Supporting Information

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Combination of Knoevenagel Polycondensation and Water-assisted Dynamic Michael-Addition-Elimination for the Synthesis of Vinylene-Linked 2D Covalent Organic Frameworks

Shunqi Xu,[a,b] Zhongquan Liao,[c] Arezoo Dianat,[d] SangWook Park,[a,g] Matthew A. Addicoat,[e] Yubin Fu,[a] Dominik L. Pastoetter,[a] Filippo Giovanni Fabozzi,[f] Yannan Liu,[a] Gianaurelio Cuniberti,[d] Marcus Richter,[a] Stefan Hecht,[f] Xinliang Feng[a,b]*

[a] Chair of Molecular Functional Materials, Center for Advancing Electronics Dresden (cfaed) and Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Mommsenstrasse 4, 01069 Dresden (Germany). E-mail: xin-liang.feng@tu-dresden.de
[b] Max-Planck Institute of Microstructure Physics, Department of Synthetic Materials and Functional Devices, 06120 Halle (Germany).
[c] Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), 01109 Dresden (Germany)
[d] Chair of Material Science and Nanotechnology, Faculty of Mechanical Science and Engineering, Technische Universität Dresden, Hallwachstraße 3, 01069 Dresden (Germany)
[e] School of Science and Technology, Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS (UK)
[f] DWI–Leibniz Institute for Interactive Materials & Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, 52074 Aachen (Germany)
[g] Leibniz-Institute for Polymer Research Dresden e.V. (IPF), 01069 Dresden (Germany)
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Section A. Materials and General Methods

General remarks: Unless otherwise stated, the commercially available reagents and dry solvents were used without further purification. The reactions were performed using standard vacuum-line and Schlenk techniques. Work-up and purification of all compounds were performed under air with reagent-grade solvents. Column chromatography was performed with silica gel (particle size 0.063-0.2 mmm from VWR) and silica-coated aluminum sheets with fluorescence indicator from Merck were used for the thin-layer chromatography. Phenylacetonitrile (M2), 2-(p-tolyl)acetonitrile (M3), benzaldehyde (M7), cesium carbonate, were purchased from TCI Deutschland GmbH; N,N-Dimethylformamide-d7 (DMF-d7) and deuterium oxide (D2O) were ordered from Sigma Aldrich and abcr GmbH. The diphenyl-acrylonitrile (M1), (Z)-3-phenyl-2-(p-tolyl)acrylonitrile (M6), and 2,3,4-triphenylpentanedinitrile (M4) were synthesized as described in the literature.1-2

In-situ high-temperature $^1$H NMR measurements were conducted via a BRUKER AVANCE III 300 spectrometer. The NMR instrument was heated up to 95 °C in advance. Afterward, all reaction mixtures were prepared and put immediately into the NMR instrument for NMR studies. The NMR spectra were then collected within 5 mins, 10 mins, 30 mins, and 1 h (and 1.5 h). Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of [H1] solvent in the corresponding deuterated solvent. The solvent signal was used as references (DMF-d7: δ(1H)=2.92 and 2.75 ppm).

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Tensor II IR spectrometer with a universal Zn-Se ATR (attenuated total reflection) accessory in the 600~4000 cm⁻¹.

$^{13}$C CP solid-state NMR spectra were recorded on a BRUKER Ascend 800 MHz spectrometer using a commercial 3.2 mm MAS NMR probe and operating at a resonance frequency of 201.2 MHz.

Scanning electron microscopy (SEM) was carried out on a field emission scanning electron microscope (FESEM, Zeiss Gemini 500).

Transmission electron microscopy (TEM) was performed on a high-resolution transmission electron microscope (HRTEM, JEM-2100, JEOL, Japan). The samples were prepared by carefully dropping powders of V-2D-COFs onto the TEM Grids Lacey Carbonfilm, 200 Mesh.

Powder X-ray diffraction measurements (P-XRD) were carried out on STOE STADI P diffractometer, using mono chromated Cu/Kα (λ = 0.1542 nm) source. The sample was pressed as a film and investigated in transmission geometry.

The modeling of V-2D-COFs: The parameters for C, N and H atoms were taken from the mio-0-1 parameter set, and Lennard-Jones dispersion was employed. The PXRD simulations and Pawley refinement of the experimental PXRD were conducted by the Reflux module in BIOVIA Materials Studio 2020.
Nitrogen adsorption-desorption isotherm measurements were carried out using a Quadrasorb SI MP. Before gas adsorption measurements, the as-prepared samples (20~50 mg) were dried under dynamic vacuum at 150~180 °C for 8 h. The resulting samples were then used for gas adsorption measurements from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory model, the pore volumes were derived from the sorption curves.

DFT calculations. DFT calculation of the model reactions was performed using the cp2k package. The geometry of all the structures in the ground state was optimized with GGA-PBE exchange-correlation functional and Goedecker-Teter-Hutter (GTH) pseudopotentials using dispersion corrections.
Section B. Synthesis of V-2D-COFs with KMAE polymerization:

V-2D-COF-TFPB-PDAN (V-2D-COF-1). A glass ampoule containing 1,3,5-tris-(4-formylphenyl)benzene (TFPB, 12.0 mg, 30.7 µmol), (1,4-phenylene)diacetonitrile (PDAN, 7.2 mg, 46.1 µmol), and 0.1 mL Cs₂CO₃ (0.1 M, aqueous solution) were added with 1.0 mL dimethylacetamide (DMAc). Then the ampoule was sealed under vacuum after three freeze-pump-thaw cycles. Afterwards, the mixture was sonicated for 1~3 minutes at room temperature and then heated at 120 °C for 3 days. After cooling down to room temperature, the precipitated sample was filtered and washed with DMF, water, and ethanol three times, respectively. The resulting powder was dried under vacuum at 100 °C for 3 hours to afford targeted V-2D-COF-1 as yellowish powder (15.4 mg, 80%).

Scheme S1. Scheme for the synthesis of V-2D-COF-1.

V-2D-COF-TFPT-PDAN (V-2D-COF-2). A glass ampoule containing (2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TFPT, 12.0 mg, 30.7 µmol), PDAN (7.15 mg, 45.7 µmol) and 0.1 mL Cs₂CO₃ (0.1 M, aqueous solution) were added with 1.0 mL DMAc. Then the ampoule was sealed under vacuum after three freeze-pump-thaw cycles. Afterwards, the mixture was sonicated for 1~3 minutes at room temperature and then heated at 120 °C for 3 days. After cooling down to room temperature, the precipitated sample was filtered and washed with DMF, water, and ethanol three times, respectively. The resulting powder was dried under vacuum at 100 °C for 3 hours to afford targeted V-2D-COF-2 as yellowish powder (14.4 mg, 75%).
Scheme S2 Scheme for the synthesis of V-2D-COF-2.

**V-2D-COF-TFPB-PDAN (V-2D-COF-3).** A glass ampoule containing TFPB (10.0 mg, 25.6 µmol), 2,2'-(1,1'-biphenyl)-4,4'-diyl)diacetonitrile (BDAN, 8.92 mg, 38.42 µmol) and 0.1 mL Cs₂CO₃ (0.1 M, aqueous solution) were added with 1.0 mL DMAc. Then the ampoule was sealed under vacuum after three freeze-pump-thaw cycles. Afterwards, the mixture was sonicated for 1~3 minutes at room temperature and then heated at 120 °C for 3 days. After cooling down to room temperature, the precipitated sample was filtered and washed with DMF, water, and ethanol three times, respectively. The resulting powder was dried under vacuum at 100 °C for 3 hours to afford targeted V-2D-COF-3 as yellow powder (13.6 mg, 72%).

Scheme S3. Scheme for the synthesis of V-2D-COF-3.
V-2D-COF-HATN-BDAN (V-2D-COF-4). A glass ampoule containing 2,3,8,9,14,15-hexa(4-formylphenyl)diquinoxalino[2,3-a:2’,3’-c]phenazine (HATN-6CHO, 11 mg, 10.9 µmol), BDAN (7.8 mg, 32.7 µmol), and 0.1 mL Cs₂CO₃ (0.1 M) were added with the mixture of 0.5 mL DMAc and 0.5 mL orthodichlorobenzene (o-DCB). Then the ampoule was sealed under vacuum after three freeze-pump-thaw cycles. Afterwards, the mixture was sonicated for 1~3 minutes at room temperature and then heated at 120 °C for 3 days. After cooling down to room temperature, the precipitated sample was filtered and washed with DMF, water, and ethanol three times, respectively. The resulting powder was dried under vacuum at 100 °C for 3 hours to afford target V-2D-COF-4 as yellow powder (15.2 mg, 81%).

Scheme S4. Scheme for the synthesis of V-2D-COF-4.
Section C. In-situ $^1$H-NMR Measurements

Model reactions for the possible C=C bonds exchange under solid Cs$_2$CO$_3$-catalyzed condition:

M3 (8 mg, 38.97 μmol), M1 (5.11 mg, 38.97 μmol), 1,3,5-trimethoxybenzene (6.56 mg, 38.97 μmol, reference), 0.5 mL DMF-$d_7$, and Cs$_2$CO$_3$ (2 mg) were added into an NMR tube. Then the reaction was heated to 95 °C and *in-situ* investigated by $^1$H NMR measurements. The $^1$H-NMR spectra were collected within 5 mins, at 10 mins, 30 mins, and 1 h.

![Diagram](image)

**Figure S1.** *In-situ* time-dependent high-temperature NMR study of the conversion from M3 and M1 to M6 and M2 under anhydrous condition. The appearance of the peaks for M6 [H(e), H(-CH$_3$)] and M2 [H(-CH$_2$)] increased slowly, indicating a slow C=C bond exchange with the yield of ~22% for M2 and M6 even at 1h.
**Retro-Knoevenagel Reaction is blocked under solid Cs$_2$CO$_3$-catalyzed condition:**

M1 (5.11 mg, 38.97 μmol), 1,3,5-trimethoxybenzene (6.56 mg, 38.97 μmol, reference), 0.5 mL DMF-đ7, and Cs$_2$CO$_3$ (2 mg) were added into an NMR tube. Then the reaction was heated to 95 °C and *in-situ* investigated by $^1$H NMR measurements. The $^1$H-NMR spectra were collected within 5mins, at 10 mins, 30 mins, 1 h, and 1.5 h. There was no reaction happening.

**Figure S2.** *In-situ* time-dependent high-temperature NMR investigation of retro-Knoevenagel reaction from M1 to M2 and M7 under anhydrous conditions. The NMR spectrum remains unchanged without the signals for M2 and M7 (-CHO at 10~10.5 ppm).
**Michael-elimination under solid Cs$_2$CO$_3$-catalyzed condition:**

Intermediate M4 (R=H, 5 mg, 15.51 μmol), 1,3,5-trimethoxybenzene (2.61 mg, 15.51 μmol, reference), 0.5 mL DMF-d$_7$, and Cs$_2$CO$_3$ (2 mg) were added into an NMR tube. Then the reaction was heated to 95 °C and *in-situ* investigated by $^1$H NMR measurements. The $^1$H-NMR spectra were collected within 5 mins, at 10 mins, 30 mins, and 1 h. The reaction finished within 5 mins.

![NMR Spectra](image)

**Figure S3.** *In-situ* time-dependent high-temperature NMR investigation of Michael-elimination from M4 to M1 and M2 under anhydrous conditions. The peaks in the NMR spectrum for M4 [especially for H(i) and H(j)] disappeared within 5 mins. Instead, the peaks belonging to M1 [H(c/d)] and M2 [H(f,g,h) and H(−CH$_2$)] can be observed and provide a yield of ~95%. Afterward, the reaction remains constant.
Michael-addition-elimination for C=C bonds exchange under 0.1 M Cs$_2$CO$_3$-catalyzed condition:

M3 (8 mg, 38.97 μmol), M1 (5.11 mg, 38.97 μmol), 1,3,5-trimethoxybenzene (6.56 mg, 38.97 μmol, reference), 0.5 mL DMF-d$_7$, and Cs$_2$CO$_3$ (0.1 M, 0.05 mL, aqueous solution) were added into an NMR tube. Then the reaction was heated to 95 °C and in-situ investigated by $^1$H NMR measurements. The $^1$H-NMR spectra were collected within 5 mins, at 10 mins, 30 mins, 1 h, and 1.5 h. The reaction reached a thermodynamic equilibrium within 5 mins. The ratio of M6(M2) and M3(M1) is 1:1.

Figure S4. In-situ high-temperature NMR investigation of Michael-addition-elimination from M3 and M1 to M6 and M2 under 0.1 Cs$_2$CO$_3$ (0.1 M) catalyzed conditions. The peaks in NMR spectrum for M3 [H(a), H(b), and H(-CH$_3$)], M1[H(c/d)], and M6[H(e) and H(-CH$_3$)] suggest that the reaction reached a thermodynamic equilibrium within 5 mins. It should be noted that the signals of -CH$_2$ in M3 and M2 could not be found due to the hydrogen deuterium exchange under 0.1M Cs$_2$CO$_3$ catalyzed conditions. The ratio of M6(M2) and M3(M1) is 1:1.
Figure S5. Mass spectrum of the mixture for (a) Michael-addition-elimination model reaction. (b) ESI spectrum showed the values of 118.1225, 132.0813, 206.0974, and 220.1123 for [M2+H]+, [M3+H]+, [M1+H]+, and [M6+H]+, respectively. Some side peaks are presented there which result from the fragment ions and adduct ions. The mass spectrum was also obtained via the machine expression CMS with three ion sources: (c) positive ASAP High, (d) positive ASAP Medium, and (e) positive ASAP Soft. The peaks at ~117, ~132, ~205, and ~220 can be found for M2, [M3+H]+, M1, and [M6+H]+, respectively. It should be mentioned that the compound M6 in the mixture was also isolated from the mixture which was confirmed by ¹H-NMR spectroscopy.
Michael-elimination under 0.1 M Cs₂CO₃-catalyzed condition:

Intermediate M₄ (R=H, 5 mg, 15.51 μmol), 1,3,5-trimethoxybenzene (2.61 mg, 15.51 μmol, reference), 0.5 mL DMF-d₇, and Cs₂CO₃ (0.1 M, 0.05 mL, aqueous solution) were added into an NMR tube. Then the reaction was heated to 95 °C and in-situ investigated by ¹H NMR measurements. The ¹H-NMR spectra were collected within 5 mins, at 10 mins, 30 mins, and 1 h. The reaction finished within 5 mins.

Figure S6. In-situ high-temperature NMR investigation of Michael-elimination from M₄ to M₁ and M₂ under 0.1 Cs₂CO₃ (0.1 M) catalyzed conditions. The peaks of M₄ [especially for H(i,j)] in the NMR spectrum disappeared within 5 mins. Instead, peaks belonging to M₁ [H(c/d)] and M₂ [H(f,g,h)] can be observed, providing a yield of ~92%. Afterward, the reaction remains constant. It should be noted that the signals of -CH₂ in M₂ cannot be found due to the hydrogen deuterium exchange under 0.1 M Cs₂CO₃ catalyzed conditions.
Retro-Knoevenagel reaction under 0.1 M aqueous Cs$_2$CO$_3$-catalyzed condition:

M1 (5.11 mg, 38.97 μmol), 1,3,5-trimethoxybenzene (6.56 mg, 38.97 μmol), 0.5 mL DMF-d$_7$, and Cs$_2$CO$_3$ (0.1 M, 0.05 mL) were added into an NMR tube. Then the reaction was heated to 95 °C and *in-situ* investigated by $^1$H NMR measurements. The $^1$H-NMR spectra were collected within 5mins, at 10 mins, 30 mins, and 1 h. The reaction reached an equilibrium at ~30 mins.

**Figure S7.** *In-situ* high-temperature NMR investigation of retro-Knoevenagel reaction from M1 to M2 and M7 under 0.1 Cs$_2$CO$_3$ (0.1 M) catalyzed conditions. Although the NMR spectrum showed peaks for M2 [H(f, g, h) and M7 (-CHO), the intensities of the peaks are quite low and keep constant after 30 mins. The yield of M2 and M7 is ~8%. It should be noted that the signals of -CH$_2$ in M2 cannot be found due to the hydrogen deuterium exchange under 0.1M Cs$_2$CO$_3$ catalyzed conditions.
Section D. DFT calculation of Model Reactions

**Figure S8.** (a) The mechanism pathway of Knoevenagel condensation from $\text{M2}$ and $\text{M7}$ to $\text{M1}$. (b) DFT calculation of corresponding Knoevenagel condensation pathway without water (black), with four water molecules (blue), and with eight water molecules (red).

**Figure S9.** (a) Molecular conformation of intermediates in DFT calculation of Michael-addition-elimination reaction without water molecules.
**Figure S10.** (a) Molecular conformation of intermediates in DFT calculation of Michael-addition-elimination reaction with four water molecules.

**Figure S11.** Molecular conformation of intermediates in DFT calculation of Michael-addition-elimination reaction with eight water molecules.
**Figure S12.** (a) Molecular conformation of intermediates in DFT calculation of Knoevenagel condensation without water molecules.

**Figure S13.** (a) Molecular conformation of intermediates in DFT calculation of Knoevenagel condensation with four water molecules.
Figure S14. (a) Molecular conformation of intermediates in DFT calculation of Knoevenagel condensation with eight water molecules.
Figure S15. FT-IR spectrum of (a) V-2D-COF-1, (b) V-2D-COF-2, (c) V-2D-COF-3, and (d) V-2D-COF-4 with their corresponding monomers. The peaks at 2214~2217 cm⁻¹ confirm the successful formation of the linkage [-CH=C(CN)-].
Figure S16. Solid-state $^{13}$C CP (cross polarization) NMR spectrum of (a) V-2D-COF-1, (b) V-2D-COF-2, (c) V-2D-COF-3, and (d) V-2D-COF-4. The peaks at around ~110 and ~120 ppm confirmed the successful formation of the linkage [-CH=C(CN)-].
Section F. Experimental and Simulated PXRD Patterns of V-2D-COFs

The V-2D-COF models were optimized using the density functional tight-binding method and mio-1-1 parameters and Lennard-Jones dispersion as implemented in DFTB+ 20.1. Both atom positions and lattice vectors were optimized. From the monolayer structure, three stacking modes were further established based on the monolayer structure, including eclipsed (AA), staggered (AB), and slipped AA stacking. All the slipped AA stacking models showed lower per-layer stabilization energies, compared to the values of AA and AB stacking models. Afterwards, these optimized slipped AA stacking structures were applied for the Pawley refinement in the Reflex module of BIOVIA Materials Studio 2020.

Figure S17. Scheme of simulated (a) slipped AA stacking, (b) AA stacking and AB stacking models for V-2D-COF-1.

Figure S18. Experimental, Pawley-refined and simulated PXRD patterns (based on slipped AA stacking) and difference plots for V-2D-COF-1.
Table S1. Optimized Interlayer distances, relevant energies and bandgaps for the V-2D-COF-1.

|                | Interlayer distance (Å) | Total Energy (a.u.) | LJ energy (a.u.) | Per layer stabilization (kcal/mol) | HOMO-LUMO gap (eV) |
|----------------|-------------------------|---------------------|------------------|------------------------------------|--------------------|
| monolayer      | -175.612823             | 0.7542              | -100.69          | 2.293                              |
| AA             | 3.61                    | -351.546562         | 1.1872           | 1.923                              |
| slipAA         | 3.61                    | -351.643923         | 1.2228           | 1.540                              |
| AB             | 3.25                    | -351.4213046        | 1.3649           | 2.115                              |
**Figure S19.** Scheme of simulated (a) slipped AA stacking, (b) AA stacking and AB stacking models for V-2D-COF-2.

**Figure S20.** Experimental, Pawley-refined and simulated PXRD patterns (based on slipped AA stacking) and difference plots for V-2D-COF-2.

**Table S2** Optimized Interlayer distances, relevant energies and bandgaps for the V-2D-COF-2.

|                | Interlayer distance (Å) | Total Energy (a.u.) | LJ energy (a.u.) | Per layer stabilization (kcal/mol) | HOMO-LUMO gap (eV) |
|----------------|-------------------------|---------------------|------------------|-------------------------------------|-------------------|
| monolayer      | -177.717867             | 0.7183              |                  |                                     | 2.175             |
| AA             | 3.49                    | -355.858670         | 1.1420           | -132.70                             | 1.748             |
| slipAA         | 3.40                    | -355.879809         | 1.1331           | -139.33                             | 1.941             |
| AB             | 2.95                    | -355.678554         | 1.3488           | -76.19                              | 2.035             |
Figure S21. Scheme of simulated (a) slipped AA stacking, (b) AA stacking and AB stacking models for V-2D-COF-3.

Figure S22. Experimental, Pawley-refined and simulated PXRD patterns (based on slipped AA stacking) and difference plots for V-2D-COF-3.

Table S3. Optimized interlayer distances, relevant energies and bandgaps for the V-2D-COF-3.

|          | Interlayer distance (Å) | Total Energy (a.u.) | LJ energy (a.u.) | Per layer stabilization (kcal/mol) | HOMO-LUMO gap (eV) |
|----------|--------------------------|---------------------|------------------|-----------------------------------|-------------------|
| monolayer| -246.223011              | 1.0405              |                  |                                   | 2.247             |
| AA       | 3.75                     | -492.801975         | 1.6531           | -111.68                           | 2.032             |
| slipAA   | 3.51                     | -492.831473         | 1.6896           | -120.94                           | 1.886             |
| AB       | 3.52                     | -492.6834752        | 1.8182           | -74.50                            | 2.010             |
Figure S23. Scheme of simulated (a) slipped AA stacking, (b) AA stacking and AB stacking models for V-2D-COF-4.

Figure S24. Experimental, Pawley-refined and simulated PXRD patterns (based on slipped AA stacking) and difference plots for V-2D-COF-4.

Table S4. Optimized Interlayer distances, relevant energies and bandgaps for the V-2D-COF-4.

| Interlayer distance (Å) | Total Energy (a.u.) | LJ energy (a.u.) | Per layer stabilization (kcal/mol) | HOMO-LUMO gap (eV) |
|------------------------|---------------------|------------------|-----------------------------------|-------------------|
| monolayer              | -246.231623         | 1.0471           |                                   | 2.206             |
| AA                     | -492.805715         | 1.6727           | -107.45                           | 1.963             |
| slipAA                 | -492.823664         | 1.7118           | -113.08                           | 1.901             |
| AB                     | -492.6784034        | 1.8405           | -67.51                            | 1.987             |
Section G. Scanning electron microscope (SEM) images of V-2D-COFs

Figure S25. SEM images of (a) V-2D-COF-1, (b) V-2D-COF-2, (c) V-2D-COF-3, and (d) V-2D-COF-4 synthesized via water-assisted KMAE polymerization.
Section H. Transmission electron microscope (TEM) images of V-2D-COFs

Figure S26. High-resolution TEM images of V-2D-COF-1 synthesized via water-assisted KMAE polymerization. (a) a large area with polycrystals; (b–d) zoomed HR-TEM images from (a) which show crystalline structures.

Figure S27. High-resolution TEM images of V-2D-COF-2 synthesized via water-assisted KMAE polymerization.
Figure S28. High-resolution TEM images of V-2D-COF-3 synthesized via water-assisted KMAE polymerization. (a) a large area with polycrystals; (b~d) zoomed HR-TEM images from (a) which show crystalline structures.

Figure S29. High-resolution TEM images of V-2D-COF-4 synthesized via water-assisted KMAE polymerization. (a) a large area with polycrystals; (b~d) zoomed HR-TEM images from (a) which show crystalline structures.
Section I. Synthesis of V-2D-COFs via only water-assisted Michael-addition-elimination

The V-2D-COF-1 and V-2D-COF-3 were also synthesized successfully via only water-assisted Michael-addition-elimination starting from the building block TFPB-Bu and linker PDAN or BDAN. Although the PXRD patterns are not good as that of V-2D-COFs synthesized via KMAE polymerization, the peaks at (100) plane also strongly confirm the dynamic nature of Michael-addition-elimination for C=C bond exchange.

V-2D-COF-1. A glass ampoule containing TFPB-Bu (TFPB-Bu, 21.93 mg, 25.61 µmol), PDAN (6.0 mg, 38.42 µmol), and 0.1 mL Cs₂CO₃ (0.1 M) were added with 1.0 mL dimethylacetamide (DMAc). Then the ampoule was sealed under vacuum after three-pump-thaw cycles. Afterwards, the mixture was sonicated for 1~3 minutes at room temperature and then heated at 120 °C for 3 days. After cooling down to room temperature, the precipitated sample was filtered and washed with DMF, water and ethanol for three times, respectively. The resulting powder was dried under vacuum at 100 °C for 3 hours to afford targeted V-2D-COF-1 as yellowish powder (8.4 mg, 53%).

Scheme S5. The synthesis of V-2D-COF-1 via only water-assisted Michael-addition-elimination.
**Figure S30.** The PXRD pattern of V-2D-COF-1 synthesized via only water-assisted Michael-addition-elimination.

**V-2D-COF-3.** A glass ampoule containing TFPB-Bu (TFPB-Bu, 21.93 mg, 25.61 µmol), BDAN (8.92 mg, 38.42 µmol), and 0.1 mL Cs₂CO₃ (0.1 M) were added with 1.0 mL dimethylacetamide (DMAc). Then the ampoule was sealed under vacuum after three-pump-thaw cycles. Afterwards, the mixture was sonicated for 1~3 minutes at room temperature and then heated at 120 °C for 3 days. After cooling down to room temperature, the precipitated sample was filtered and washed with DMF, water and ethanol for three times, respectively. The resulting powder was dried under vacuum at 100 °C for 3 hours to afford targeted V-2D-COF-3 as green powder (9.4mg, 50%).

**Scheme S6.** The synthesis of V-2D-COF-3 via only water-assisted Michael-addition-elimination.
The PXRD pattern of V-2D-COF-3 synthesized via only water-assisted Michael-addition-elimination.

Section J. Synthesis of V-2D-COFs via only water-assisted Michael-addition-elimination
A kinetic study was conducted by collecting time-dependent yields, FT-IR, and PXRD patterns to prove the existence of dynamic Michael-addition-elimination for error-correction process during the COF synthesis. To obtain a time-depended PXRD studies, a series of polymerizations of V-2D-COF-1 between TFPB and PDAN under the same reaction conditions was performed. The reaction mixtures were quenched with water after 30 mins, 1h, 3 h, 6 h, 12 h, 24 h, 48 h, and 72 h. Afterwards, the precipitation was washed in different organic solvents and dried under vacuum. For each sample, the yield was determined and the crystallinity was investigated by PXRD measurements. These results suggest an efficient self-error correction process involved, which can be attributed to the in-situ dynamic Michael-addition-elimination.

Figure S32. The KMAE polymerization showed that the yields increased during the first day and further kept constant after one reaction day.
Figure S33. The PXRD patterns of the precipitated powders were collected with same measured parameters (step: 1, times: 60s, same volume of samples). After one-hour reaction time, crystalline V-2D-COF-1 was formed due to the present of significant (100) peak at 2.86°. The intensity of (100) planes increased from ~800 to ~6380 a.u. within 3 days, indicating an increased crystallinity of all time.
Section K. NMR spectrum of Compounds M1~M7

Figure S34. $^1$H-NMR spectrum of M1 measured in DMF-$d_7$ at 95 °C.

Figure S35. $^1$H-NMR spectrum of M1 measured in DMF-$d_7$/D$_2$O=10/1 at 95 °C.
Figure S36. $^1$H-NMR spectrum of M2 measured in DMF-$d_7$ at 95 °C.

Figure S37. $^1$H-NMR spectrum of M2 measured in DMF-$d_7$/D$_2$O=10/1 at 95 °C.
Figure S38. $^1$H-NMR spectrum of M3 measured in DMF-d$_7$ at 95 °C.

Figure S39. $^1$H-NMR spectrum of M3 measured in DMF-d$_7$/D$_2$O=10/1 at 95 °C.
Figure S40. $^1$H-NMR spectrum of M4 measured in CD$_2$Cl$_2$ at room temperature (There are diastereomers).

Figure S41. $^1$H-NMR spectrum of M4 measured in DMF-d$_7$ at 95 °C (There are diastereomers).
Figure S42. $^1$H-NMR spectrum of M4 measured in DMF-d$_7$/D$_2$O=10/1 at 95 °C (There are diastereomers).

Figure S43. $^1$H-NMR spectrum of M6 measured in DMF-d$_7$ at 95 °C.
**Figure S44.** $^1$H-NMR spectrum of M6 measured in DMF-d$_7$/D$_2$O=10/1 at 95 °C.

**Figure S45.** $^1$H-NMR spectrum of M7 measured in DMF-d$_7$ at 95 °C.
Figure S46. $^1$H-NMR spectrum of M7 measured in DMF-d$_7$/D$_2$O=10/1 at 95 °C.

Section L. References

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