Supporting Information

An Efficient Modulated Synthesis of Zirconium Metal-Organic Framework UiO-66

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1. Synthesis

The amount of each reagent added to the 28 different syntheses is summarized in Table S1, where the quantities are provided in terms of their molar ratio with ZrCl₄ and by the actual mass or volume added. And the masses of products are also listed in Table S1.

Table S1 Molar ratio and masses or volume of the various reagents and mass of UiO-66 products.

| Sample designation | Molar equivalents / Masses (g) or volume (mL) | Mass of products/g |
|--------------------|---------------------------------------------|-------------------|
|                    | ZrCl₄/g H₂BDC DMF Haloid acid               |                   |
| UiO-66-free        | 1 / 0.9325 1 / 0.6602 64.6 / 20.0 0        | 0.29              |
| UiO-66-1HBr        | 1 / 0.9325 1 / 0.6602 “ 1 / 0.215          | 1.53              |
| UiO-66-2 HBr       | 1 / 0.9325 1 / 0.6602 “ 2 / 0.430          | 1.52              |
| UiO-66-3 HBr       | 1 / 0.9325 1 / 0.6602 “ 3 / 0.645          | 1.55              |
| UiO-66-4 HBr       | 1 / 0.9229 1 / 0.6603 “ 4 / 0.865          | 1.77              |
| UiO-66-5 HBr       | 1 / 0.9229 1 / 0.6603 “ 5 / 1.080          | 1.50              |
| UiO-66-6 HBr       | 1 / 0.9229 1 / 0.6603 “ 6 / 1.300          | 1.49              |
| UiO-66-7 HBr       | 1 / 0.9229 1 / 0.6603 “ 7 / 1.520          | 1.44              |
| UiO-66-8 HBr       | 1 / 0.9229 1 / 0.6603 “ 8 / 1.735          | 1.35              |
| UiO-66-9 HBr       | 1 / 0.9229 1 / 0.6603 “ 9 / 1.950          | 1.27              |
| UiO-66-1HF         | 1 / 0.9328 1 / 0.6615 “ 1 / 0.070          | 0.64              |
| UiO-66-2 HF        | 1 / 0.9330 1 / 0.6614 “ 2 / 0.140          | 0.63              |
| UiO-66-3 HF        | 1 / 0.9330 1 / 0.6614 “ 3 / 0.210          | 0.57              |
| UiO-66-4 HF        | 1 / 0.9330 1 / 0.6640 “ 4 / 0.275          | 0.55              |
| UiO-66-5 HF        | 1 / 0.9330 1 / 0.6640 “ 5 / 0.345          | 0.48              |
2. Characterization

2.1. X-ray Diffraction Profiles Analysis

The crystalline structure of UiO-66 was analyzed by X-ray diffraction (XRD, D8-ADVANCED, Bruker) using Cu-Kα radiation in the range of 2θ = 3-50° at the step of 0.2° s⁻¹. The relatively intensity of the broad peak was calculated as the following Eq. and the relevant data were listed in Table S2. Table S3 showed the crystallite size derived from (111) reflection (FWHM the reflection) according to Schaler's formula.

\[ \text{Rel}(I)_\text{BP} = \frac{I_{\text{BP}}}{I(111) + I(200) + I(600)} \times 100 \]

Table S2 Intensity of three most intense reflections and relatively intensity of the broad peaks of UiO-66 samples obtained with different amounts of haloid acid additive.

| Sample designation | Intensity of the most intense reflections\(^a\) | Rel(I)\(_{\text{BP}}\), % |
|--------------------|-----------------------------------------------|------------------------|
|                    | 2-7° (111)7.3° (200)8.5° 25.8°                  |                        |
| UiO-66-free        | 1318  8054  2565  3347                      | 28.31                  |
| UiO-66-1HBr        | 1197  7937  2058  2733                      | 28.21                  |
| UiO-66-2 HBr       | 1804  8462  1852  2403                      | 42.56                  |
| UiO-66-3 HBr       | 1597  10829 2105  1082                     | 34.18                  |
| UiO-66-4 HBr       | 18    4342  939   270                      | 0.97                   |
| UiO-66-5 HBr       | 1203  8333  1513  1011                     | 33.24                  |
Table S3 Crystallite size of UiO-66 samples synthesized with different amount of modulator.

| Sample designation | 20θ  | FWHM (111) | D/nm | λ   |
|--------------------|------|------------|------|-----|
| UiO-66-free        |      |            |      |     |
| UiO-66-1 HBr       | 7.360| 0.198      | 39.8 |     |
| UiO-66-2 HBr       | 7.379| 0.252      | 31.3 |     |
| UiO-66-3 HBr       | 7.400| 0.287      | 27.4 |     |
| UiO-66-4 HBr       | 7.422| 0.270      | 29.2 |     |
| UiO-66-5 HBr       | 7.359| 0.235      | 33.5 |     |
| UiO-66-6 HBr       | 7.420| 0.257      | 30.6 | 0.154056 |
| UiO-66-7 HBr       | 7.419| 0.274      | 28.7 |     |
| UiO-66-8 HBr       | 7.420| 0.282      | 27.9 |     |
| UiO-66-9 HBr       | 7.480| 0.243      | 32.4 |     |
| UiO-66-2 HF        | 7.418| 0.238      | 33.1 |     |
| UiO-66-2 HCl       | 7.441| 0.325      | 24.2 |     |

2.2. TGA Calculations

Table S4 Missing-linker deficiency of obtained samples synthesized with haloid acid additive.

| Sample designation | TGA |          | BDC | Missing linkers, % |
|--------------------|-----|----------|-----|-------------------|
|                    | Theoretical value, % | Experimental value, % |     |                   |
| UiO-66-free        | 195.78 | 4.8       | 20.32 |
| UiO-66-1 HBr       | 188.02 | 4.4       | 26.78 |
| UiO-66-2 HBr       | 197.95 | 4.9       | 18.51 |
| UiO-66-3 HBr       | 220.25 | 4.8       | 19.91 |
| UiO-66-4 HBr       | 195.22 | 4.8       | 20.78 |
| UiO-66-5 HBr       | 191.5  | 4.6       | 23.88 |
| UiO-66-6 HBr       | 191.82 | 4.6       | 23.61 |
2.3. Nitrogen Adsorption

$\text{N}_2$ adsorption and desorption isotherms of UiO-66 were recorded at 77 K using an ASAP 2460 analyzer (Micromeritics). 200–250 mg of one sample was outgassed at 120 ºC for 12 h in vacuo prior to the measurement. The total surface area and the mesoporous surface area were respectively calculated from the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. The microporous surface area was obtained by subtracting the mesoporous surface from the total surface area.

The micropore size distribution was calculated using the NLDFT method.

| Sample designation | SSA(BET), $\text{m}^2/\text{g}$ | Microporous area, $\text{m}^2/\text{g}$ | Micropore volume, $\text{cm}^3/\text{g}$ | Total pore volume, $\text{cm}^3/\text{g}$ |
|--------------------|----------------------------------|----------------------------------------|------------------------------------------|------------------------------------------|
| UiO-66-free        | 325                              | 331                                    | 0.132                                    | 0.377                                    |
| UiO-66-1HBr        | 1527                             | 1397                                   | 0.537                                    | 0.632                                    |
| UiO-66-2HBr        | 1451                             | 1273                                   | 0.516                                    | 0.639                                    |
| UiO-66-3HBr        | 1401                             | 1184                                   | 0.512                                    | 0.672                                    |
| UiO-66-4HBr        | 1411                             | 1227                                   | 0.453                                    | 0.580                                    |
| UiO-66-5HBr        | 1309                             | 1127                                   | 0.427                                    | 0.553                                    |
| UiO-66-6HBr        | 1249                             | 1065                                   | 0.412                                    | 0.540                                    |
| UiO-66-7HBr        | 1216                             | 1030                                   | 0.393                                    | 0.538                                    |
| UiO-66-8HBr        | 1088                             | 887                                    | 0.384                                    | 0.543                                    |
| UiO-66-9HBr        | 1134                             | 935                                    | 0.371                                    | 0.535                                    |
| UiO-66-2HF         | 1442                             | 1355                                   | 0.501                                    | 0.561                                    |
| UiO-66-2HCl        | 1630                             | 1486                                   | 0.532                                    | 0.636                                    |