

Electronic Supplementary Information

Strongly coupled and highly-compacted Zirconium Aminobenzenedicarboxylate crystal membranes for accelerating carbon dioxide capture

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Experimental Section

2.1. Chemicals and Reagents

Pyrrole ($\geq 98.0\%$) was of chemical grade and purchased from Sinopharm Chemical Reagent Co., Ltd, and were distilled under vacuum before use. 1,4-Dibromobutane ($\geq 98.0\%$), 2-methylimidazole (MI), and 2-amino-1,4-benzene dicarboxylic acid ($\text{NH}_2\text{-BDC}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All other reagents were of analytical grade and used without further purification, such as methyl orange (MO) (Tianjin Damao Chemical Factory, IND); ammonium persulfate ($\geq 99.0\%$), KOH ($\geq 85.0\%$), and dimethylformamide (DMF) (98.0%) obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol and ethanol were obtained from Tianjin Damao Chemical Factory, 99.7% . Deionized water was used for all experiments. Zirconium tetrachloride (ZrCl_4 , $\geq 99.5\%$) was obtained from Sigma-Aldrich Co., Ltd. Carbon cloth was acquired from All starting materials and solvents, unless otherwise specified, were used without further purification.

2.2. Depositing PPy coatings onto carbon cloth (CC-PPy)

Carbon cloth (CC) is washed with dilute sulfuric acid prior to use in the experiment. PPy coatings were deposited onto the surface of CC via emulsion polymerization as reported in the literature. Briefly, a piece of CC (5 cm x 5cm) was put into 50 mL deionized water, followed by the addition of 0.1 mL pyrrole monomer under stirring. Ammonium persulfate (0.243 g, 1.5 mmol) was dissolved in 30 mL deionized water and added to the above solution drop by drop, and the mixture was stirred at room temperature for 24 h. The formed CC-PPy composite substrate was washed with deionized water/ethanol several times. The produced substrate was dried under

vacuum at 60 °C for 24 h.

2.3. *CC-PPy chemically grafting 1,4-dibromobutane*

A mixture of CC-PPy, KOH powder (0.050 g), and 1,4-dibromobutane (0.143 g) was dispersed in 25.0 mL DMF, sonicated for 5 min and then held at 60 °C for 24 h under vigorous agitation. The product was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed KOH and unreacted 1,4-dibromobutane from the surface of CC-PPy. The final product, denoted as CC-PPy-(CH₂)₄Br, was then dried in a vacuum oven at 60 °C overnight to remove residual solvent.

2.4. *CC-PPy-(CH₂)₄Br chemically grafting 2-methylimidazole*

A mixture containing CC-PPy-(CH₂)₄Br (0.025 g) and MI (0.200 g) in 25.0 mL DMF with KOH (0.050 g) was sonicated for 5 min and then held at 80 °C for 24 h under vigorous agitation. The product was concentrated and washed with ethanol several times to thoroughly remove physically absorbed MI. Then the black precipitate was denoted as CC-PPy-(CH₂)₄-MIBr and was dried in a vacuum oven at 60 °C overnight to remove the residual solvent.

2.5. *CC-PPy-(CH₂)₄Br chemically grafting NH₂-BDC*

As can be seen from Figure 1, a mixture containing CC-PPy-(CH₂)₄Br, K₂CO₃ (0.050g) powder, and dimethyl 2-aminoterephthalate (prepared by BDC and methanol, 0.050g) was dispersed in 25.0 mL DMF and sonicated for 5 min and then held at 80 °C for 24 h under vigorous agitation. The product was filtrated and washed with deionized water and ethanol to thoroughly remove physically absorbed K₂CO₃ and unreacted dimethyl 2-aminoisophthalate from the surface of CC-PPy-(CH₂)₄Br. The final product, denoted as CC-PPy-(CH₂)₄Br-aminoisophthalate, was then dried

in a vacuum oven at 60 °C overnight to remove residual solvent. Subsequently, a mixture containing CC-PPy-(CH₂)₄Br-aminoisophthalate (0.025 g) and H₂SO₄ (0.200 g) in 25.0 mL H₂O was sonicated for 5 min and then held at 80 °C for 24 h under vigorous agitation. The product was concentrated and washed with deionized water several times. Then the black precipitate, denoted as CC-PPy-(CH₂)₄-NH₂-BDC, was dried in a vacuum oven at 60 °C overnight to remove residual solvent.

2.6. *Synthesis of CC-PPy@UiO-66-NH₂ crystal membrane*

A mixture containing ZrCl₄ (28.80 mg, 0.12 mmol), CC-PPy-(CH₂)₄-NH₂-BDC (50.00 mg), and acetic acid (0.34 mL) was firstly added to DMF (5 mL) and sonicated for 10 min. Subsequently, NH₂-BDC (19.94 mg, 0.12 mmol) was added to the clear dispersion in an equimolar ratio with regard to ZrCl₄. Afterwards, the mixed solution was transferred into a Teflon-lined stainless steel autoclave and kept in an oven for 24 h at 120 °C under static conditions. When the reaction temperature cooled to room temperature, the precipitate was isolated by centrifugation. Finally, the sample dried in air at 80 °C, and the product was denoted as CC-PPy@UiO-66-NH₂.

2.7. *Characterization*

The crystal structures were determined using a powder X-ray diffraction (XRD) analysis (Philips X'Pert PRO) with Cu K α radiation. The Ni content of Ni/PCNF and S loading of Ni/PCNF-S were determined using thermogravimetric analysis (TGA 4000 PerkinElmer Co., Ltd) under N₂ and air at a heating rate of 5 °C min⁻¹. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM Hitachi S-4700) and high-resolution transmission electron

microscopy (HRTEM FEI Tecnai G2 F20) fitted with an energy dispersive spectrometer (EDS) detector, STEM, and selected area electron diffraction (SAED). N₂ (at 77K) and CO₂ (at 298 K) sorption isotherms measurements were performed with a Micromeritics ASAP 2020 Plus HD88. The samples were dried and degassed at 120 °C for 24h before the measurement. The pore-size distributions (PSD) was calculated based on the Barrett–Joyner–Halenda (BJH) model. Infrared thermal imager (ZJJY, CEL-NP2000-2A, China) was used to measure the surface temperature of the sample.

2.8. Calculations of IAST selectivity

The IAST selectivity was calculated according to a simple equation:

$$K = \frac{q_{CO_2}}{q_{N_2}}$$

Where K was denoted as IAST selectivity, q_{CO_2} and q_{N_2} were the adsorption capacity measured at the same pressure.

2.9. Vacuum vapor/gas sorption test

Typically, the samples were firstly vacuum degassed at 120 °C for 6 hours, then placing the samples in a vacuum environment. Subsequently, CO₂ flow was injected into the vacuum system and controlled at the specified partial pressure P/P_0 (0.05, 0.2, 0.3, 0.5, 0.6, 0.8, 0.9, 0.95) according to the set program. The adsorption time and corresponding weight data were continuously recorded until adsorption equilibrium was reached.

2.10. Molecular models and computational methodology

Atomistic molecular dynamics simulations of adsorption and spatial orientation of the combination of bridging molecules grafted with BDC molecules on the substrate surface were performed using the GROMACS package with two-dimensional periodic boundary conditions. Construct an initial structural model with a polypyrrole substrate and BDC molecules connected (to simplify calculations, a planar substrate is used instead of the polypyrrole surface), with approximately 800-1500 atoms, and periodic boundary conditions are applied. There are a total of 9 grafting points on the substrate surface per unit area in the simulated space, ensuring that BDC molecules can freely orient in space. Select appropriate classical potential functions to calculate the interactions between atoms in the system. Adopting spin polarized GGA PBE functional, all electron plane wave basis set with energy cutoff of 520 eV, and projection augmented wave (PAW) method. The Brillouin zone integration to be sampled adopts a (3x3x1) Monkhorst Pack grid. The conjugate gradient algorithm was used in the optimization. The convergence threshold is set to a total energy of 1×10^{-5} eV, with each atom subjected to a force of 0.02 eV/Å. By providing a detailed description of the simulated dynamic processes and physical quantity changes, reveal the molecular spatial orientation mechanism at the atomic scale, and explain the experimental results. If there are difficulties in conducting one-step simulation of the entire process, an initial model can be established step by step based on actual conditions for step-by-step simulation.

Synthesis route:

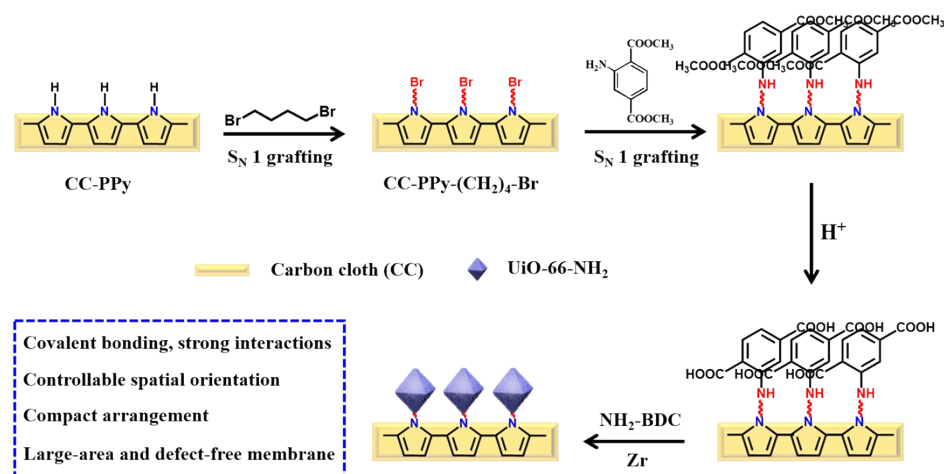


Figure S1. Synthesis route for the carbon cloth-supported UiO-66-NH₂ hybrid membrane (CC-PPy@UiO-66-NH₂).

Initially, PPy coatings were deposited on the surface of carbon cloth to form a composite substrate (CC-PPy) via emulsion polymerization. Subsequently, 1,4-dibromutane, serving as a bridged molecule, reacted with the N site of PPy on one side and the NH₂ group of dimethyl terephthalate molecules on the other side via covalent grafting through an S_N 1 reaction. Finally, in situ growth of densely packed UiO-66-NH₂ nanocrystals with strong interactions on the CC was achieved through the surface confinement effect. To the best of our knowledge, there are no similar reports of the fabrication of octahedral-shaped UiO-66-NH₂ (<100 nm) monolayer hybrid membranes. Notably, chemically grafting ligand molecules onto the CC substrate via the connection of 1,4-dibromutane as a bridged molecule, and in situ growth of UiO-66-NH₂ nanocrystals within a surface-confined space contributed to the fabrication of the hybrid membrane (CC-PPy@UiO-66-NH₂) with optimized configurations. Gas separation results indicated that the as-prepared CC-PPy@UiO-66-NH₂ hybrid membrane exhibited superior CO₂/N₂ separation performance compared with bulk UiO-66-NH₂ powder under similar conditions.

Fig. S1 illustrates the synthesis route for the CC-PPy@UiO-66-NH₂ hybrid membrane (details provided in the Supporting Information). Initially, positively

charged PPy coatings were deposited onto the CC, which had been cleaned with sulfuric acid, based on electrostatic interactions, the morphologies as demonstrated by scanning electron microscopy (SEM)–electron dispersive spectroscopy analysis (Fig. S2). During the subsequent fabrication process, the chemically grafted 1,4-dibromobutane and NH₂-BDC molecules are challenging to detect via infrared spectroscopy and nuclear magnetic resonance spectroscopy owing to their low content. Instead, we confirmed the successful grafting of these molecules using elemental mappings (Fig. S3). After the addition of Zr and NH₂-BDC sources, the surface-confined growth of UiO-66-NH₂ crystals began on the grafting sites within the same period and arranged orderly on the surface of substrate through a simple solvothermal method.

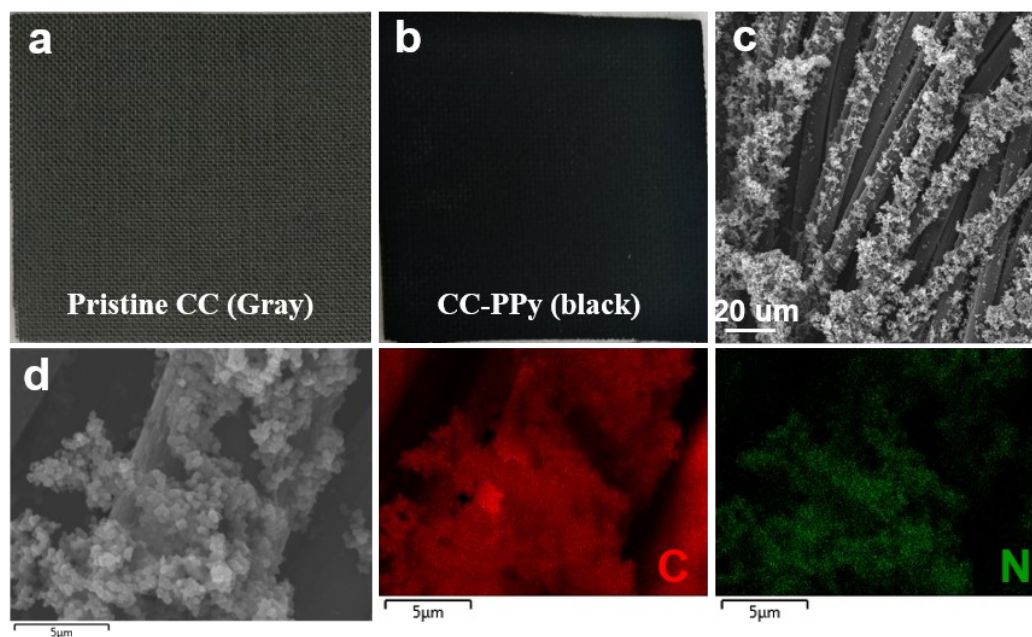


Figure S2. Digital photos of pristine (a) CC and (b) CC–PPy composites. (c, d) SEM images and corresponding elemental mappings of C and N elements.

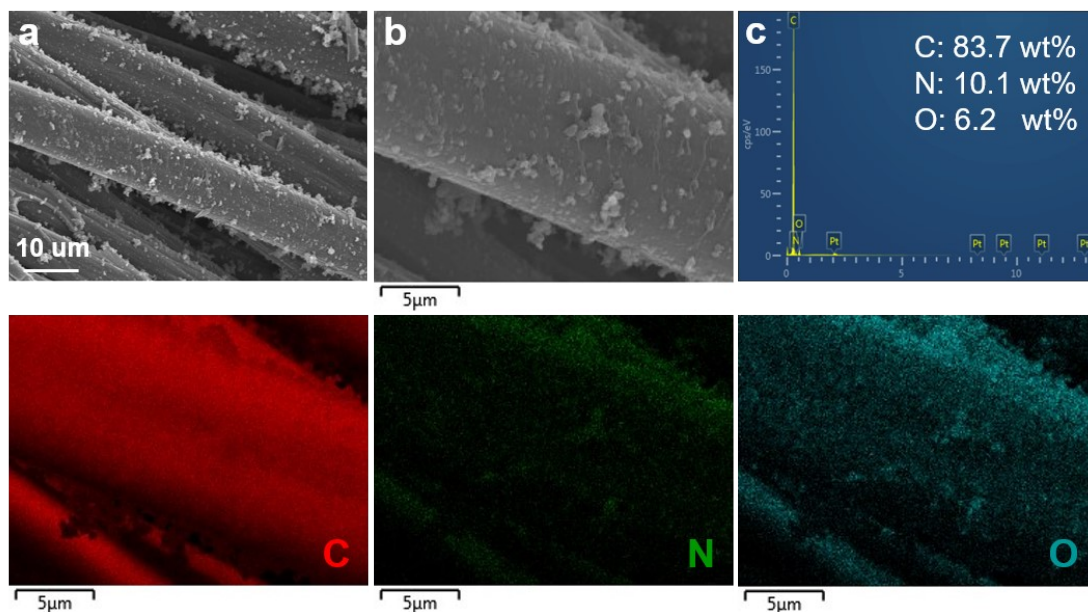


Figure S3. (a, b) SEM images of CC-PPy-(CH₂)₄-BDC-NH₂ and corresponding elemental mappings of C, N, and O elements. (c) EDS analysis of C, N, and O elements.

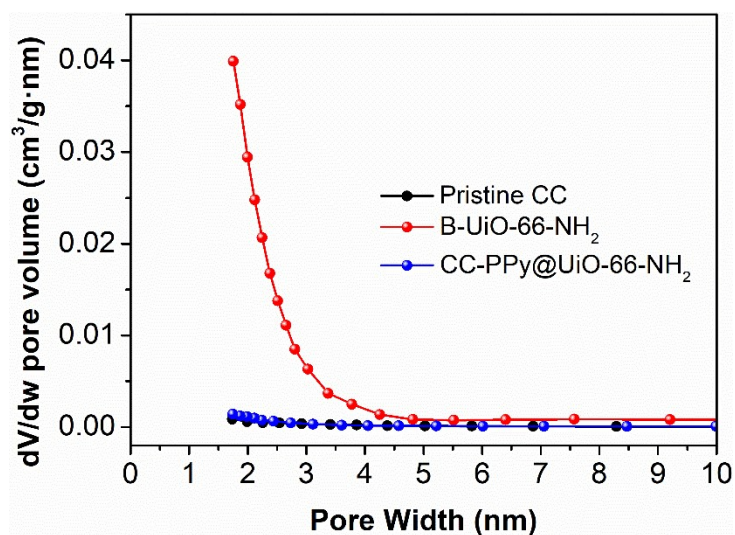


Figure S4. Pore size distribution of pristine CC, B-UiO-66-NH₂, and CC-PPy@UiO-66-NH₂ based on the Barrett–Joyner–Halenda (BJH) model.

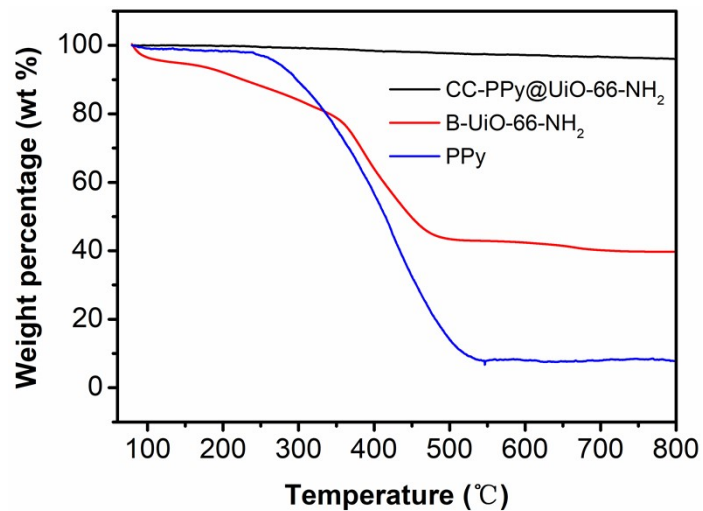


Figure S5. TG curves of B-UiO-66-NH₂ and CC-PPy@UiO-66-NH₂ at N₂ flow with a heating rate of 5 °C min⁻¹.

PPy is stable before 253 °C, and it can maintain 85% of its initial weight at 300 degrees.

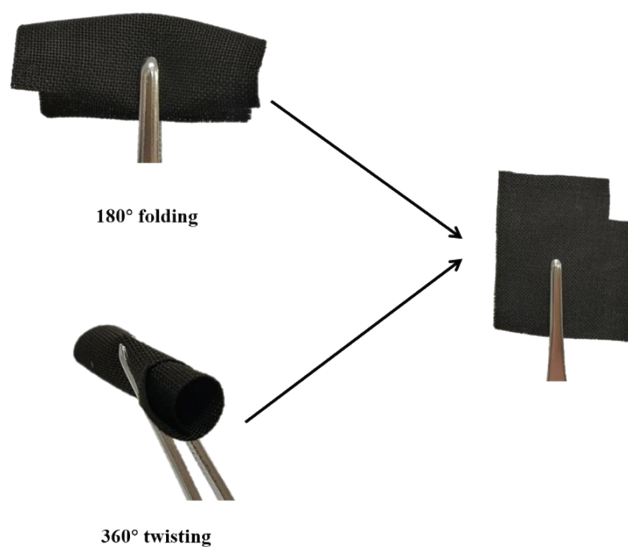


Figure S6. The folding and twisting tests of CC-PPy@UiO-66-NH₂ hybrid membrane.

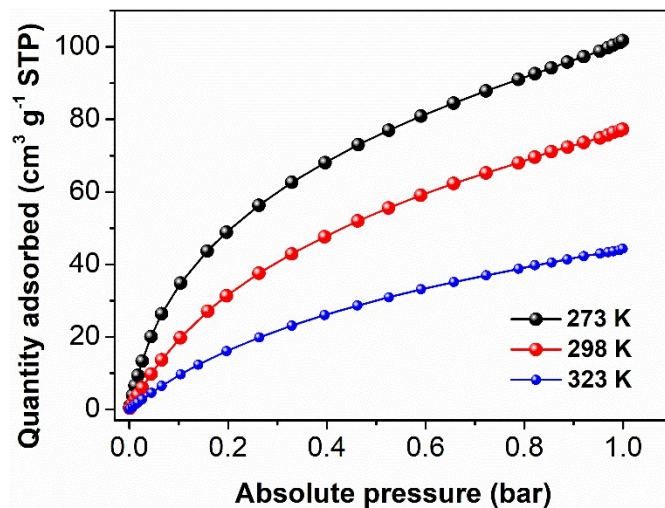


Figure S7. CO₂ adsorption isotherms of B-UiO-66-NH₂ at 273, 298, and 323 K.

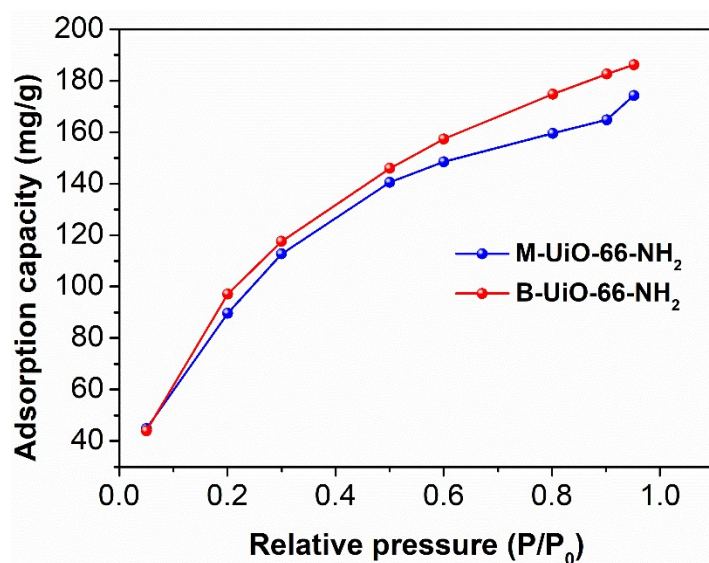


Figure S8. Adsorption capacity of M-UiO-66-NH₂ and B-UiO-66-NH₂ measured at different relative pressure.

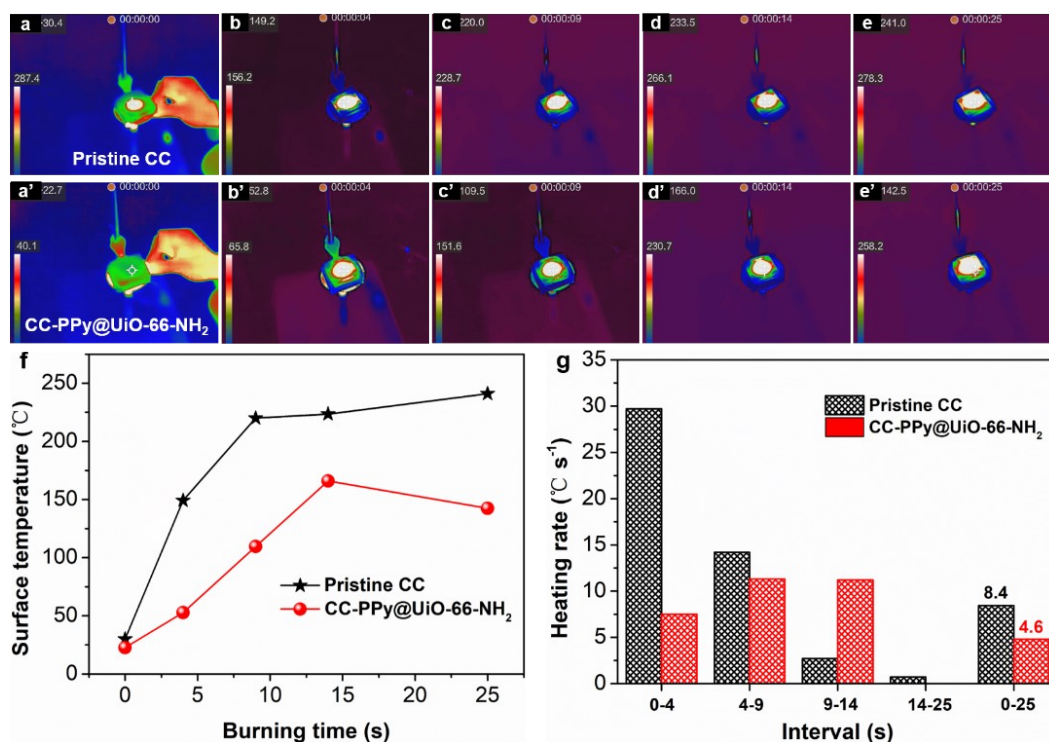


Figure S9. Infrared thermal imaging views of (a-e) pristine CC and (a'-e') CC-PPy@UiO-66-NH₂ hybrid membrane using a lighted candle as a heat source. (f) Details the surface temperature of the two samples versus the burning time of the candle. (g) Heating rate diagram for the specific intervals.

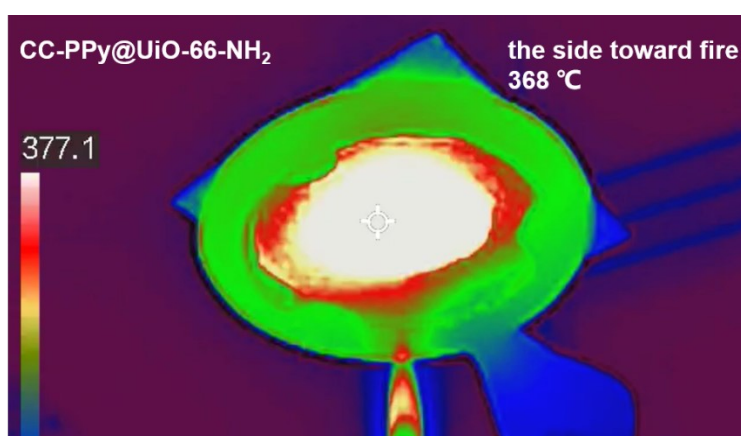


Figure S10. Infrared thermal imaging view of CC-PPy@UiO-66-NH₂ hybrid membrane by using a lighted candle.

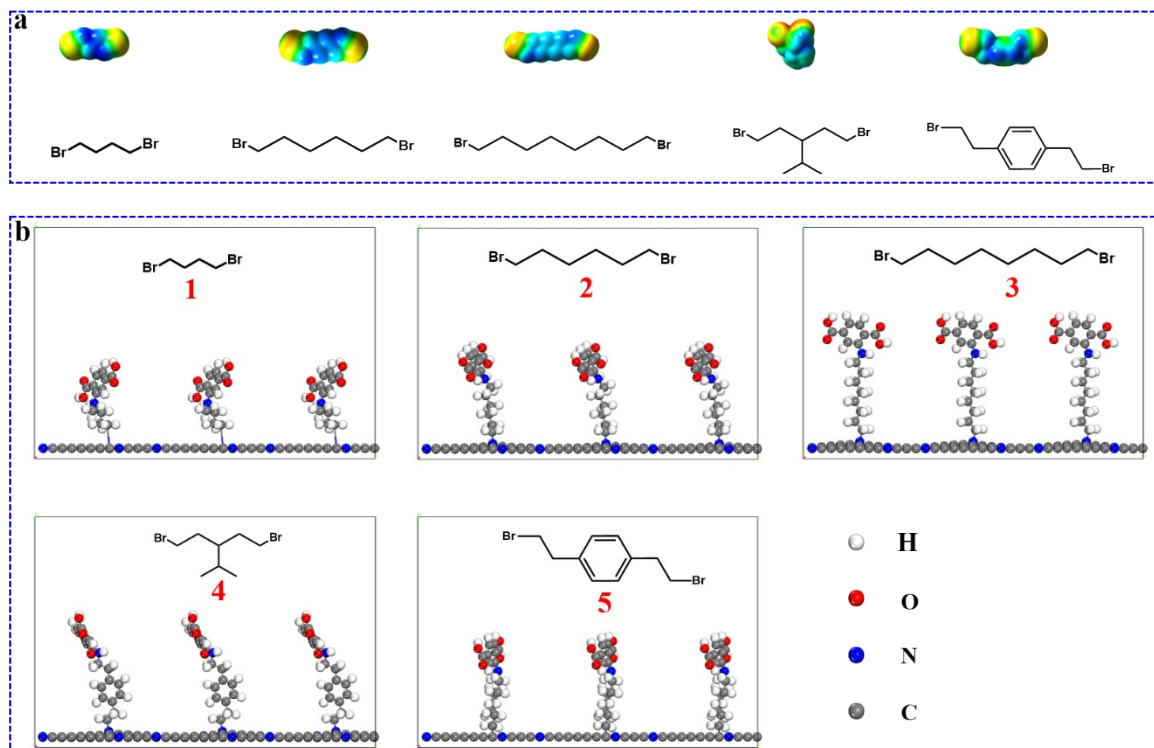


Figure S11. Theoretical calculation results. (a) Theoretical simulation of molecular electrostatic potentials of five bridged molecules represented by brominated hydrocarbons. (b) Spatial orientation molecular dynamics simulation of different brominated hydrocarbon bridged molecules grafted with terephthalic acid.