

Converting metal-organic framework particles from hydrophilic to hydrophobic by an interfacial assembling route

Fanyu Zhang,^{1,2} Xinxin Sang,^{1,2} Xiuniang Tan,^{1,2} Chengcheng Liu,^{1,2} Jianling

Zhang,^{*1,2} Tian Luo,¹ Lifei Liu,^{1,2} Buxing Han,^{1,2} Guanying Yang¹ and

Bernard P. Binks^{*3}

¹Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P.R. China

²School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, P.R. China

³School of Mathematics and Physical Sciences, University of Hull, Hull HU6 7RX, UK

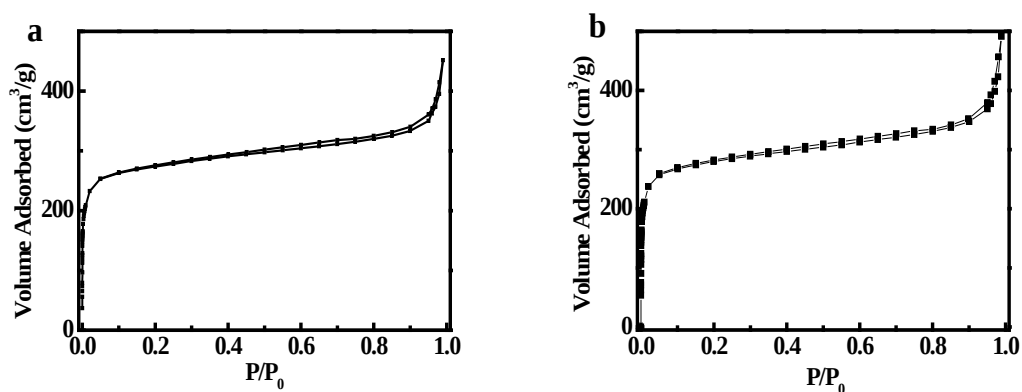


Figure S1. N₂ adsorption-desorption isotherms of (a) pristine UiO-66-NH₂ particles and (b) modified UiO-66-NH₂ particles from an emulsion with particle concentration of 1.58 mg mL⁻¹. The BET surface area and the total pore volume of pristine and modified UiO-66-NH₂ are 1079 m² g⁻¹ and 0.7006 cm³ g⁻¹ and 1098 m² g⁻¹ and 0.7628 cm³ g⁻¹, respectively.

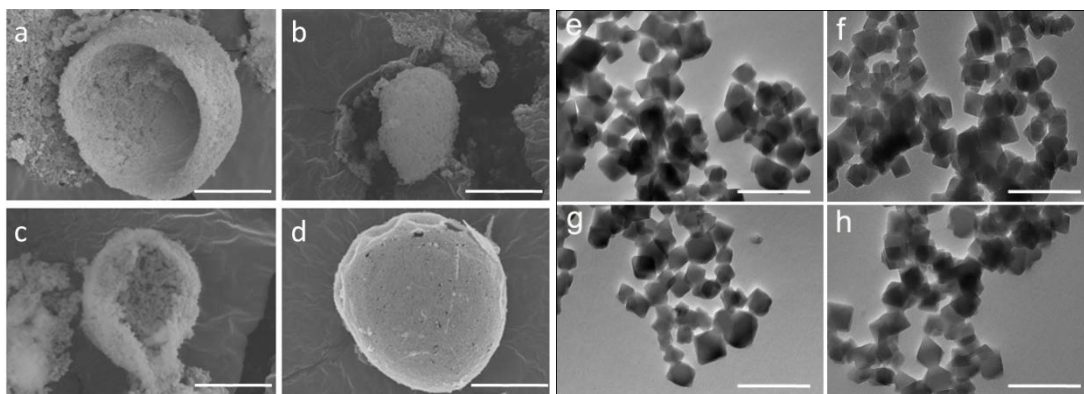


Figure S2. SEM (a-d) and TEM images (e-h) of modified UiO-66-NH₂ nanocrystals obtained from emulsions at particle concentrations (mg mL⁻¹) of (a, e) 14.29, (b, f) 7.27, (c, g) 4.69 and (d, h) 1.94. Scale bars: 10 μ m in a, 3 μ m in b and c, 8 μ m in d, 200 nm in e-h.

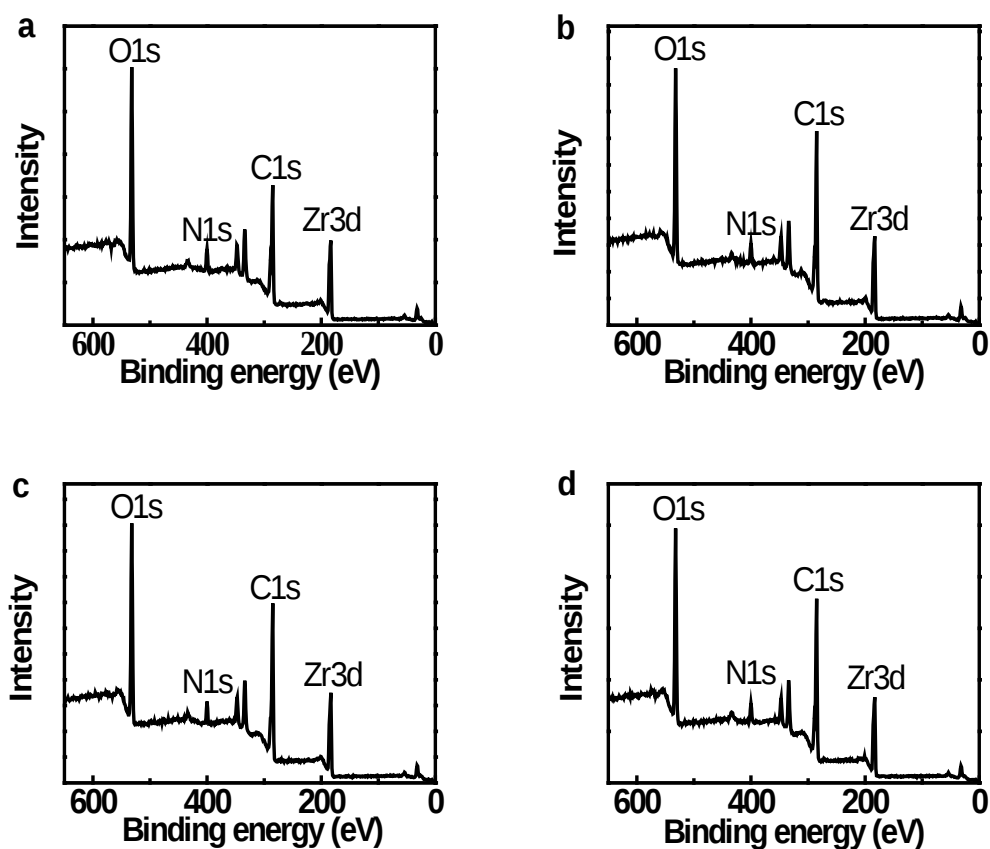


Figure S3. Wide-range XPS spectra of (a) pristine UiO-66-NH₂ nanocrystals and modified UiO-66-NH₂ nanocrystals obtained from emulsions at particle concentrations (mg mL⁻¹) of (b) 14.29, (c) 7.27 and (d) 4.69.

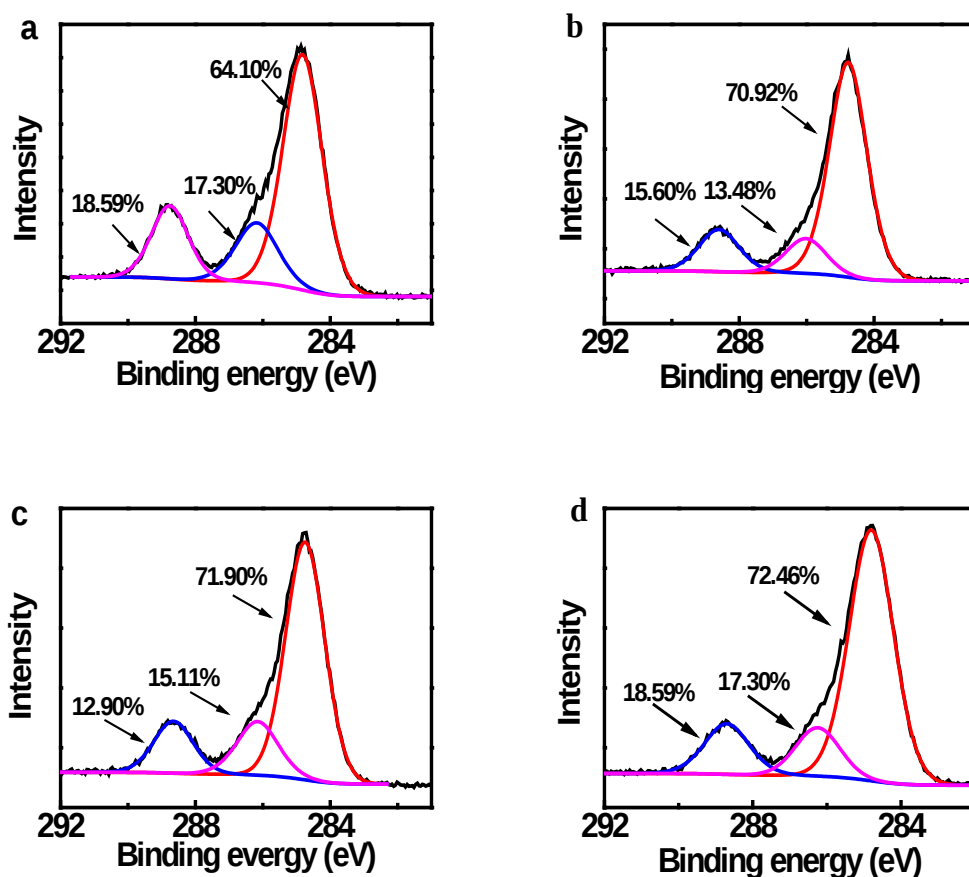
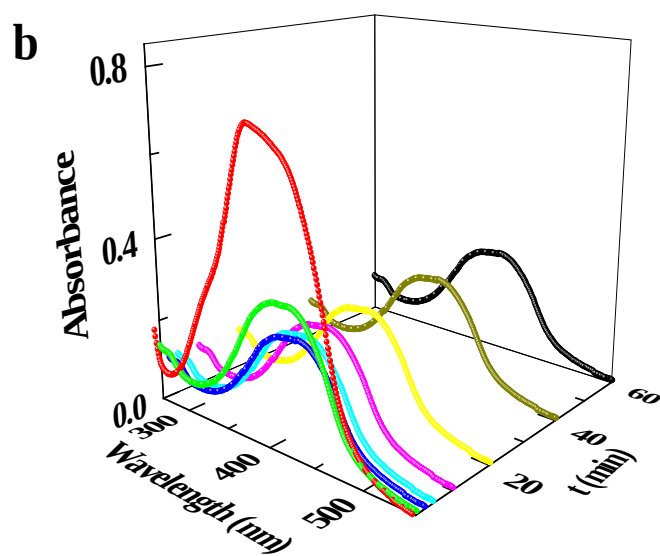
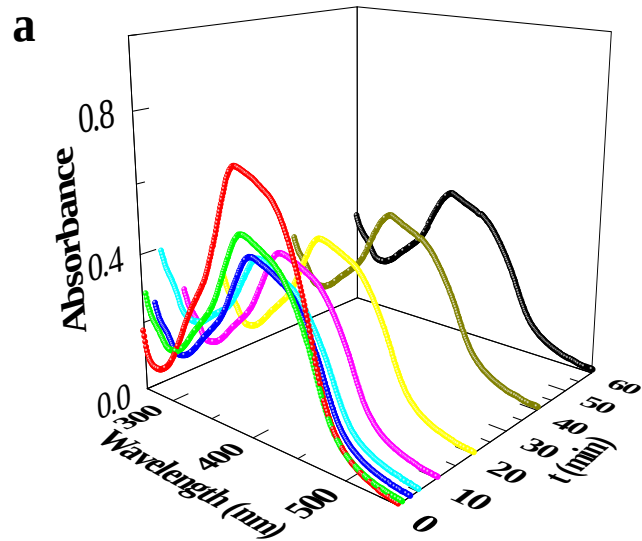


Figure S4. C1s XPS spectra of (a) pristine UiO-66-NH₂ nanocrystals and modified UiO-66-NH₂ nanocrystals obtained from emulsions at particle concentrations (mg mL⁻¹) of (b) 14.29, (c) 7.27 and (d) 4.69. The labels (%) refer to the three types of carbon bond: C-C or C=C (284.8 eV), C-O or C-N (286.3 eV) and COOH (288.7 eV).



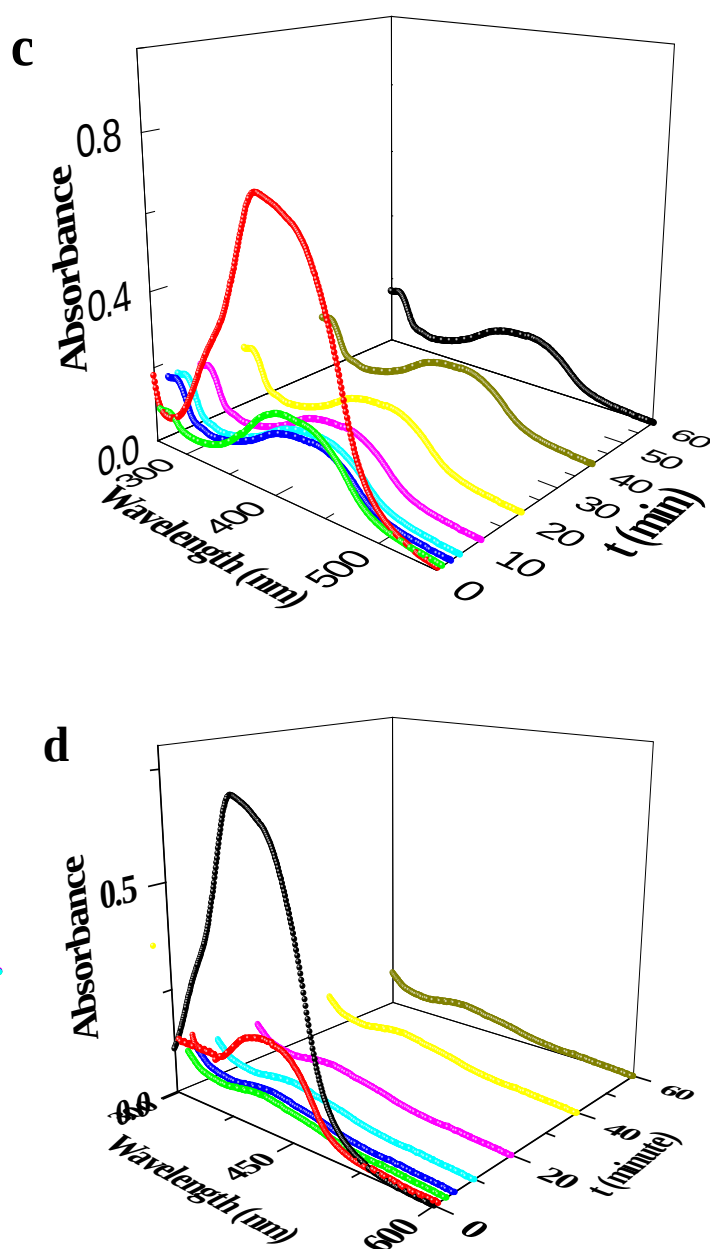


Figure S5. UV-Vis spectra of solutions of 4.6×10^{-5} mol L⁻¹ Sudan Orange G in hexane containing (a) pristine UiO-66-NH₂ particles and modified UiO-66-NH₂ particles obtained from emulsions at particle concentrations (mg mL⁻¹) of (b) 14.29, (c) 4.69 and (d) 1.58 at different times. The particle concentration in hexane was 2 mg mL⁻¹.

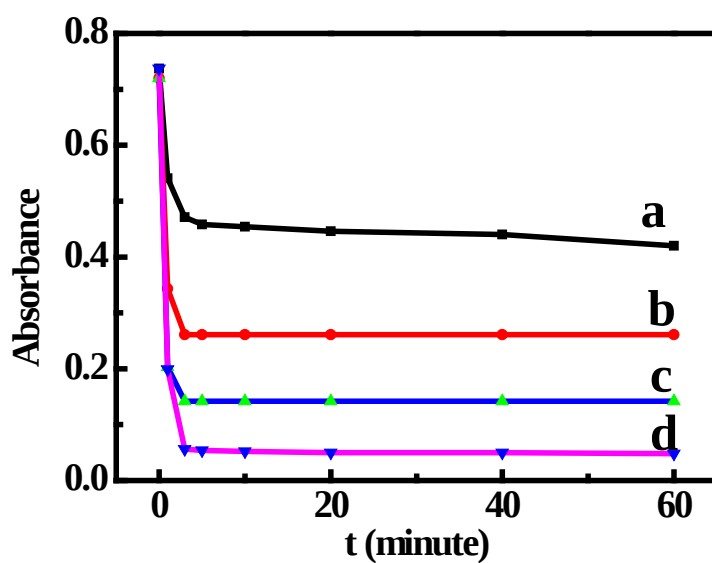


Figure S6. Dependence of the absorbance of Sudan Orange G in hexane ($4.6 \times 10^{-5} \text{ mol L}^{-1}$) with time in the presence of (a) pristine UiO-66-NH₂ particles and modified UiO-66-NH₂ particles obtained from emulsions at particle concentrations (mg mL^{-1}) of (b) 14.29, (c) 4.69 and (d) 1.58.

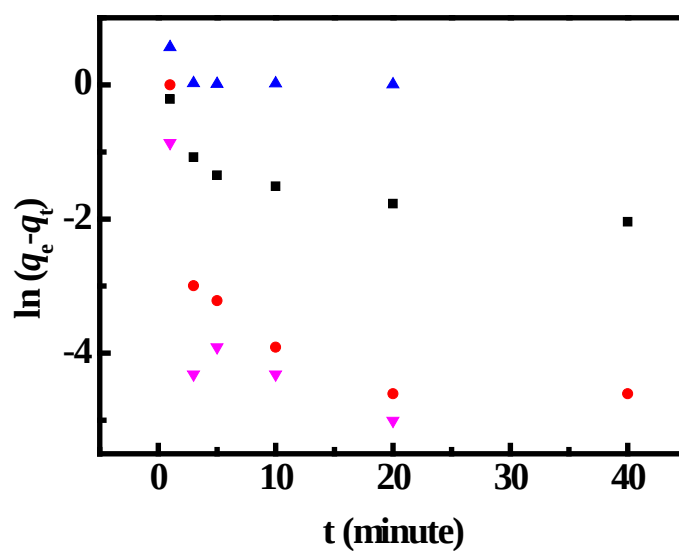


Figure S7. Pseudo-first order kinetic plot for Sudan Orange G adsorption on (red) pristine UiO-66-NH₂ particles and modified UiO-66-NH₂ particles obtained from emulsions at particle concentrations (mg mL⁻¹) of (pink) 14.29, (blue) 4.69 and (black) 1.58. The poor linearity proves that the adsorption doesn't follow pseudo-first order kinetics.

Table S1. Parameters relating to the adsorption of Sudan Orange G on pristine UiO-66-NH₂ and modified UiO-66-NH₂ nanocrystals.

Adsorbent	$q_{e,exp}^{[c]}$ (mg g ⁻¹)	k_1 (min ⁻¹) or k_2 (g mg ⁻¹ min ⁻¹) ^[d]	$q_{e,cal}^{[e]}$ (mg g ⁻¹)	R^2 ^[f] (%)
UiO-66-NH ₂	2.12 ^[a]	3.43×10^{-2}	2.40	62.7
M-UiO-66-NH ₂ ^[g]	3.07 ^[a]	7.85×10^{-2}	1.29	27.1
M-UiO-66-NH ₂ ^[h]	3.87 ^[a]	0.0167	13.02	44.9
M-UiO-66-NH ₂ ^[i]	4.60 ^[a]	0.1432	8.93	45.7
UiO-66-NH ₂	2.12 ^[b]	0.48	2.11	99.8
M-UiO-66-NH ₂ ^[g]	3.07 ^[b]	4.78	3.08	100.0
M-UiO-66-NH ₂ ^[h]	3.87 ^[b]	4.30	3.88	100.0
M-UiO-66-NH ₂ ^[i]	4.60 ^[b]	1.98	4.61	100.0

^[a] Calculated using pseudo-first order model. ^[b] Calculated using pseudo-second order model. ^[c] The amount of dye adsorbed on the adsorbent (mg g⁻¹) at equilibrium. ^[d] k_1 is the first order rate constant, k_2 is the second order rate constant. ^{[e],[f]} Calculated from linear plot of $\ln(q_e - q_t)$ vs t for the pseudo-first order model and linear plot of t/q_t vs t for the pseudo-second order model. ^{[g],[h],[i]} Modified UiO-66-NH₂ particles obtained from emulsions at particle concentrations of 14.29, 4.69 and 1.58 mg mL⁻¹, respectively.