (%) |
|---|---|---|
| 1 | Catalyst-free | 0 |
| 2 | 2-$NH_2$-$H_2$BDC | 1 |
| 3 | $Py_2$TTz | 72 |
| 4 | 2-$NH_2$-$H_2$BDC + $Py_2$TTz | 54 |
| 5 | $Ph_2$TTz | 48 |
| 6 | **1a** | 99.9 |
| 7 | **2a** | 99.8 |

**Table S5.** Recyclable experiments of **1a** and **2a** as catalyst for Knoevenagel reaction.

| Entry | Yield (%, **1a** as catalyst) | Yield (%, **2a** as catalyst) |
|---|---|---|
| Round 1 | 99.9 | 99.8 |
| Round 2 | 98.5 | 98.1 |
| Round 3 | 97.8 | 98.3 |
| Round 4 | 97.3 | 97.6 |
| Round 5 | 96.7 | 97.3 |

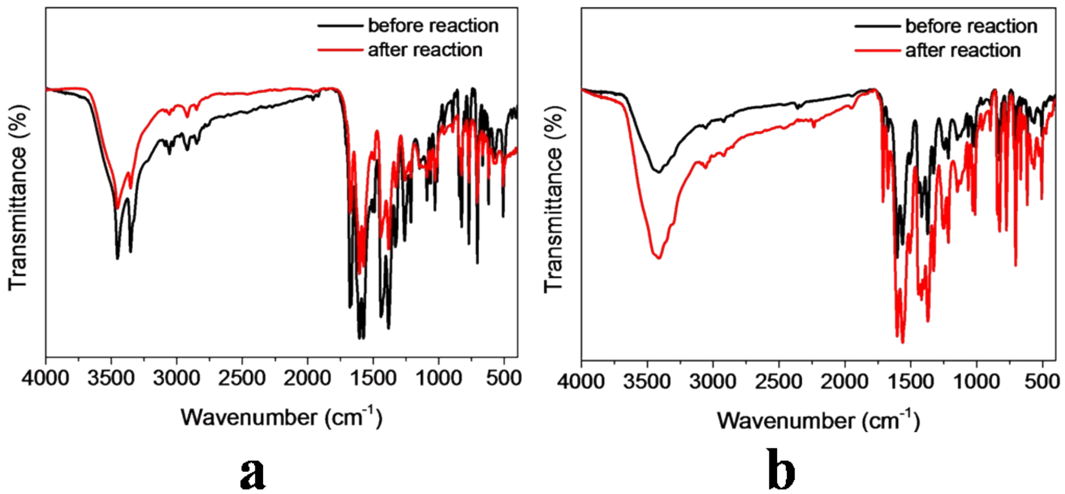



**Figure S12.** (a) IR spectra of **1a** before and after five round catalytic experiments. (b) IR spectra of **2a** before and after five round catalytic experiments.

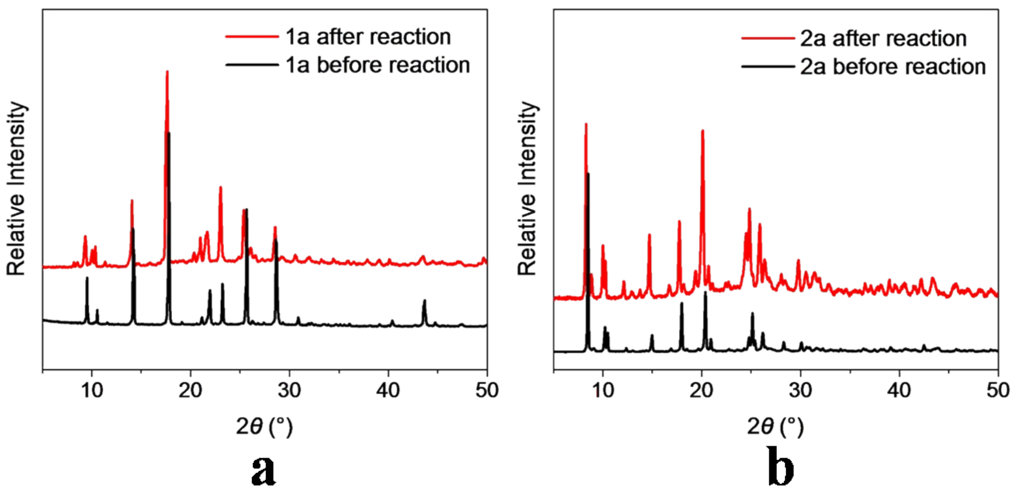



**Figure S13.** (a) PXRD patterns of **1a** before and after five round catalytic experiments. (b) PXRD patterns of **2a** before and after five round catalytic experiments.

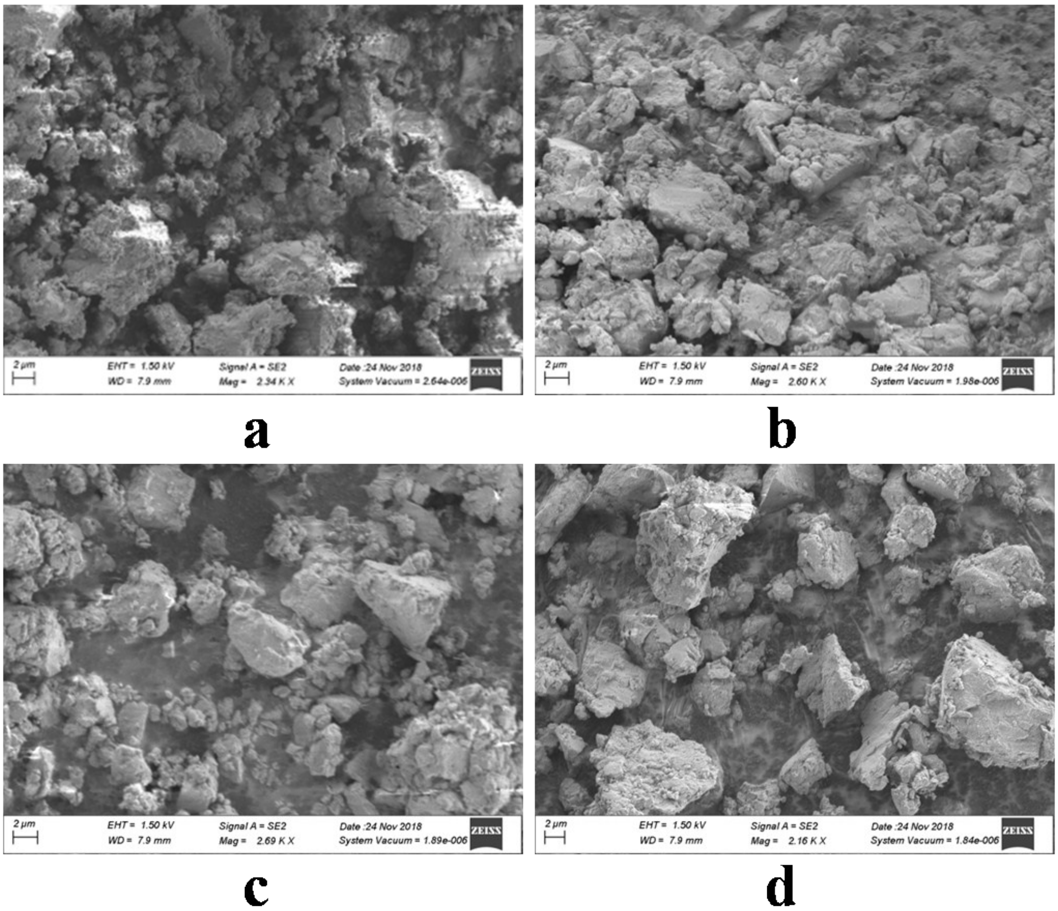



**Figure S14.** (a) SEM images of **1a** before catalytic experiment. (b) SEM images of **1a** after five round catalytic experiments. (c) SEM images of **2a** before catalytic experiment. (d) SEM images of **2a** after five round catalytic experiments.