Supporting Information

Removal of diclofenac by adsorption process studied in free-base porphyrins Zr-metal organic frameworks (Zr-MOFs)

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A comparison of the NU-902 PXRD pattern when synthesized using 4-methoxybenzoic acid and benzoic acid as the modulator is given in ***Figure S 1***. As can be seen, the PXRD pattern of the NU-902 that was synthesized using benzoic acid as the modulator shows a mixed phase between NU-902 and MOF-525. Therefore, we chose to synthesize NU-902 by employing 4-methoxybenzoic acid as the modulator.

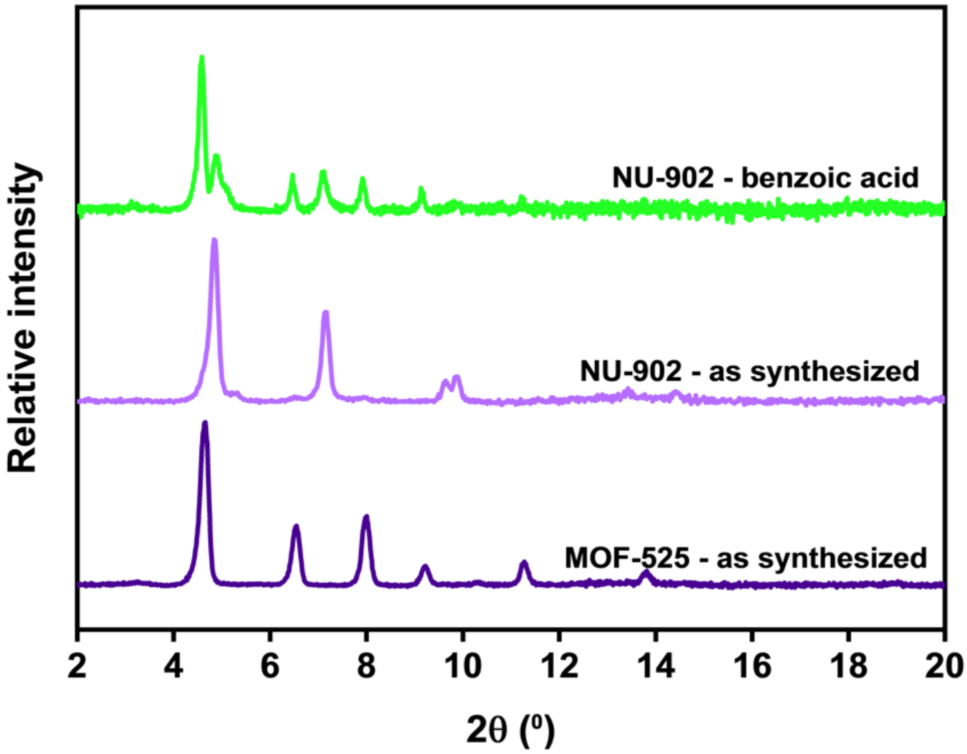

Figure S 1. The PXRD pattern of MOF-525 and NU-902 synthesized using 4-methoxybenzoic acid and benzoic acid as the modulator

The SEM micrograph of all the base-free porphyrin Zr-MOFs is given in ***Figure S 2***.

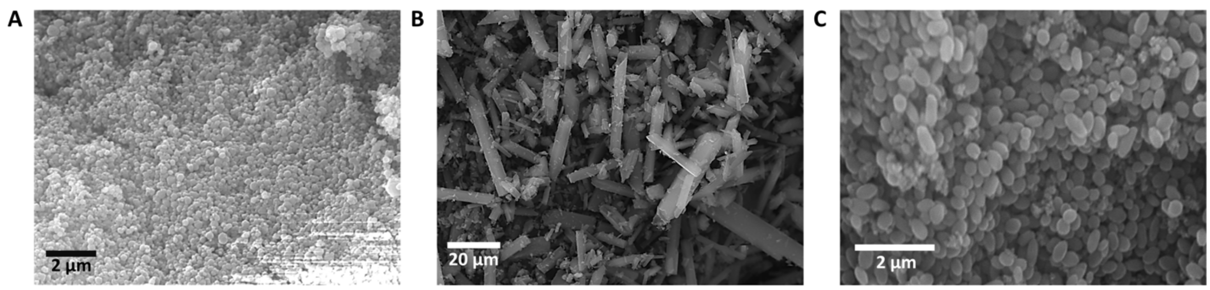

Figure S 2. SEM micrograph of MOF-525 (A), MOF-545 (B) and NU-902 (C)

The non-linear form of the pseudo first order and pseudo second order kinetic of adsorption is given below

$$q_t = q_{eq}(1 - e^{-k_1 t})$$

$$q_t = \frac{k_2 q_{eq}^2 t}{1 + k_2 q_{eq} t}$$

The analysis for the adsorption kinetic is based on the four different equations to assess whether the adsorption kinetic is limited by the film diffusion or the intraparticle diffusion. To assess the adsorption kinetic that is limited by film-diffusion, the first equation is used based on Yao and Chen [1].

$$At = -\left(1 - \frac{q_{eq}}{q_{max}}\right)\ln\left(1 - \frac{q_t}{q_{eq}}\right) - \left(\frac{VC_0}{mq_{eq}} - 1\right)\ln\left(1 - \frac{mq_{eq}\ q_t}{VC_0\ q_{max}}\right)$$

The At value is then plotted against t and when a linear plot through the origin is obtained, it can be concluded that the adsorption kinetic is limited by the film-diffusion process.

The second evaluation when the adsorption process is limited by film diffusion process is based on the Boyd model [2] and is given based on the equation below

$$ln(1 - \frac{q_t}{q_{eq}}) = -k_B t$$

Meanwhile, both the intraparticle diffusion and Boyd model are used to evaluate whether the kinetic of the adsorption process is limited by the intraparticle diffusion process. The equation for the intraparticle diffusion model, which is based on Weber and Morris study [1,3], is given below

$$q_t = k_p t^{0.5} + c$$

For the Boyd model [2], where the adsorption process is limited by intraparticle diffusion process, the equations are given below and the plot is obtained by plotting B_t value against time.

$$F = 1 - \frac{6}{\pi^2} - \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 B_t\right)$$

$$B_t = -ln\frac{\pi^2}{6} - \ln\left(1 - F(t)\right),\ F(t) > 0.85$$

$$B_t = \left(\sqrt{\pi} - \sqrt{\pi - \frac{\pi^2 F(t)}{3}}\right)^2,\ F(t) \le 0.85$$

The equation for Langmuir, Freundlich and Sips adsorption isotherm is given below.

$$q_{eq} = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}}$$

$$q_{eq} = K_F C_{eq}^{1/n})$$

$$q_{eq} = \frac{q_{max}(K_{Sips} C_{eq})^n}{1 + (K_{Sips} C_{eq})^n}$$

The adsorption thermodynamics is evaluated by firstly calculating the distribution coefficient of the diclofenac in the adsorbed and bulk phase as given in the equation below.

$$K_d = \frac{q_{eq}}{C_{eq}}$$

The value of ΔH and ΔS can then be obtained by applying the below equation after plotting the K_d against 1/T

$$lnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

Meanwhile, to obtain the Δ*G* value at each temperature, the below equation is used.

$$\Delta G = \Delta H - T\Delta S$$

The recyclability of the samples was also evaluated for 4 adsorption cycles and the results are presented in ***Figure S 3***.

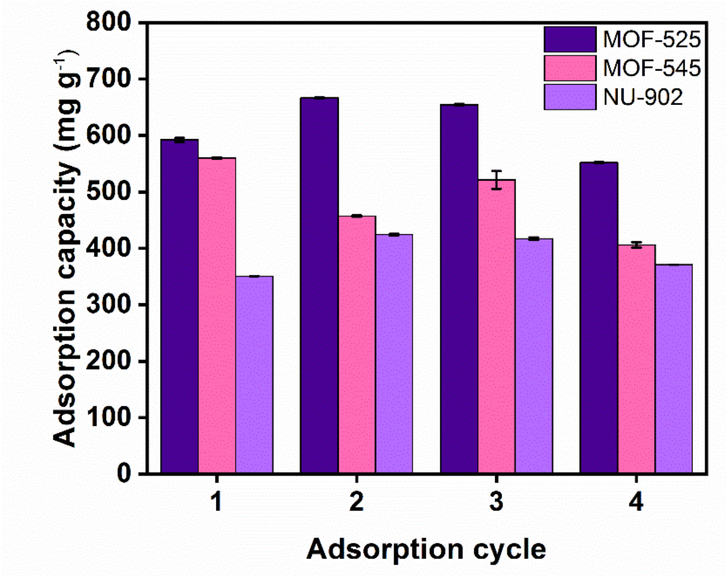

Figure S 3. Diclofenac adsorption capacity of MOF-525, MOF-545 and NU-902 during the recyclability test

References

[1] C. Yao, T. Chen, A new simplified method for estimating film mass transfer and surface diffusion coefficients from batch adsorption kinetic data, Chem. Eng. J. 265 (2015) 93–99.

[2] G. Boyd, A.W. Adamson, L. Myers Jr, The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics1, J. Am. Chem. Soc. 69 (1947) 2836–2848.

[3] W.J. Weber Jr, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. 89 (1963) 31–59.