Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Continuous-flow Synthesis of MIL-53(Cr) with Polar Linker: Probing Nanoscale Piezoelectric Effect

*Feifei Xue[a], Jian Cao[b], Xiaoting Li[a], Jingjing Feng[a], Minli Tao[*a] and Bin Xue[*c]*

[a] Department of Chemistry, School of Science, Tianjin University, No.135 Yaguan Road, Haihe Education Park, Tianjin, 300350, P. R. China.

[b]Department of Chemistry and Material Science, Langfang Normal University, Langfang 065000, Hebei, P.R. China

[c]Department of Marine Technology, School of Marine Science and Technology, Tianjin University, No.92 Weijin Road, Tianjin, 300072, P. R. China.

*Corresponding author: Minli Tao

Department of Chemistry, School of Science, Tianjin University, No.135 Yaguan Road, Haihe Education Park, Tianjin, 300350, P. R. China.

E-mail: mltao@tju.edu.cn

*Corresponding author: Bin Xue

Department of Marine Technology, School of Marine Science and Technology, Tianjin University, No.92 Weijin Road, Tianjin, 300072, P. R. China.

E-mail: xuebin@tju.edu.cn

General experimental information

Materials. Commercially available chemical reactants were purchased from J&K Chemicals, Bidepharm, and Solarbio, and used without any further purification. All reagents were analytical grade.

Characterization and measurements.

The shapes and surface morphologies of the samples were observed with a Hitachi-S-4800 scanning electron microscope. FTIR spectrometer (AVATAR 360 Thermo Nicolet) was employed using pressed KBr discs. D/MAX-2500 X-ray diffract meter was performed to determine the crystallinity of the original and modified samples. Dynamic light scattering (DLS) was used to characterize the stability of the solution and aggregation of the nanoparticles (0.25 mg/mL, methanol). The zeta potential analyzer apparatus (Malvern instruments Co., Nano-ZS90) was used to measure for potentials of the nanoparticles in ultrapure water.

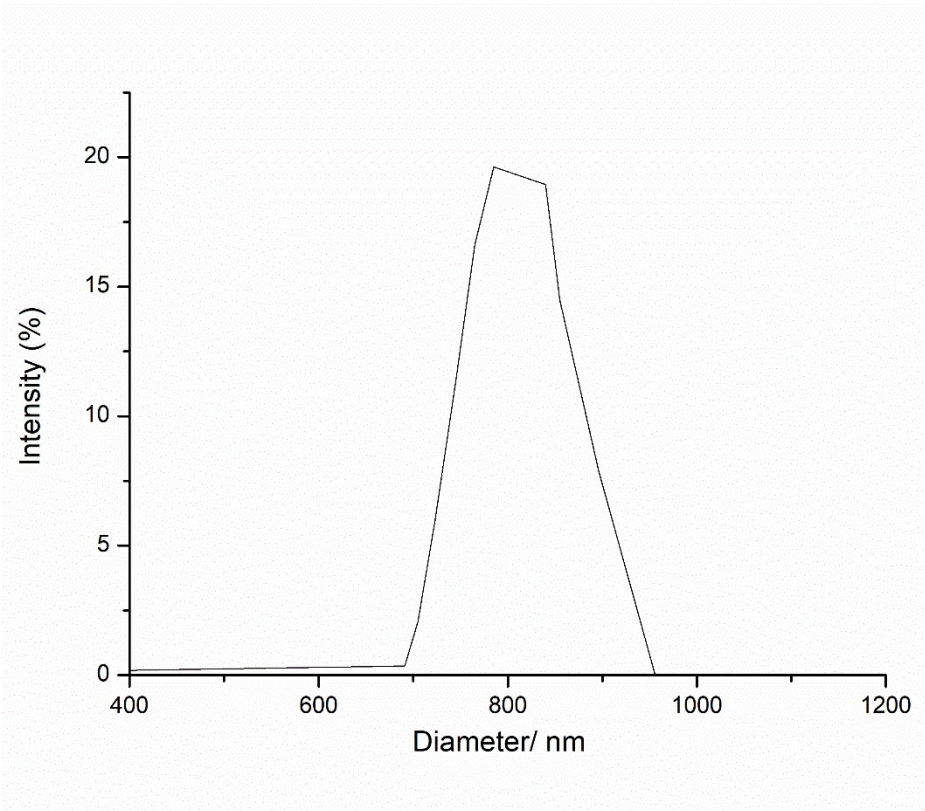

Figure S1 Dynamic light scattering measurements of MOF samples in water.

Table S1 The surface area and porosity of MOFs.

	S_{BET}(m^2 g^{-1})	V_{Tot}(cm^3 g^{-1})
MIL-53(Cr)-F (Batch method)	625	0.84
MIL-53(Cr)-F (Flow method)	615	0.82
MIL-53(Cr)-F (Flow method with high flow rate)	285	0.56

Evaluation of crystallinity by full width half maximum

The crystallinity is the degree of structural order in the product. Crystallinity depends on several factors, the most relevant commonly considered are the crystallite size and

lattice defects. Both features contribute to the broadening of the peaks in the diffraction pattern, although with a different dependence on the diffraction angle θ. However, for a series of isostructural samples, their relative crystallinity can be evaluated by means of the full width half maximum (FWHM) of a selected peak. The (020) reflection, located at 9.2° 2θ, was chosen because it has appreciable intensity and is not affected by overlapping with other reflections. The use of the same instrument for collecting the PXRD patterns of all the samples ensures that the instrumental contribution to the broadening is constant and therefore non influent. In this discussion the indicator (1/ FWHM) is used for comparing relative crystallinity of the samples. Full width at half maximum (FWHM) of the (020) reflection was estimated with the aid of the *PHILIPS PROFIT* software.

Response surface method

Design-Expert software version 6 (Stat-Ease, Inc., USA) and SAS software version 9.1 (SAS Institute) were used for analysis and optimization from Table S5, three levels of Box-Behnken experimental design (1, 0, -1) were performed with a total of 17 experiments and five replications at the central point to estimate pure error. Flow rate (A: 0.5, 1.0, 2.5), concentration (B: 0.04, 0.08, 0.12), and reaction temperature (C:130, 150, 180), were the key independent variables, whereas 1/FWHM was the response variable.

Table S2 Box-Behnken design matrix with experimental responses.

Std	Run	Factor1 A	Factor2 B:	Factor3 C:	Response 1/FWHM
8	1	1.000	0.000	1.000	4.87
15	2	0.000	0.000	0.000	7.86
2	3	1.000	-1.000	0.000	7.02
17	4	0.000	0.000	0.000	7.8
10	5	0.000	1.000	-1.000	2.98
6	6	1.000	0.000	-1.000	3.68
16	7	0.000	0.000	0.000	7.68
7	8	-1.000	0.000	1.000	6.21
3	9	-1.000	1.000	0.000	7.9
5	10	-1.000	0.000	-1.000	4.1
13	11	0.000	0.000	0.000	7.78
12	12	0.000	1.000	1.000	4.93
9	13	0.000	-1.000	-1.000	7.4
11	14	0.000	-1.000	1.000	6.19
1	15	-1.000	-1.000	0.000	5.31
14	16	0.000	0.000	0.000	7.85
4	17	1.000	1.000	0.000	6.16

Table S3 Analysis of variance table

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob >F
Model	34.95	9	3.88	3.37	<0.0001 significant
A-A	0.40	1	0.40	0.35	0.5743
B-B	1.95	1	1.95	1.69	0.2348
C-C	2.04	1	2.04	1.77	0.2253
AB	2.98	1	2.98	2.58	0.1523
AC	0.21	1	0.21	0.18	0.6814
BC	2.50	1	2.50	2.16	0.1848
A^2	3.63	1	3.63	3.14	0.1195
B^2	0.30	1	0.30	0.26	0.6241
C^2	19.48	1	19.48	16.88	0.0045
Residual	8.08	7	1.15		
Lack of Fit	8.06	3	2.69	518.46	<0.0001 significant
Pure Error	0.021	4	5.180E-003		
Cor Total	43.03	16			

Dual AC Resonance Tracking Piezoresponse Force Microscopy (DART-PFM)

PFM is the most widely used scanning probe microscopy (SPM) method for imaging piezoelectric materials and ferroelectrics. This technique is based on monitoring surface displacement of the piezoelectric materials induced by electric bias[1]. A functional generator is used to apply an AC voltage between the tip and the sample surface. The voltage induced deflection of probe cantilever is detected by a reflected laser beam on a four-quadrant photodiode. DART-PFM technique can reduce the crosstalk with topography due to the shift in the resonant frequency, and using a feedback loop to adjust the drive frequency of the cantilever to match the resonance frequency. Rather than using the phase (ϕ) information as the input to the frequency ϕ feedback, DART-PFM uses the difference between the two amplitudes as the input feedback. Fig. S2 shows the schematic of the two frequencies, and the resulting amplitudes (A_1 and A_2) when the resonant frequency changes. For example, if the frequency shifts downward, A_1 moves to A_3 and A_2 moves to A_4. The change in the $A_2 - A_1$ signal causes the feedback loop to respond by changing the drive frequency until the $A_2 - A_1$ signal is zero again.

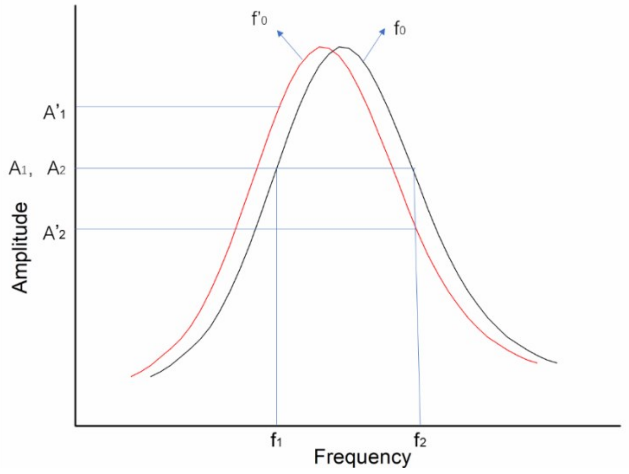

Figure S2 Principle of DART-PFM method.

Piezoresponse Force Spectroscopy (PFS)

PFS is the technique to acquire the local ferroelectric hysteresis loop from the sample surface. In this technique, the optimal signal-to-noise ratio is achieved at frequencies near the contact resonances of the cantilever. The tip approaches the sample surface in the vertical direction with the deflection set point (trigger force) used as a feedback. When the set point is reached, a hysteresis loop is acquired by swept the bias.

During the PFS experiment, the tip is fixed at a given location on the sample surface and an electric wave is applied to the tip. The ac voltage V_{ac} is the PFM driving amplitude. The $V_{dc}(t)$ is comprised of a sequence of pulses with amplitude V_{i} and length τ_1 (high state/dc-on) separated by intervals of zero bias with the duration of τ_2 (low state/dc-off). The envelope for the voltage pulses is specified by a triangular wave having amplitude $Vmax$ and time periodic T. The waveform of PFS is shown in Fig. S3.

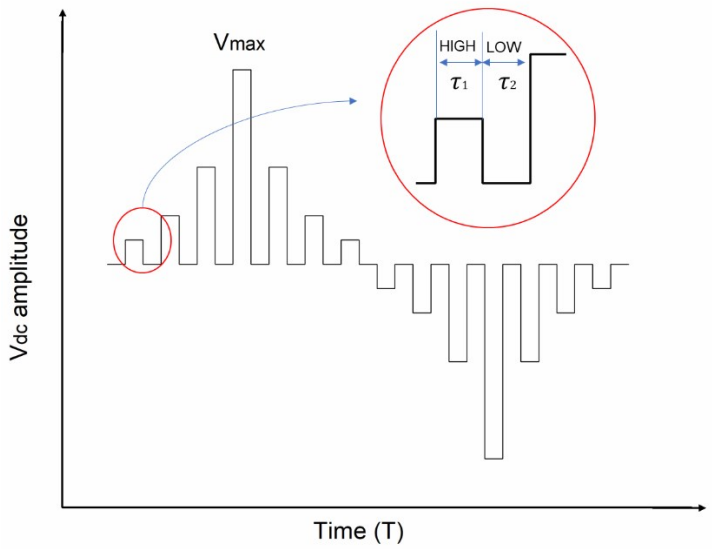

Figure S3 The switching and driving waveform of PFS

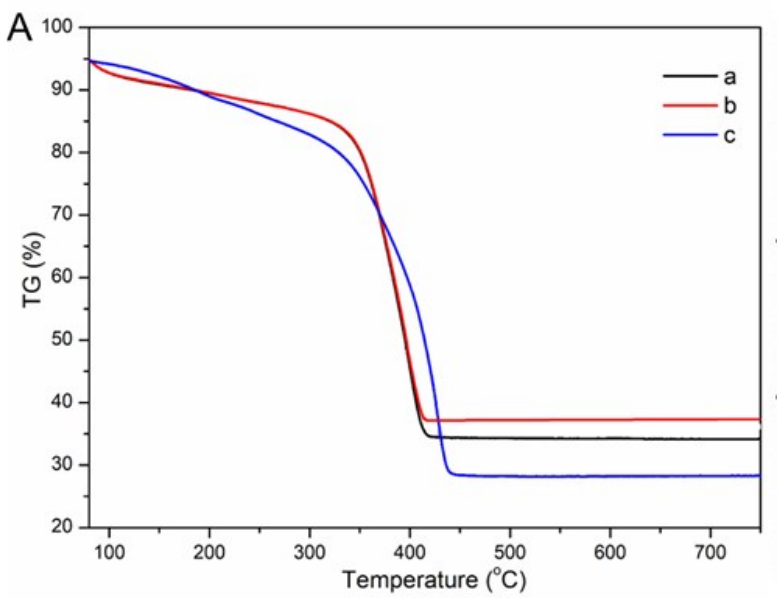

Figure S4. Thermogravimetric analyses (TGA) of (a) MIL-53(Cr)-F (Batch method); (b) MIL-53(Cr)-F (Flow method); and (c) MIL-53(Cr)-F (lp).

Table S4 Preparation of MIL series MOF by continuous-flow method.

MOF	Yield (%)	BET (m^2/g)	STY (kg m^{-3} d^{-1})	Ref
MIL-53(Al)	N/A	919	1300	[1]
MIL-53(Al)	65	1376	3618	[2]
MIL-100(Fe)	89.71	1981	771.6	[3]
MIL-100	78	1039	19.6*	[4]
MIL-53(Cr)-F	82	625	7188	This work

* spray drying for UiO-66

1. Gannepalli, A., et al., *Mapping nanoscale elasticity and dissipation using dual frequency contact resonance AFM.* Nanotechnology, 2011. **22**(35): 355705.
2. Bayliss, P.A., et al., *Synthesis of metal-organic frameworks by continuous flow.* Green Chemistry, 2014. **16**(8): 3796-3802.
3. Taddei, M., et al., *Continuous-Flow Microwave Synthesis of Metal–Organic Frameworks: A Highly Efficient Method for Large-Scale Production.* Chemistry – A European Journal, 2016. **22**(10): 3245-3249.
4. Van Nhieu, L., et al., *Microwave-assisted continuous flow synthesis of mesoporous metal-organic framework MIL-100 (Fe) and its application to Cu(I)-loaded adsorbent for CO/CO_2*

separation. Materials Chemistry and Physics, 2020: 253.

5. Garzon-Tovar, L., et al., *A spray-drying continuous-flow method for simultaneous synthesis and shaping of microspherical high nuclearity MOF beads.* Reaction Chemistry & Engineering, 2016. **1**(5): 533-539.