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Electronic Supplementary Information

Growth of high-quality covalent organic framework nanosheets at the interface of two miscible organic solvents

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1. Materials

1,3,5-Triformylphloroglucinol were prepared according to the published procedure.[1] Generally, 90 mL trifluoroacetic acid was added to hexamethylenetetraamine (15.098 g, 108 mmol) and dried phloroglucinol (6.014 g, 49 mmol) under N_2. The solution was heated at 100 ºC for ca. 2.5 h. Approximately 150 mL of 3 M HCl was added and the solution was heated at 100 ºC for 1 h. After cooling to room temperature, the solution was filtered through Celite, extracted with ca. 350 mL dichloromethane, dried over magnesium sulfate, and filtered. Rotary evaporation of the solution afforded ~ 1 g of an off-white powder. Dihydroxybenzidine, all metal salts and other reagents and solvents were commercially available and used as received.

2. Characterization Methods

FT-IR spectra (KBr pellet) of the samples were measured by a NEXUS 670 FT-IR spectrometer (USA) in the region of 400-4000 cm^{-1}. A Raman analyzer (Horiba/Jobin,Yvon, Longjumeau, France) was used to record the Raman spectra of the samples. Thermogravimetric analyses (TGA) were carried out on a DTG-60(H) analyzer (Shimadzu,Japan) under N_2 atmosphere at a heating rate of 10 ºC min^{-1} within a temperature range of 30-600 °C. Solid-state cross polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra were recorded on a Bruker Avance III 400 WB (400 MHz) NMR spectrometer using a standard cross-polarization pulse sequence. Element analysis (EA) was performed on a CARLO ERBA 1106 (Italy). XPS measurement was performed with a Kratos ASAM800 spectrometer (Kratos Analytical Limited, U.K.). Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance diffractometer using Cu Kα radiation at 40 kV, 40 mA power. SEM images were obtained with a JSM-7500F Scanning Electron Microscope with tungsten filament as electron source. The samples were sputtered with Au before tested. HR-TEM images were recorded using Tecnai G2 F20 S-TWIN TEM at an accelerating voltage of 300 kV. Atomic Force Microscopy (Innova) scans were collected at 512 points/lines under tapping mode in air. Fluorescence spectra were recorded at room temperature using a RF-5301PC fluorescence spectrophotometer. Stock solutions of $UO_2(NO_3)_2$ (2 mmol/L) was prepared in DMF, and dispersions of NS-COF was also prepared in DMF. The fluorescence spectra were recorded immediately after an appropriate aliquot of the stock solution of uranyl ions was added. Each test was repeated at least for three times to get concordant values. All the measurements, unless otherwise noted, were excited at λex = 360 nm and the corresponding emission wavelength was tested from λem = 420 to 740 nm. The concentrations of the all metal ions used in this work were analyzed by ICP-AES (PerkinElmer, USA) using the standard curve method.

3. Preparation of a Simulated Nuclear Industry Effluent Sample[2-3]

The simulated nuclear industry effluent samples containing 12 metal ions including uranyl, as listed in Table S1, was prepared according to the following procedures: 5 mmol of the desired metal oxides or nitrates was weighed, respectively, using an electronic balance (AL204, Mettler-Toledo, Switzerland) to the nearest 0.1 mg, and the weighed salts were dissolved in 2 mL of concentrated nitric acid, which was transferred to a 1000 mL volumetric flask, then diluted to volume with deionized water and mixed well to obtain the multiple ion stock solution. The preparation of the multi-ion working solutions were concocted by suitable dilution of the above stock solution with deionized water to the demanded concentrations. The pH of each test solution was regulated to the desired value with dilute and concentrated HNO_3 and NaOH solutions.[2]

Table S1. Compositions of the simulated nuclear industrial effluents.

Coexistent ion	Added as	Reagent purity
UO_2^{2+}	$UO_2(NO_3)_2 \cdot 6H_2O$	Standard reagent
La^{3+}	$La(NO_3)_3 \cdot 6H_2O$	99.9% metal basis
Ce^{3+}	$Ce(NO_3)_3 \cdot 6H_2O$	99.9% metal basis
Nd^{3+}	$Nd(NO_3)_3 \cdot 6H_2O$	AR
Sm^{3+}	$Sm(NO_3)_3 \cdot 6H_2O$	AR
Gd^{3+}	$Gd(NO_3)_3 \cdot 6H_2O$	AR
Mn^{2+}	MnO	99.5%

Co^{2+}	$Co(NO_3)_2 \cdot 6H_2O$	99.9% metal basis
Ni^{2+}	$Ni(NO_3)_2 \cdot 6H_2O$	Spectrum pure
Zn^{2+}	$Zn(NO_3)_2 \cdot 6H_2O$	99.9% metal basis
Sr^{2+}	$Sr(NO_3)_2$	99.9% metal basis
Ba^{2+}	$Ba(NO_3)_2$	99.999%

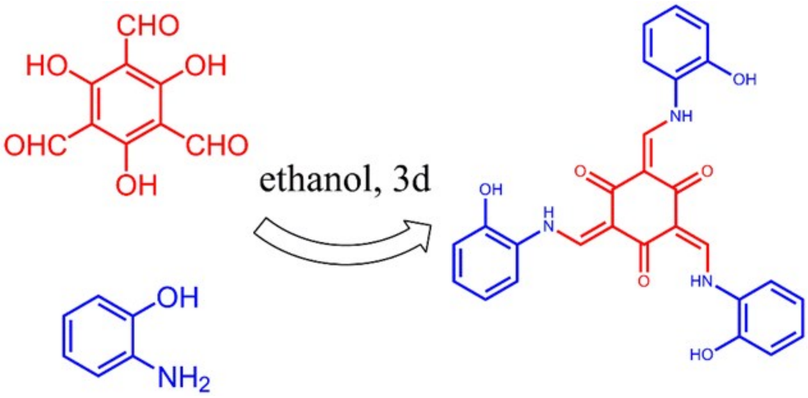
4. Synthetic Procedures for NS-COF Nanosheets and Reference Compound

NS-COF

Firstly, a certain amount of TFP was dissolved in 80 mL methylene chloride (1.325 g/mL at 25 °C) to give the aldehyde solution (A); then 20 mL of 12 M acetic acid solution (buffer C, 1.06 g/mL at 25 °C) was added slowly until the surface of A was completely covered. Amine solution (B) was prepared by dissolving a certain amount of DHBD in a mixed solution of 80 mL dichloromethane and 20 mL DMF (0.944 g/mL at 25 °C). Next, the solution B was added dropwise to the surface of buffer C. After a period of time, the product was collected and washed thoroughly with dichloromethane, ethanol, acetone and DMF in turn, and put aside for further investigation.

Reference Compound (RC)

The RC was synthesized by the reaction between 1,3,5-triformylphloroglucinol (21 mg, 0.1 mmol) and 2-aminophenol (35 mg, 0.3 mmol) in 10 mL ethanol at 80 °C for three day. After the reaction was finished, the solution was cooled to room temperature and the precipitate was collected by filtration, then washed thoroughly with ethanol and dried under vacuum to get final product (2,4,6-tris[(phenylamino)methylene]cyclohexane-1,3,5-trione, yellow solid).



Scheme S1 Representation of the synthesis of the reference compound.

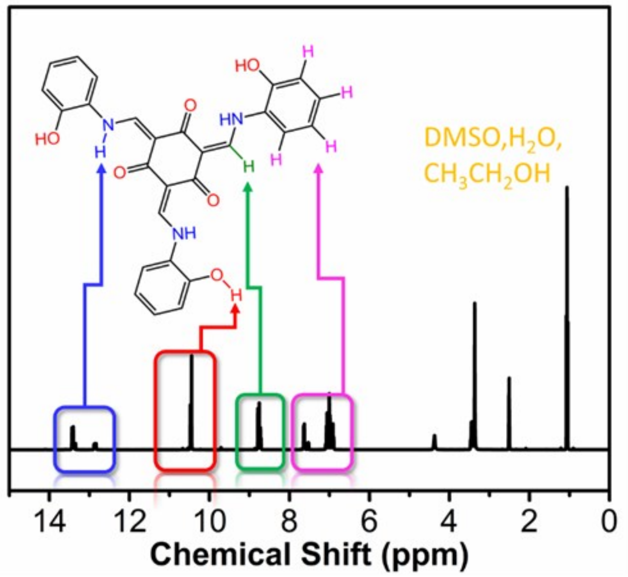


Fig. S1 ^{1}H NMR of 2,4,6-tris[(phenylamino) methylene]cyclohexane-1,3,5-trione (RC).

5. Raman Spectra

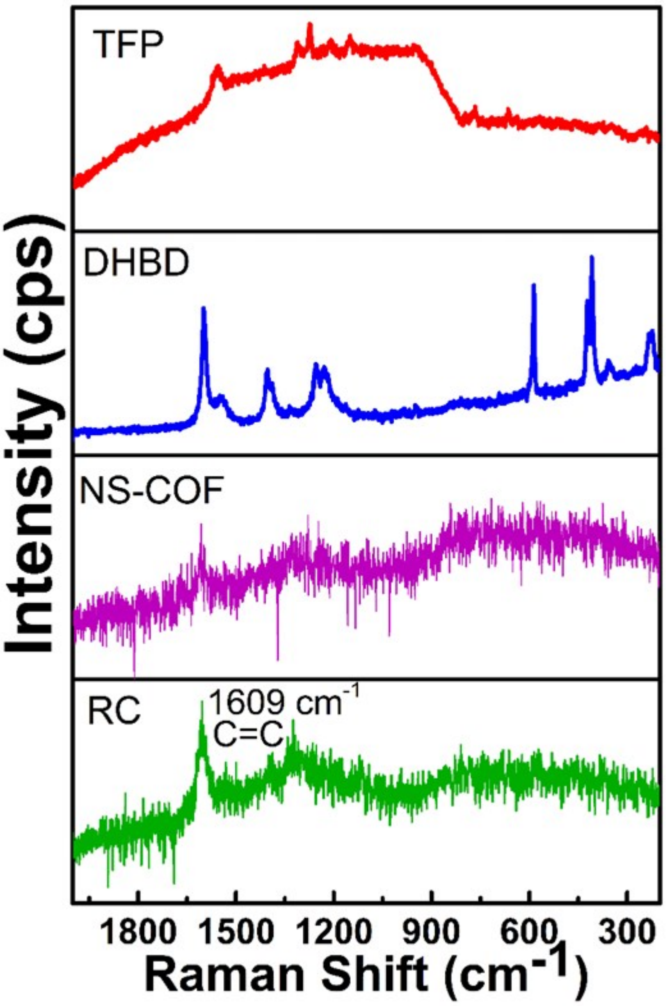


Fig. S2 Raman spectra of TFP, DHBD, NS-COF and RC.

6. Elemental Analysis

Table S2. Elemental Analysis of NS-COF

	C wt%	N wt%	H wt%
Exp.	**60.71**	**6.81**	**5.55**
Anal. Calcd.	**67.22**	**8.71**	**4.18**

7. Powder X-Ray Diffraction Analysis (PXRD) and Structural Modeling

Molecular modeling of NS-COF was generated with the Materials Studio (ver. 6.0) suite of programs. Firstly, we degraded the symmetry of the lattice to P1, inserted the optimized monomer in the empty cell, then the lattice model was geometry-optimized using the MS Forcite molecular dynamics module and promoted the symmetry to P6/m.

A staggered arrangement for NS-COF was constructed wherein the alternating stacked units were offset by a/2 and b/2.

The energies of the different stacking modes were calculated by using Self-Consistent Charge Density Functional Tight-Binding (SCC-DFTB) method as implemented in DFTB+.[4]

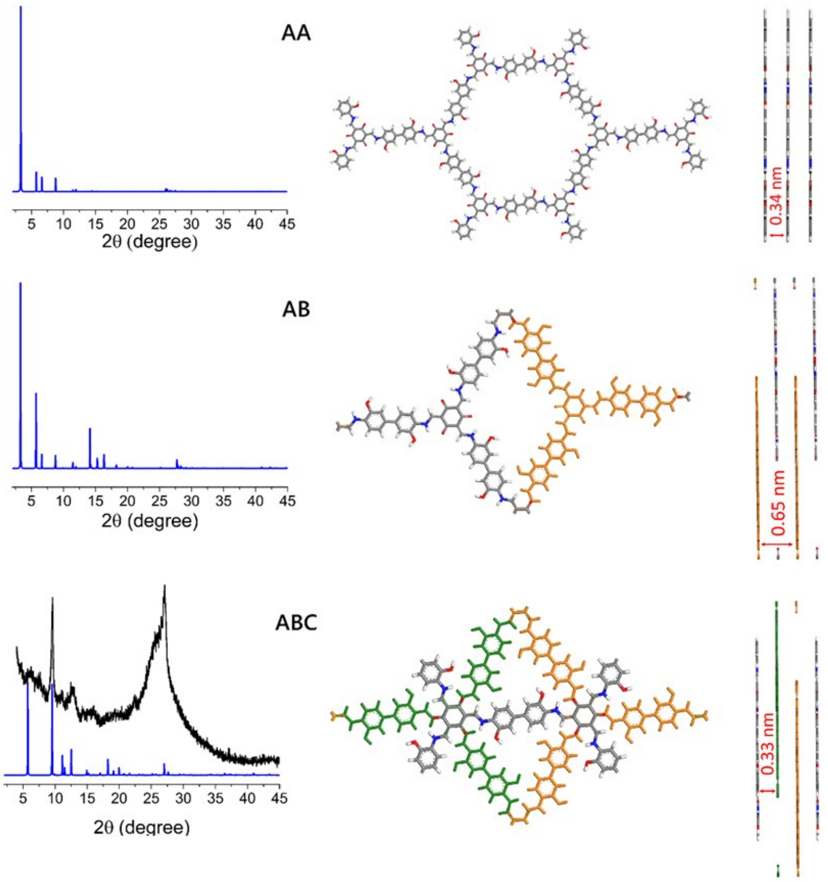


Fig. S3 Simulated and experimental PXRD patterns and view of the AA, AB and ABC stacking structure of NS-COF (O, red; N, blue; C, gray).

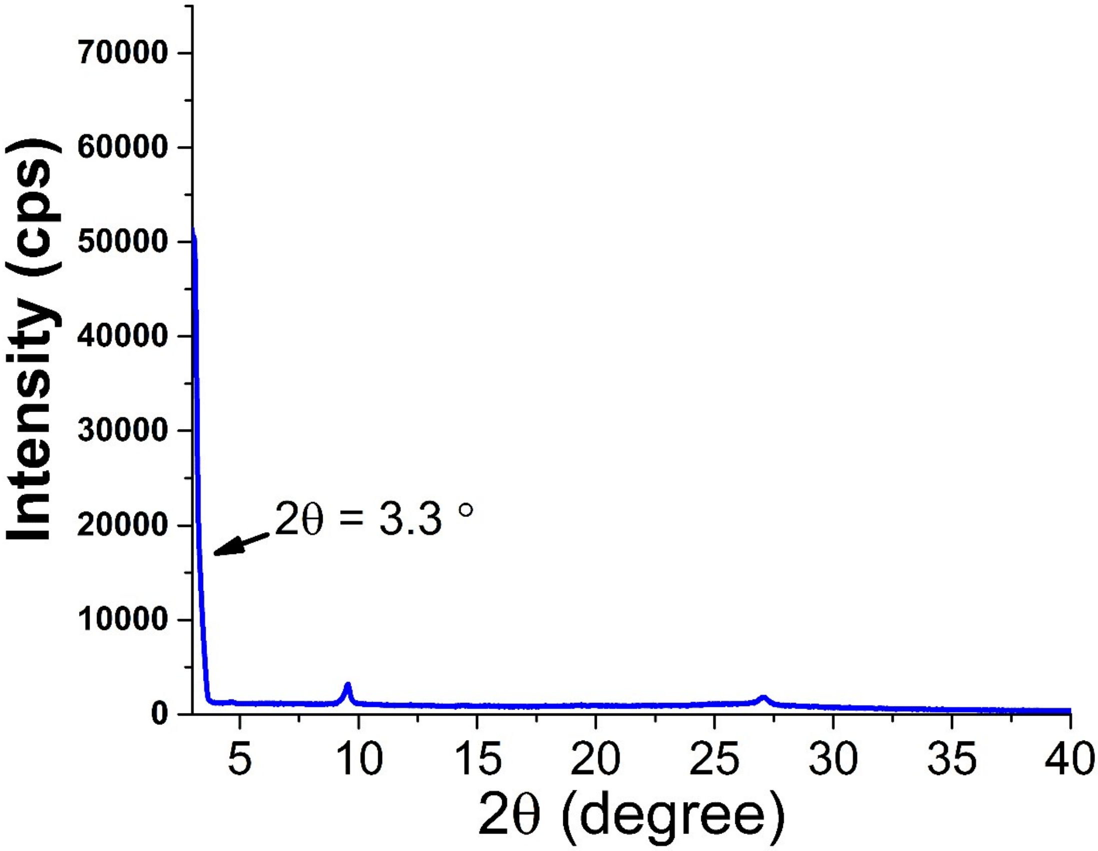


Fig. S4 Experimental PXRD patterns of the NS-COF.

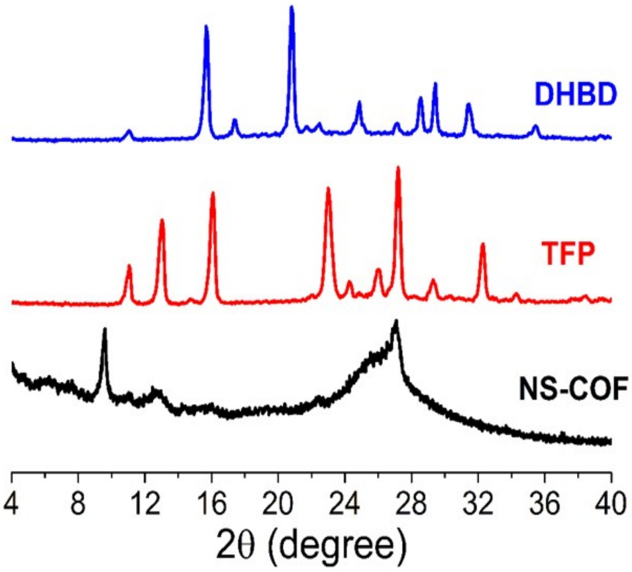


Fig. S5 Experimental PXRD patterns of the DHBD, TFP and NS-COF.

Table S3 The total DFTB energies, the crystal stacking energies and the corresponding HOMO-LUMO energy gap for NS-COF.

Staking	Symmetry Group	Total DFTB energy (kcal/mol)	Crystal stacking energy (kcal/mol)	HOMO-LUMO gap (eV)
AA	P6/m	-203261.179274	-21.27	1.991
AB	P63/m	-203261.307361	-21.40	1.852
ABC	R-3	-304892.792069	-32.93	1.825

Table S4 Fractional atomic coordinates for the unit cell of NS-COF

Atom	x	y	z
C1	-0.63512	-0.27688	0
C2	-0.69103	-0.30244	0
O3	-0.56592	-0.28827	0
C4	-0.62216	-0.39619	0
N5	-0.56967	-0.38163	0
C6	-0.5506	-0.41616	0
C7	-0.58221	-0.46845	0
C8	-0.56269	-0.50066	0
C9	-0.51058	-0.48242	0
C10	-0.4791	-0.42981	0
C11	-0.49847	-0.39712	0
O12	-0.46589	-0.34528	0
H13	-0.42911	-0.33494	0
H14	-0.19812	-0.54236	0
H15	-0.58737	-0.02638	0
H16	-0.46005	-0.04995	0
H17	-0.51413	-0.13651	0
H18	-0.56435	-0.21282	0

8. Morphology

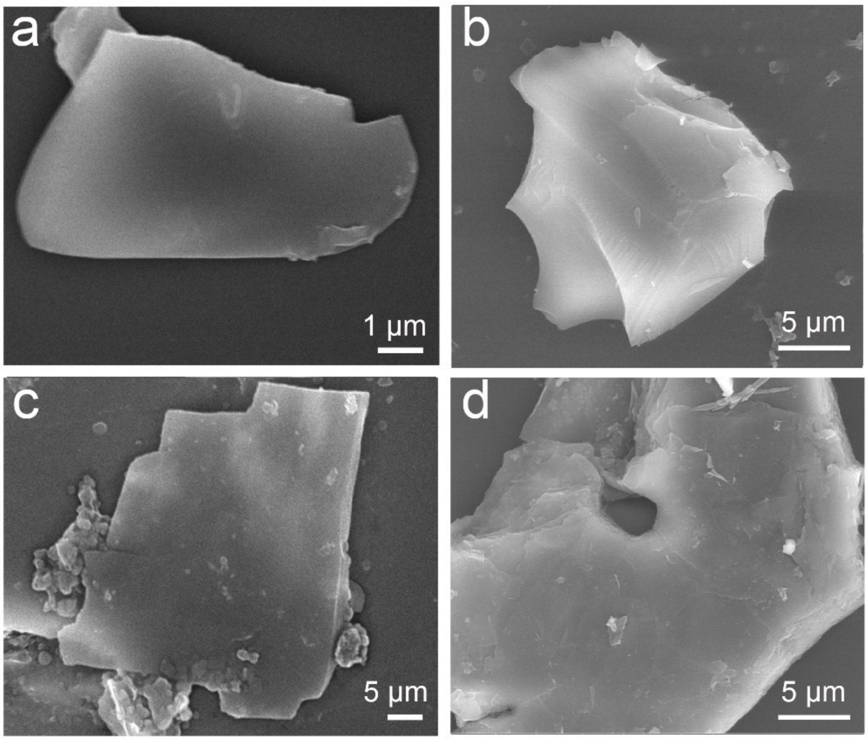


Fig. S6 SEM images of NS-COF.

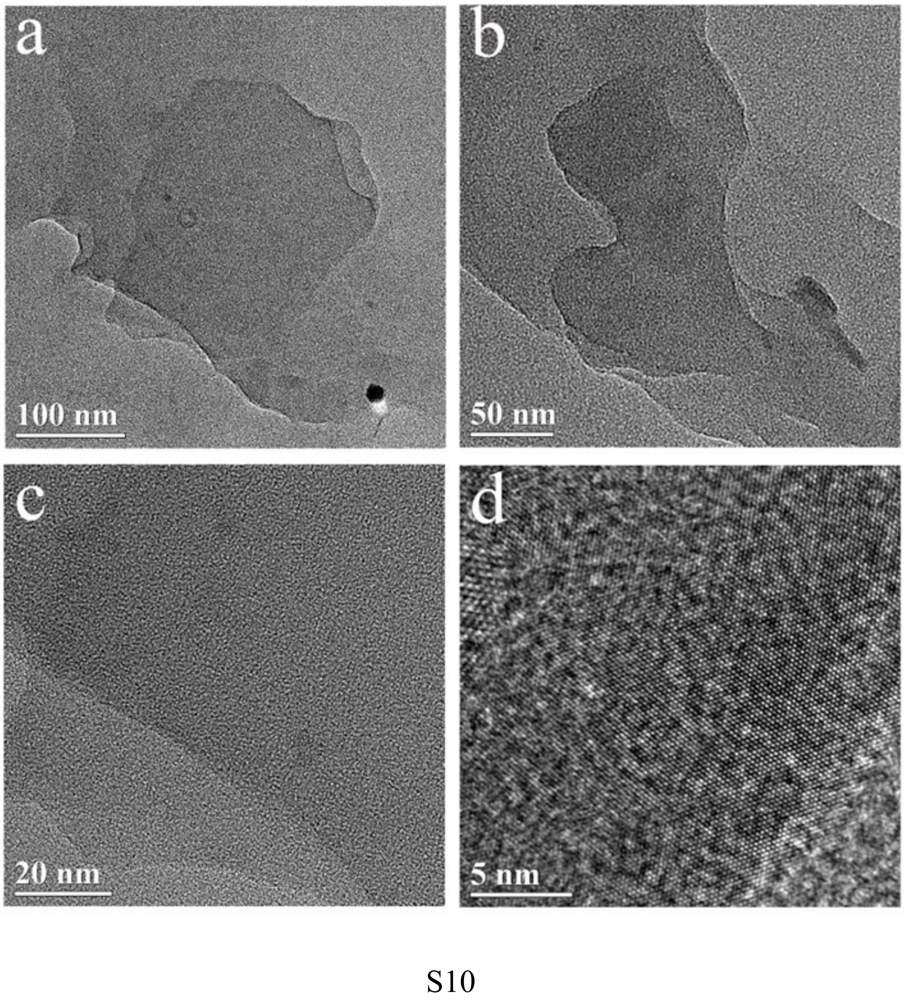


Fig. S7 TEM images of NS-COF.

9. Thermogravimetric Analysis

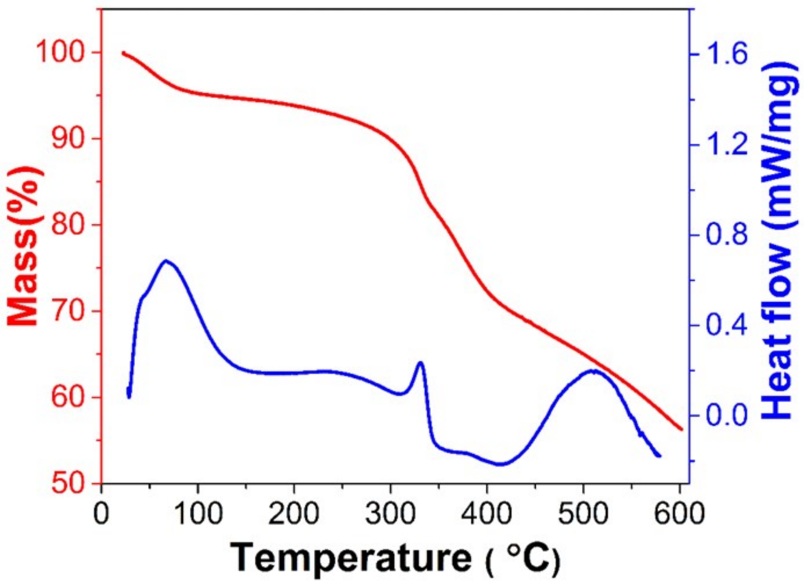


Fig. S8 TGA and DSC curves of NS-COF.

10. Solvent Stability Test

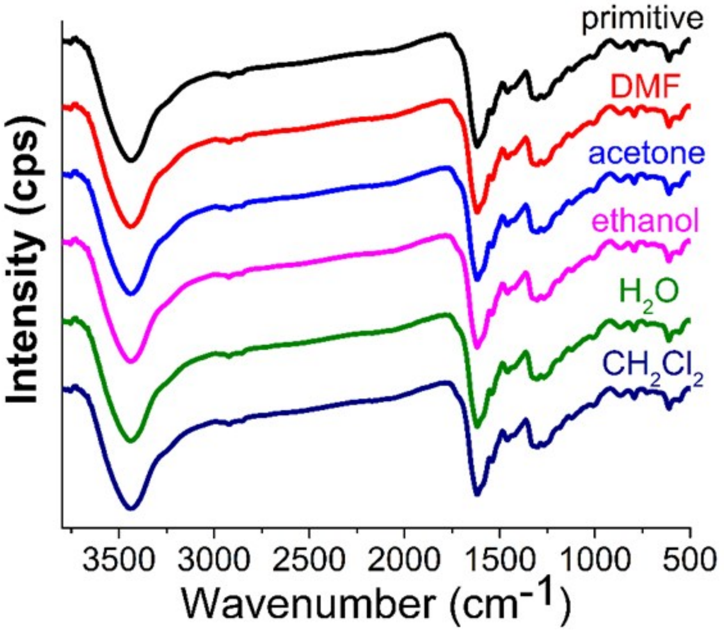


Fig. S9 Solvent stability of NS-COF.

11. Batch Adsorption Experiments

10 mg of sorbent was added into a 50 mL Erlenmeyer flask along with 25 mL of simulated

nuclear industrial effluent sample containing 12 co-existing cations (see Table S1) with a designed metal ion concentration and pH value. Then the mixture sample was shaken for a certain time at specified temperatures. Then the solid was separated from the supernatant by filtration, and the concentrations of metal ions before and after adsorption were determined by ICP-AES. All tests were carried out at least in duplicates. The adsorption capacity (q_e, mg/g or mmol/g) of U(VI) or other metal ions was calculated by using the following eqn (1) :[2-3]

$$q_e = \frac{(c_0 - c_e) \times V}{w} \qquad (1)$$

where c_0 and c_e are the initial and equilibrium concentrations of metal ions respectively; V is the volume of testing solution; and w is the weight of the sorbent.

Uranium selectivity (S_U), was coined to describe the degree of selectivity of the adsorbents to uranium：

$$S_U = \frac{q_{e-U}}{q_{e-tol}} \times 100\% \qquad (2)$$

where $q_{e\text{-}U}$ is the amount of uranium sorbed (mmol/g) and $q_{e\text{-}tol}$ is amount of all cations sorbed (mmol/g) in multi-ion solution

12. XPS

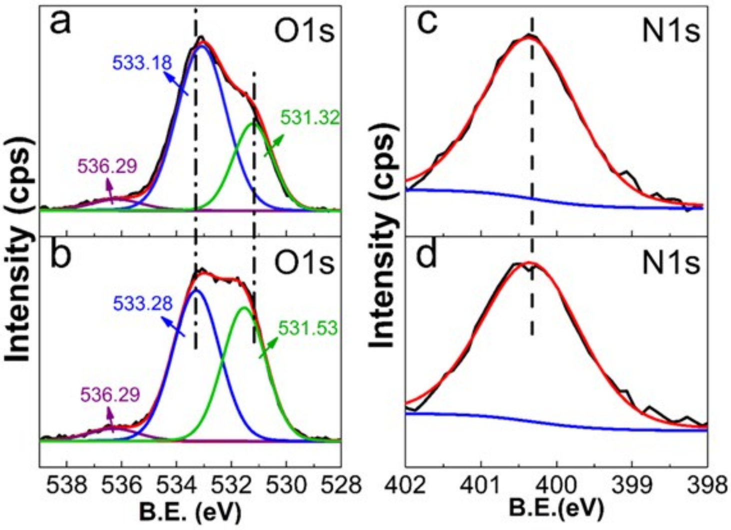


Fig. S10 O1s and N1s signals of XPS for NS-COF before (a, c) and after (b, d) uranium loading.

13. Applicability of the proposed method

Preparation of 2D COFs nanosheets with other different amines

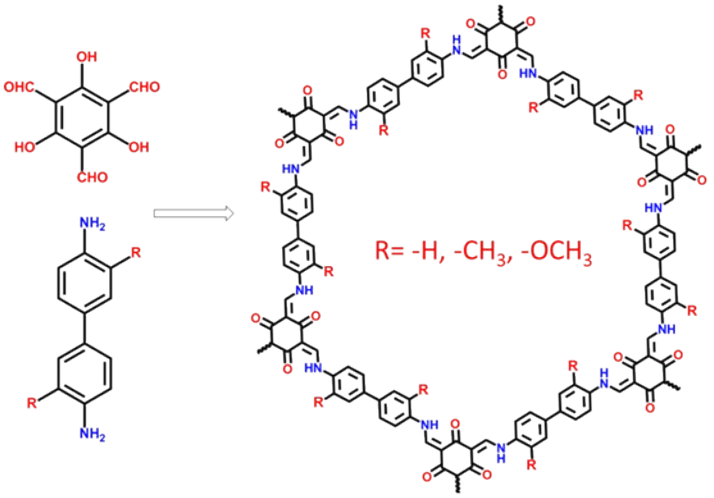


Fig. S11 Reaction scheme of the prepared COFs with different amine monomers in the supplementary experiments.

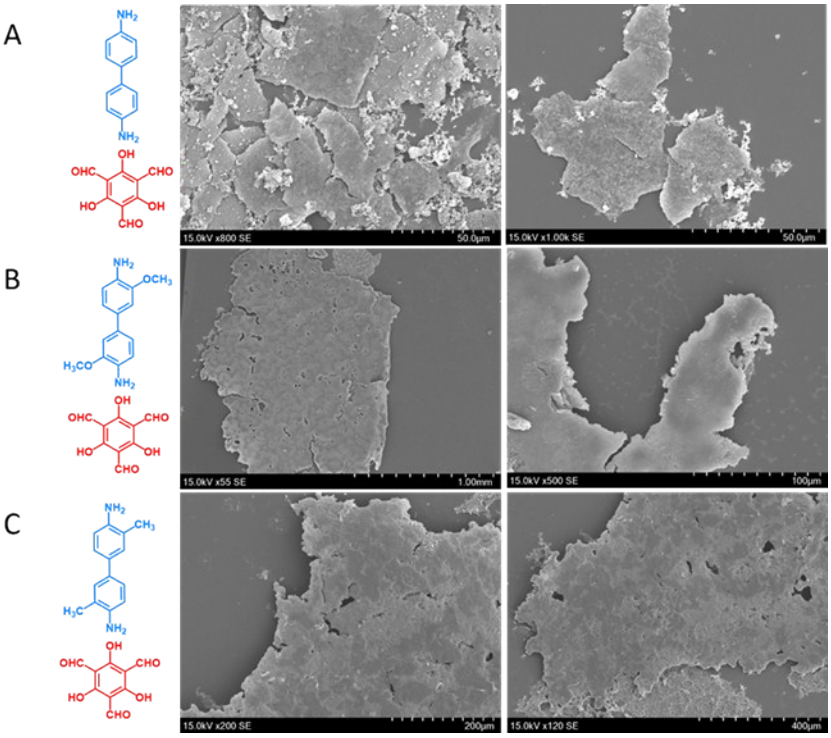


Fig. S12 SEM images of different COFs with different amine monomers.

Preparation of 2D COFs nanosheets with different combination of solvents

The results of different combination of solvents are as follows, it is noteworthy that the solubility of DHBD (amine monomer used in the manuscript) is poor in common organic solvents due to the strong hydrogen bonds between the molecules. In order to show the impact of changes in solvent combinations more intuitively, we chose a new amine monomer with better solubility as a substitution, here are the results:

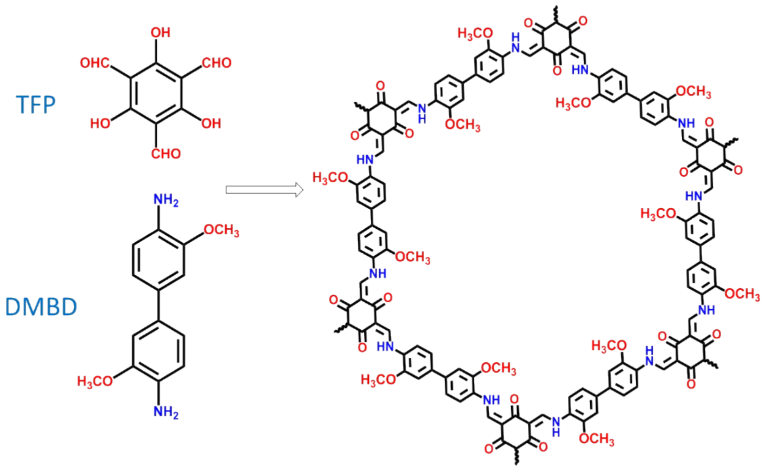


Fig. S13 The structure of the COF for testing other combinations of solvents.

Typically, two samples (EtOH + CH_2Cl_2; acetone + $CHCl_3$) were taken to be characterized, the results are as follows:

1) EtOH + CH_2Cl_2

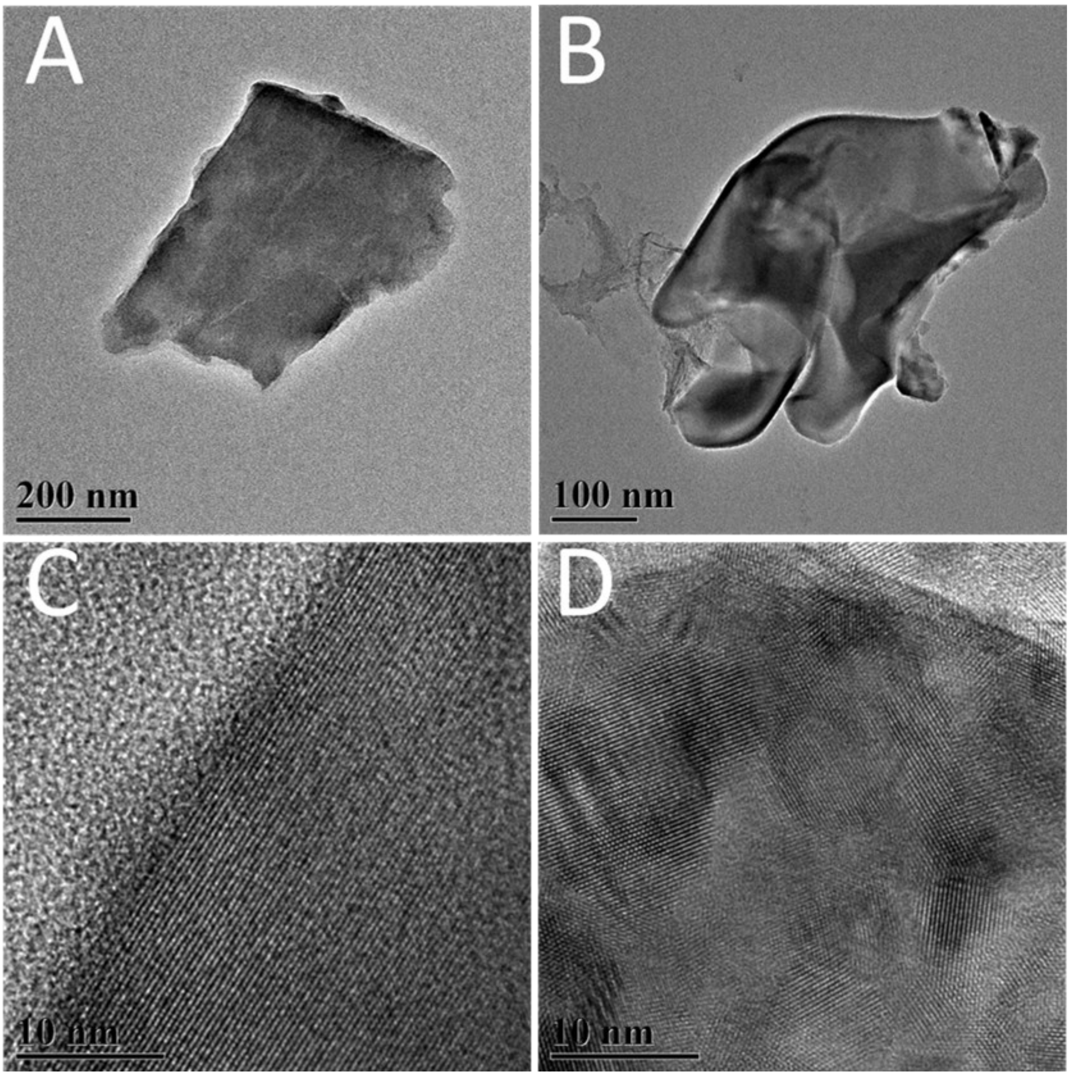


Fig. S14 TEM images of 2D COF nanosheets prepared with different solvent combination (EtOH + CH_2Cl_2).

2) acetone + $CHCl_3$

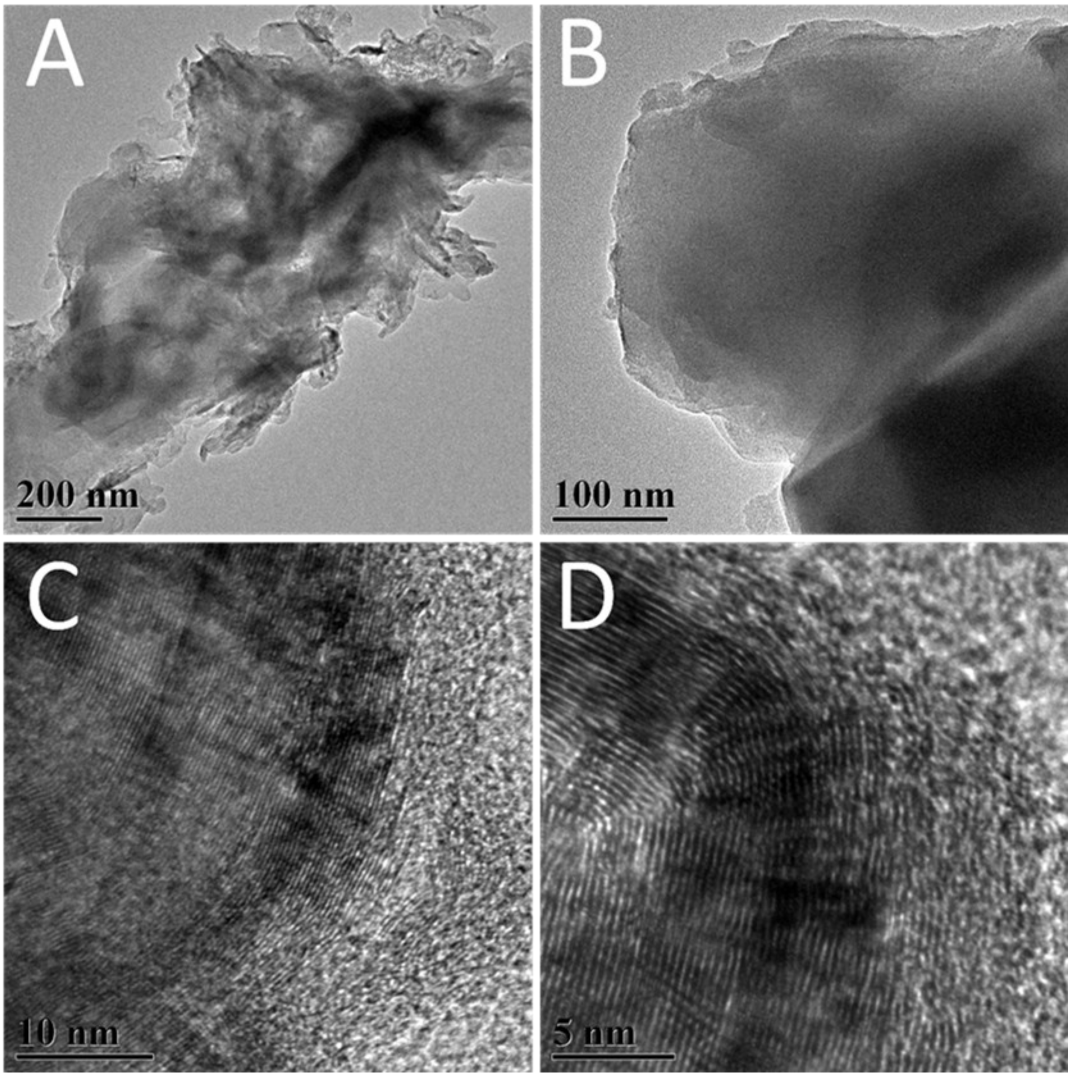


Fig. S15 TEM images of 2D COF nanosheets prepared with different solvent combination (acetone + $CHCl_3$).

The above results of the additional experiments could validate that our strategy are feasible and practicable within a certain range.

Reference

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