

Electronic Supplementary Information (ESI)

## **Metal–organic framework functionalized poly-cyclodextrin membranes confining polyaniline for charge storage**

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## **S1. Experimental section**

### **1. Chemicals**

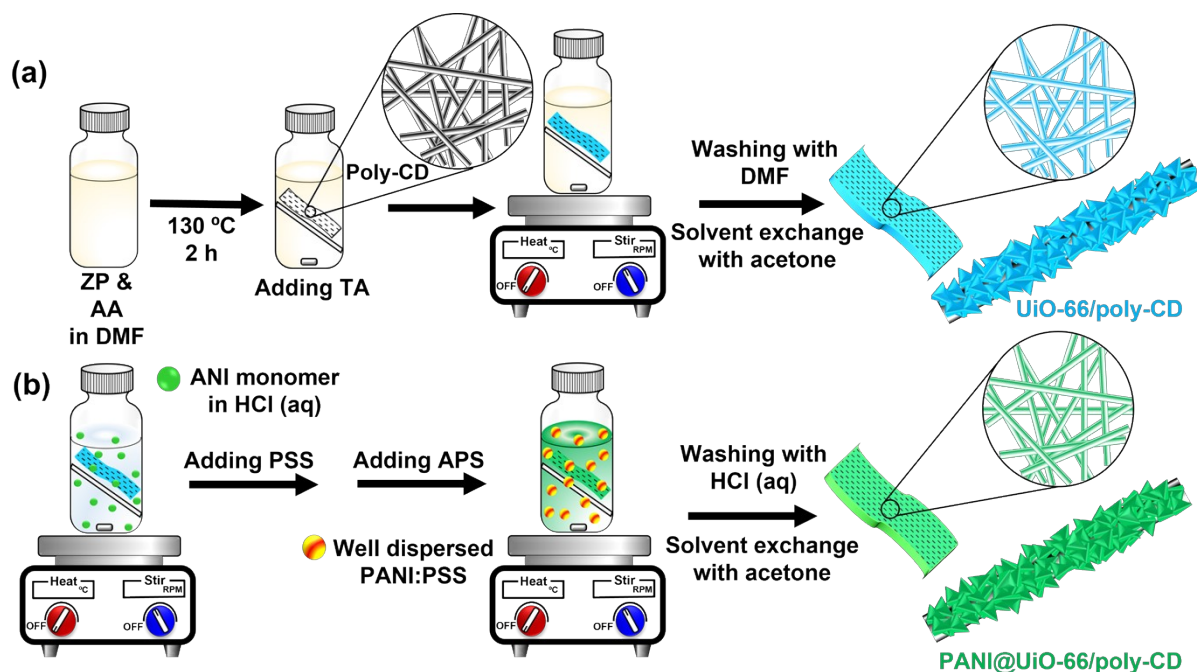
Hydroxypropyl- $\beta$ -cyclodextrin (HP $\beta$ CD), molar substitution:  $\sim 0.6$ ), was obtained from Wacker Chemie AG, Germany. 1,2,3,4-butanetetracarboxylic acid (BTCA, 99%), sodium hypophosphite hydrate (SHP,  $\sim 95\%$ ), zirconium(IV) propoxide solution (ZP, 70 wt.% in 1-propanol), terephthalic acid (TA, 99%), aniline (ANI,  $\geq 99.5\%$ ), ammonium persulfate (APS,  $\geq 98\%$ ), and poly(sodium 4-styrenesulfonate) (PSS, average MW = 70,000) were purchased from Sigma–Aldrich. Nitric acid ( $\geq 65\%$ ), acetic acid (AA,  $\geq 99.8\%$ ), and sulfuric acid (95.0–98.0%) were purchased from Honeywell Fluka. Hydrochloric acid (HCl, 36.5–38.0%) was purchased from J. T. Baker. The solvents such as dimethylformamide (DMF,  $\geq 99.8\%$ ), ethanol ( $\geq 99.5\%$ ), and acetone ( $\geq 99.0\%$ ) were purchased from ECHO Chemical Co., Ltd., Taiwan. All the chemicals were used as received without any further treatments. Deionized water was used as the water source throughout the work.

### **2. Preparation of electrospun crosslinked poly-cyclodextrin (CD) fibrous membranes**

Electrospinning poly-CD fibres was achieved similar to the reported procedure by a slight modification.<sup>1</sup> HP $\beta$ CD (280% w/v) was dissolved in deionised water under the continuous stirring at 50 °C for 4 h. After the complete dissolution, BTCA (20% w/w, according to CD) and SHP (2% w/w, according to CD) were added to the HP $\beta$ CD solution. The mixture was further stirred at 50 °C for 2 h to achieve complete dissolution. The solution was degassed for half an hour to remove all the bubbles from the solution. Then, it was transferred into a plastic syringe (1 mL) equipped with an 18 G blunt needle. The syringe was placed horizontally on a syringe pump (KD Scientific, KDS-101), and fibres were collected on aluminium foil with the help of a high voltage power supply (You-Shang Tech. Cor.). The electrospinning was performed with the following parameters. Applied voltage: 20-21 kV, tip-to-collector distance: 10-12 cm and the solution flow rate: 0.5-1.0 mL/h. The electrospinning was carried out at 22–24 °C at 55-60% relative humidity. Then, the electrospun fibres were detached from the aluminium surface with the help of a tweezer. Finally, a self-standing water-soluble fibrous membrane of (HP $\beta$ CD/BTCA/SHP) was placed in an oven at 175 °C for 4 h to obtain crosslinked poly(HP $\beta$ CD/BTCA/SHP) fibrous membrane. The term poly-CD membrane was used to define electrospun crosslinked poly(HP $\beta$ CD/BTCA/SHP) fibrous membrane in further studies and discussion.

### 3. Growth of UiO-66 nanocrystals on poly-CD membranes

UiO-66 nanocrystals were grown on the poly-CD membrane at room temperature by following the procedure slightly modified from those reported in previous studies.<sup>2,3</sup> Prior to the crystal growth, 86  $\mu\text{L}$  of ZP, 8.4 mL of DMF, and 4.8 mL of AA were added into a 20 mL scintillation glass vial, and the vial sealed with a poly(tetrafluoroethylene) (PTFE)-lined polyurethane cap was placed in an oven at 130  $^{\circ}\text{C}$  for 2 h; a clear solution with a light yellow colour could be obtained. After cooling down the obtained solution to room temperature, 90 mg of TA and a stir bar (length = 15 mm; diameter = 6 mm) were added into the solution. It should be noticed that to prevent the stir bar from hitting the poly-CD membrane during the MOF growth, a glass slide with the size of 3 cm  $\times$  1.5 cm was then placed into the vial in the slanting position above the stir bar. Thereafter, poly-CD membrane (2 cm  $\times$  1 cm) was carefully placed into the solution above the glass slide, and the mixture was stirred at 120 rpm for 20 h at room temperature. The resulting membrane was then removed from the suspension by a tweezer, rinsed with DMF for several times, and immediately immersed in 10 mL of acetone. The membrane was then washed with 10 mL of acetone for three times with the immersing periods of 2 h, overnight, and 2 h in between, respectively, in order to allow the completion of the solvent-exchange process. Thereafter, the obtained membrane was carefully removed from acetone by a tweezer and placed on a glass slide, and was then dried in an oven at 60  $^{\circ}\text{C}$  overnight; the membrane of UiO-66/poly-CD was thus obtained. The experimental procedure is illustrated in Figure S1(a). For comparison, the powder of UiO-66 nanocrystals was also synthesized for characterization by following the procedure reported previously.<sup>3</sup>



**Figure S1.** Schematic representations for the experimental procedures regarding the (a) growth of UiO-66 nanocrystals on the poly-CD membrane and (b) selective polymerisation of ANI within the UiO-66 crystals to prepare the PANI@UiO-66/poly-CD membrane.

#### 4. Polymerisation of ANI in the presence of UiO-66/poly-CD or poly-CD membranes

Synthesis of the PANI solely confined within the pores of a Zr-MOF has been demonstrated in our recent work for powder samples,<sup>4</sup> and a similar procedure with slight modifications was used here for membranes. Initially, 5 mL of deionized water, 0.207 mL of concentrated HCl, 19  $\mu$ L of ANI, and a small magnetic stir bar (length = 10 mm; diameter = 3 mm) were added into a 20 mL glass vial. A glass slide with the size of 2 cm  $\times$  1.5 cm along with one UiO-66/poly-CD membrane above it was then immersed in the obtained solution; this setup is quite similar to that used for the growth of UiO-66 on the poly-CD membrane mentioned in the previous part. The solution was allowed to stir at 1000 rpm for 30 min to fully acidize the ANI monomer. After that, 0.167 g of PSS was dissolved in 5 mL of deionized water by sonication, and the obtained PSS solution was added into the ANI solution under stirring. The solution was allowed to stir for 6 h. Thereafter, 0.052 g of APS was dissolved in 3.33 mL of deionized water, and the obtained solution was added slowly drop by drop into the solution containing PSS and ANI to initiate the polymerisation, with a slow injecting rate of 1 mL/min under stirring. The solution was kept aside under constant stirring at 1000 rpm overnight, and a homogeneous PANI:PSS polymer solution with a dark green colour was obtained. Then, this

polymer solution was discarded, and the obtained membrane was rinsed with 0.2 M HCl aqueous solutions for several times to completely remove the residual PANI:PSS and other reagents. The resulting membrane was further immersed in 10 mL of 0.2 M HCl aqueous solution and kept for 1 h before the last time of rinsing to ensure the complete removal of PANI that was not attached on the membrane. Finally, the membrane was immersed in 10 mL of acetone and washed with acetone for three times to complete the solvent exchange, with the immersing periods of 2 h, overnight, and 2 h in order, respectively. The resulting membrane with a uniform light green colour was carefully removed from acetone by a tweezer and placed on a glass slide, and was then dried in an oven at 60 °C overnight; the membrane of PANI@UiO-66/poly-CD was thus obtained. The experimental procedure is illustrated in Figure S1(b). For comparison, the same polymerisation process was also performed by replacing the UiO-66/poly-CD with the pristine poly-CD membrane, and the obtained membrane after polymerisation was named as “PANI/poly-CD”.

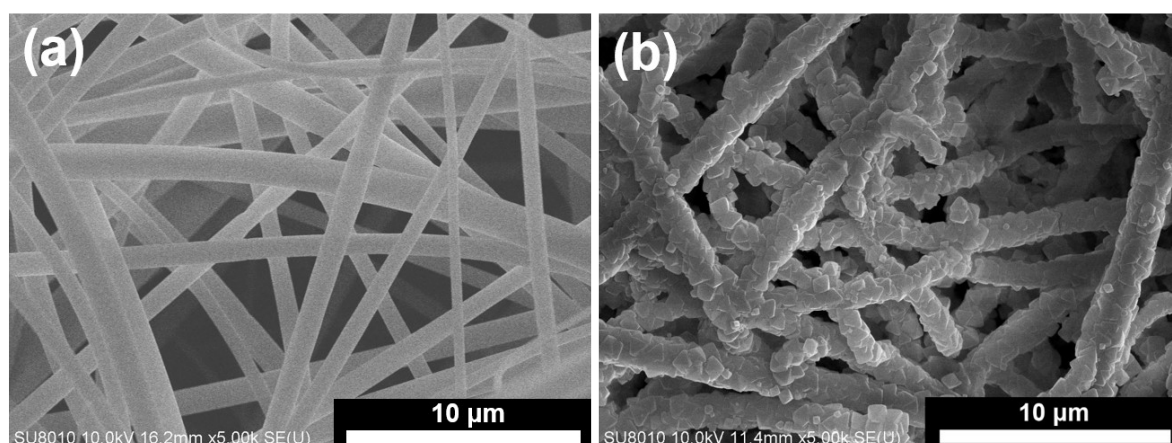
## 5. Instrumentations

Grazing incidence X-ray diffraction (GIXRD) patterns of various membranes were collected by a D8 DISCOVER system (Bruker, Germany) at room temperature. Scanning electron microscopic (SEM) images were collected by using a SEM SU-8010 (Hitachi). Energy-dispersive X-ray spectroscopic (EDS) elemental analysis was performed on the same SEM instrument. Nitrogen adsorption-desorption isotherms were collected by an ASAP 2020 (Micromeritics). Prior to each nitrogen adsorption-desorption experiment, the membrane sample was cut into small pieces and degassed at 60 °C. Fourier-transform infrared spectroscopy (FTIR) was investigated by using a Nicolet 6700 (Thermo Scientific). Thermogravimetric analysis (TGA) was performed by using a TGA4000 (Perkin Elmer) in a nitrogen flow at a heating rate of 10 °C /min.

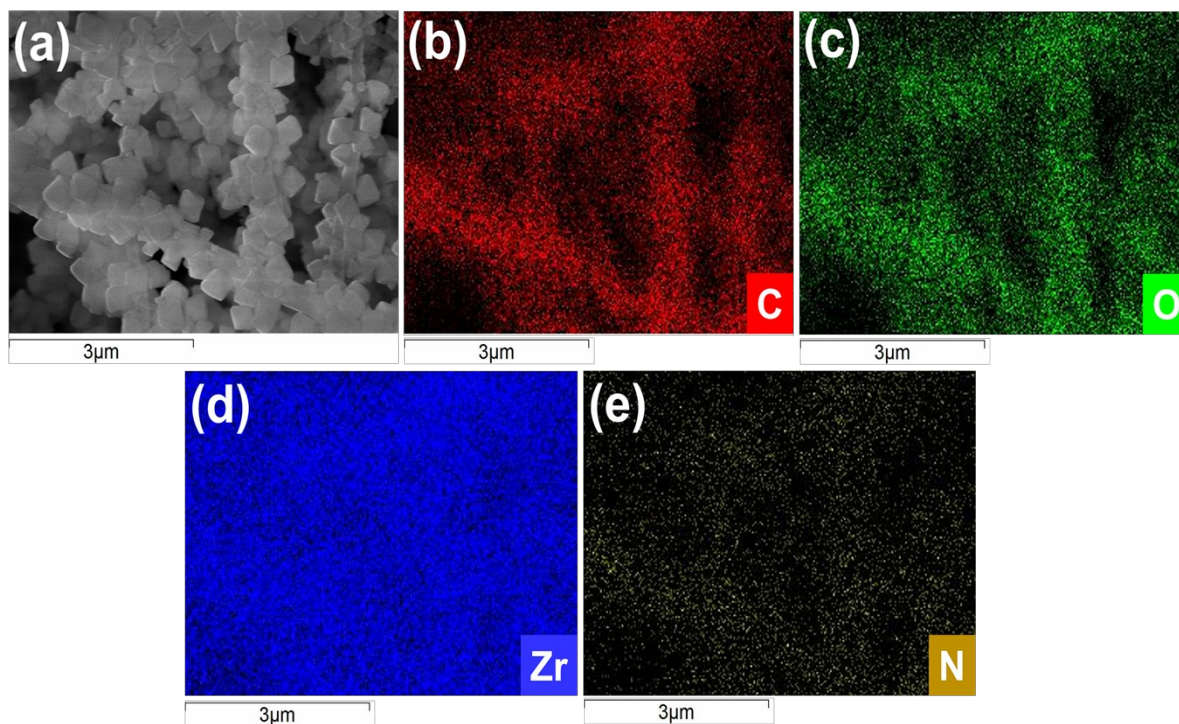
All electrochemical measurements were performed by using a CHI6273E (CH Instruments Inc.) at room temperature. The standard three-electrode setup was employed, with a platinum wire as the counter electrode and an Ag/AgCl/NaCl (3 M) as the reference electrode. A single-compartment cell with 20 mL of 0.2 M HCl aqueous solution was used for every electrochemical test. The membrane with a size of 1 cm × 1 cm was sandwiched between two fluorine-doped tin oxide (FTO) conducting glass electrodes (7 Ω/sq.; 1 cm × 5 cm and 1 cm × 6 cm in size, respectively) by Elliot folder to prepare the working electrode for electrochemical

measurements. Electrochemical impedance spectroscopy (EIS) measurements were performed with the same three-electrode system at the applied potential equal to the formal potential of PANI@UiO-66/poly-CD obtained from its CV curve shown in Figure 3(a) of the main text, *i.e.*, +0.37 V vs. Ag/AgCl/NaCl (3 M). The amplitude of 20 mV and a frequency range of 1 MHz-0.01 Hz were used for collecting EIS data.

## S2. Additional data for materials characterization



**Figure S2.** Low-magnification SEM images of (a) poly-CD and (b) UiO-66/poly-CD.



**Figure S3.** (a) SEM image of PANI@UiO-66/poly-CD. The corresponding EDS elemental mapping images for (b) carbon-C, (c) oxygen-O, (d) zirconium-Zr and (e) nitrogen-N.

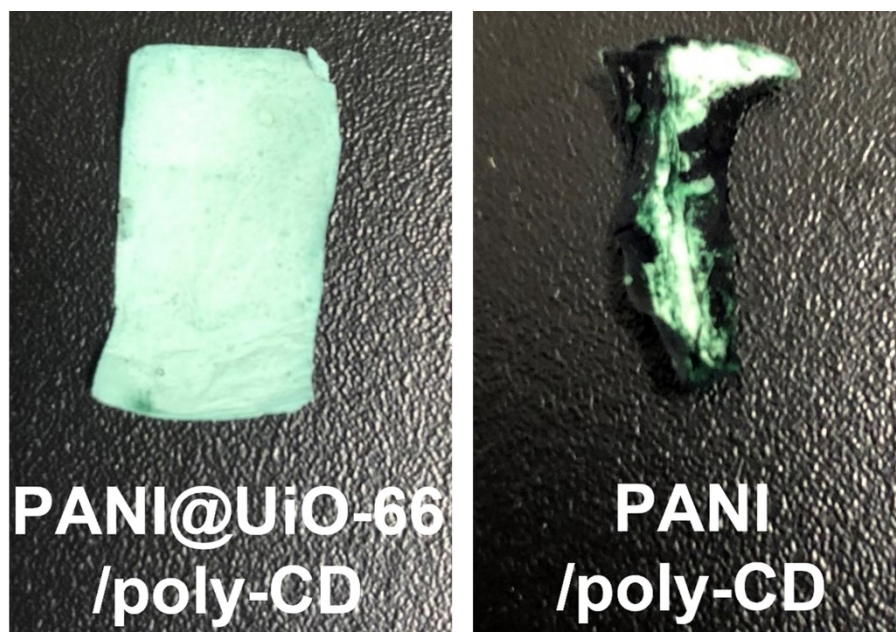


Figure S4. Photos of PANI@UiO-66/poly-CD and PANI/poly-CD.

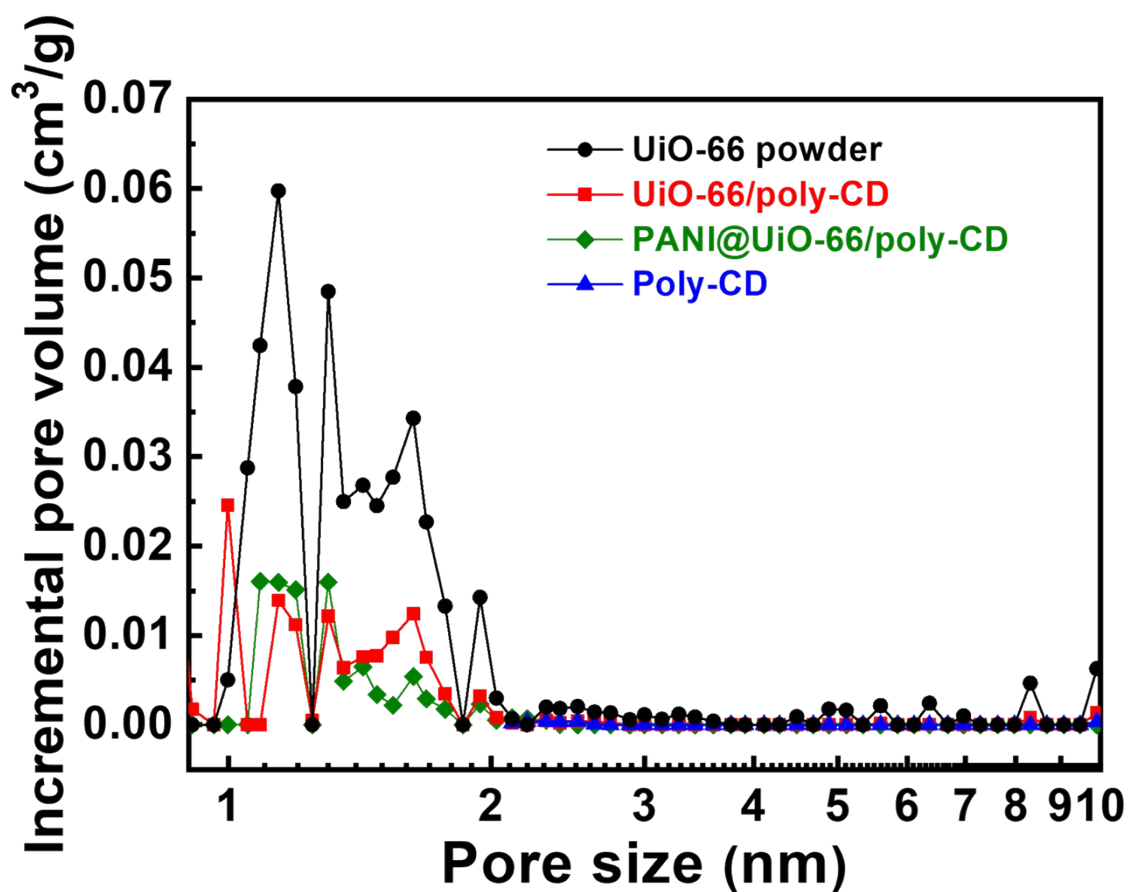


Figure S5. DFT pore size distributions of poly-CD, UiO-66/poly-CD, PANI@UiO-66/poly-CD, and UiO-66 powder.



FTIR spectra of poly-CD, UiO-66/poly-CD, and PANI@UiO-66/poly-CD are shown in Figure S6. The spectrum of poly-CD shows prominent absorption peaks located at  $1,035\text{ cm}^{-1}$  (C-O-C stretching),  $1,157\text{ cm}^{-1}$  (C-O stretching), and  $1,643\text{ cm}^{-1}$  (H-O-H bending), which are consistent with those reported for poly-CD in previous work.<sup>5</sup> The spectrum of UiO-66/poly-CD shows the similar absorption peaks of poly-CD along with additional major peaks located at  $1,400\text{ cm}^{-1}$ ,  $1,506\text{ cm}^{-1}$ , and  $1,581\text{ cm}^{-1}$ ; these peaks agree well with those originated from the symmetric vibration of O-C-O, C=C in the aromatic ring of the linker, and asymmetric vibration of O-C-O reported for UiO-66, respectively.<sup>6</sup> This result again confirms the successful growth of UiO-66 on the poly-CD membrane. On the other hand, for PANI@UiO-66/poly-CD, two additional peaks located at  $1,300\text{ cm}^{-1}$  and  $1,127\text{ cm}^{-1}$  can be observed in its FTIR spectrum, which correspond to the C-N/C-N<sup>+</sup> vibration and C-H bending of the quinoid ring present in PANI, respectively.<sup>4</sup> The FTIR finding here indicates that polyaniline is present within the membrane of PANI@UiO-66/poly-CD.

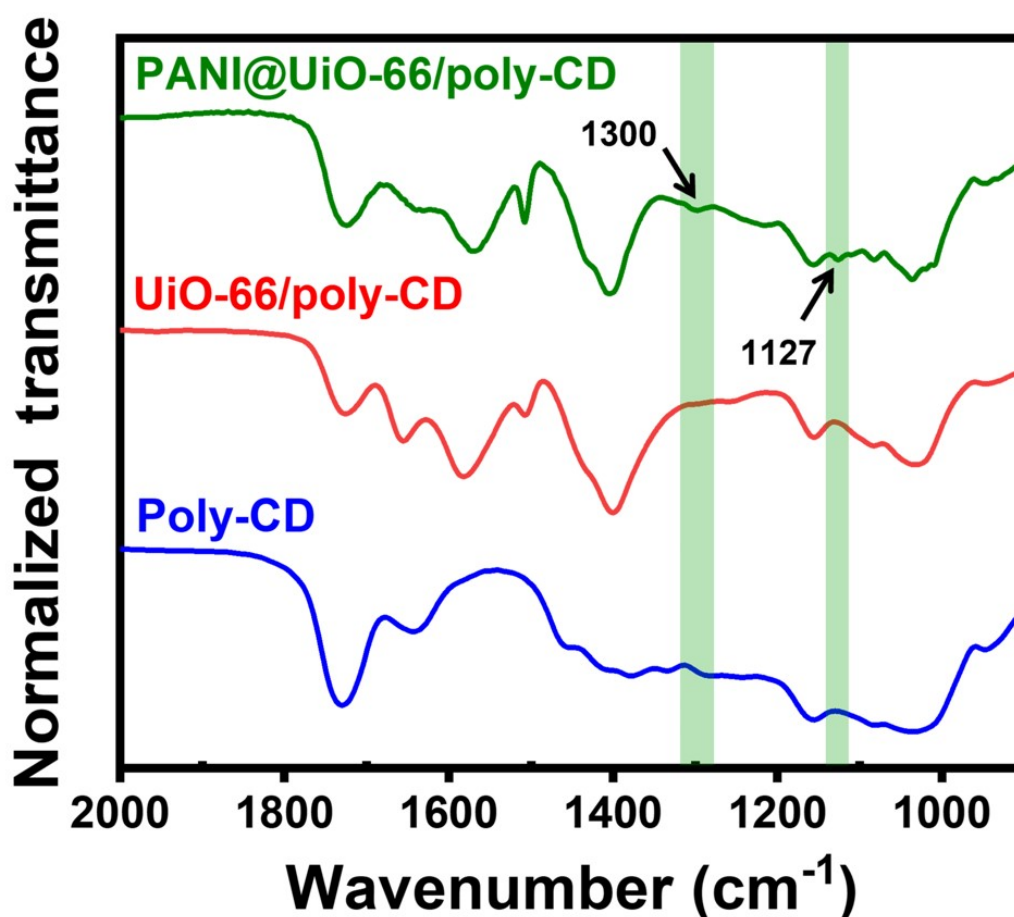
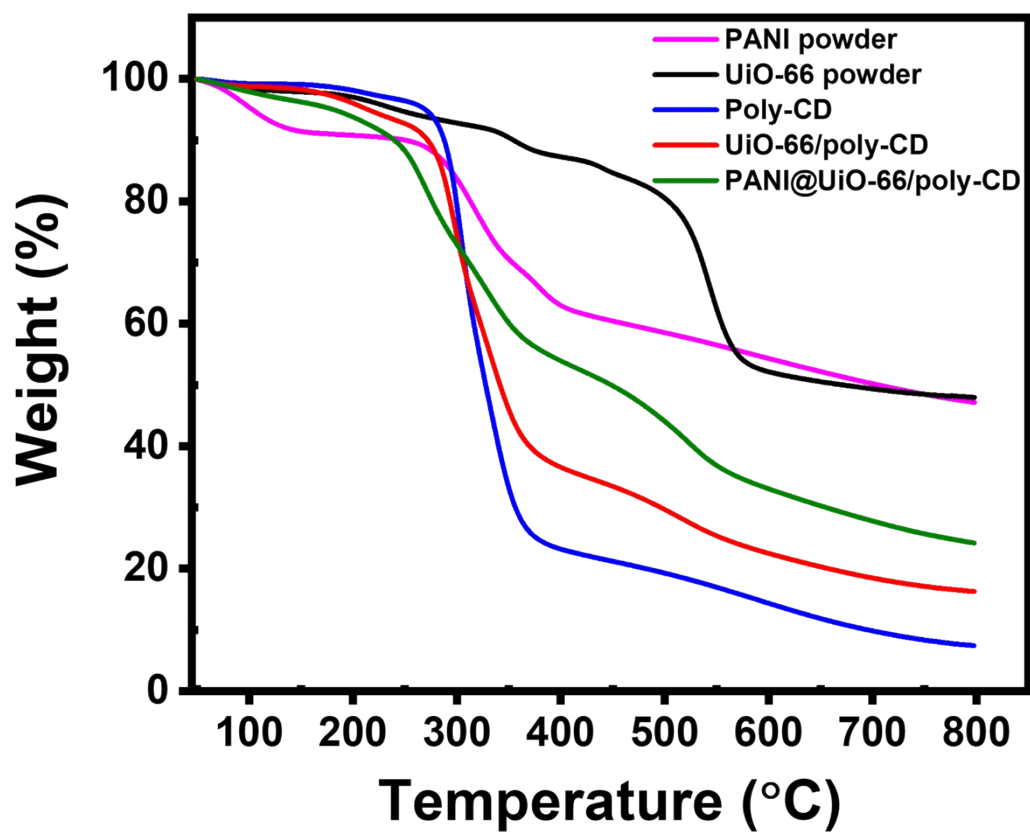


Figure S6. FTIR spectra of poly-CD, UiO-66/poly-CD, and PANI@UiO-66/poly-CD.

TGA was utilized to quantify the mass fraction of UiO-66 within UiO-66/poly-CD as well as the mass fraction of PANI within PANI@UiO-66/poly-CD, respectively. The referencing TGA samples, namely, “UiO-66 powder” and “PANI powder”, were synthesized by following the experimental procedures which are quite similar to those used in this study for membranes reported in our previous studies.<sup>4,7</sup> Figure S7 shows the TGA curves of PANI powder, UiO-66 powder, poly-CD, UiO-66/poly-CD, and PANI@UiO-66/poly-CD. The pristine poly-CD shows an obvious decomposition at around 300 °C, and its residual weight is 7.5% at 800 °C. For UiO-66 powder, the major decomposition of the MOF occurs at around 500 °C, and the residual weight at 800 °C is 48.0%. TGA curve of UiO-66/poly-CD reveals mixed characteristics from those of UiO-66 powder and poly-CD, with a residual weight of 16.3% at 800 °C. According to the residual weights at 800 °C in the TGA data, the mass fraction of UiO-66 present in the membrane of UiO-66/poly-CD was calculated as 21.6%. For the pristine PANI powder, its TGA curve shows the first weight loss before 150 °C and another major weight loss starting from around 300 °C, which are associated with the removal of oligomers/solvent molecules and the decomposition of polyaniline, respectively.<sup>8</sup> The residual weight for PANI powder is 47.1% at 800 °C in the TGA data. On the other hand, TGA curve of PANI@UiO-66/poly-CD reveals a residual weight of 24.2% at 800 °C. According to the residual weights of PANI powder, UiO-66/poly-CD, and PANI@UiO-66/poly-CD at 800 °C, the mass fraction of polyaniline present within PANI@UiO-66/poly-CD was determined as 25.8%.



**Figure S7.** TGA curves of poly-CD, UiO-66/poly-CD, PANI@UiO-66/poly-CD, UiO-66 powder, and PANI powder.

### S3. Additional electrochemical data

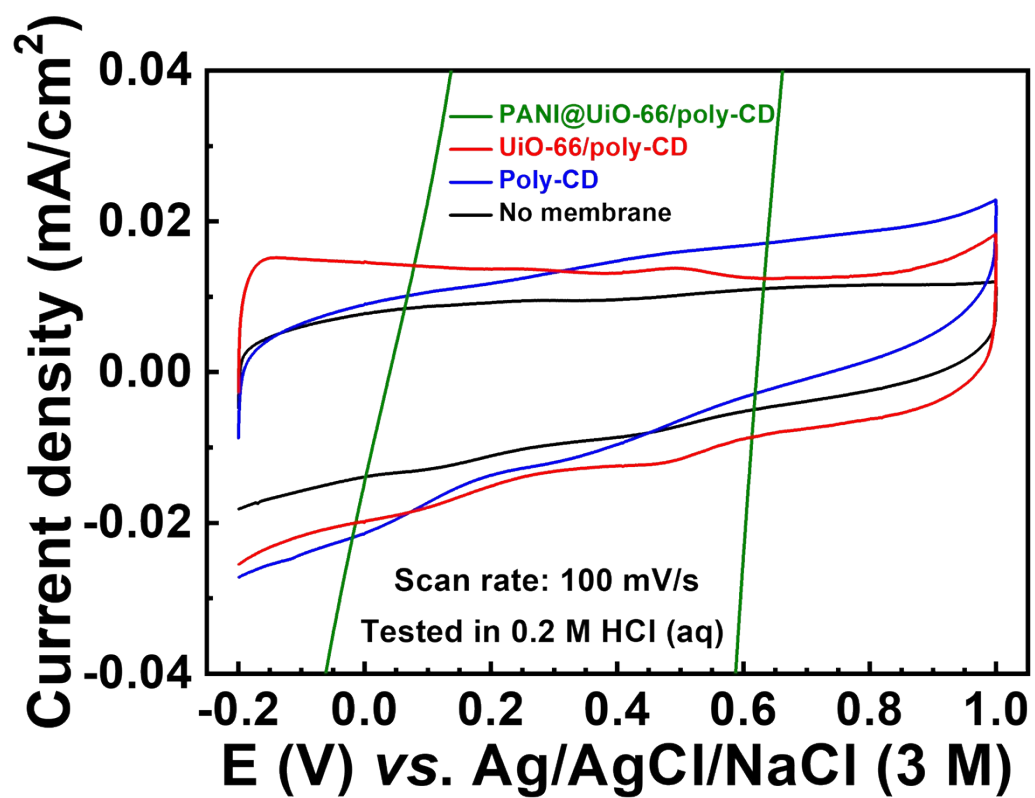
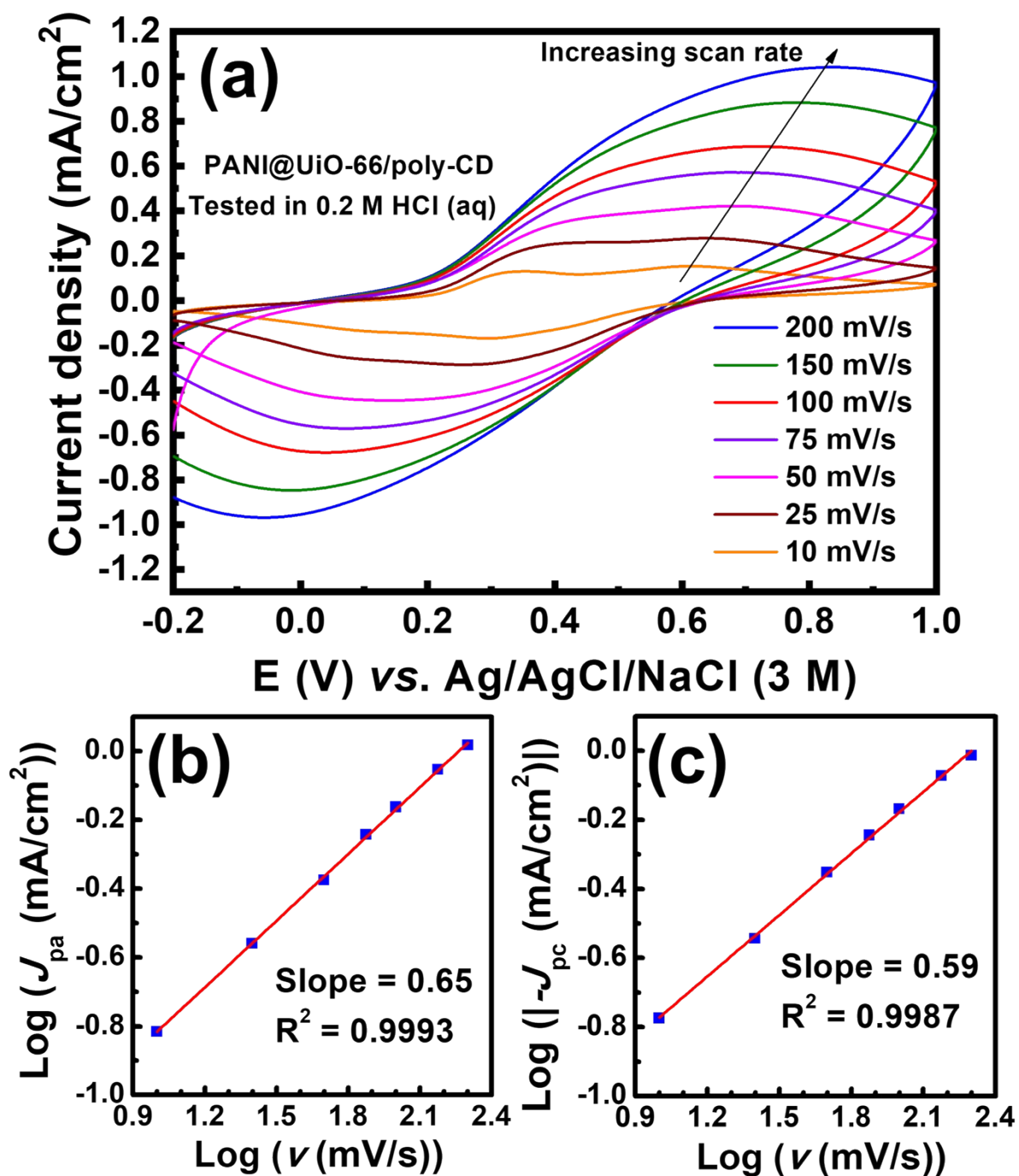
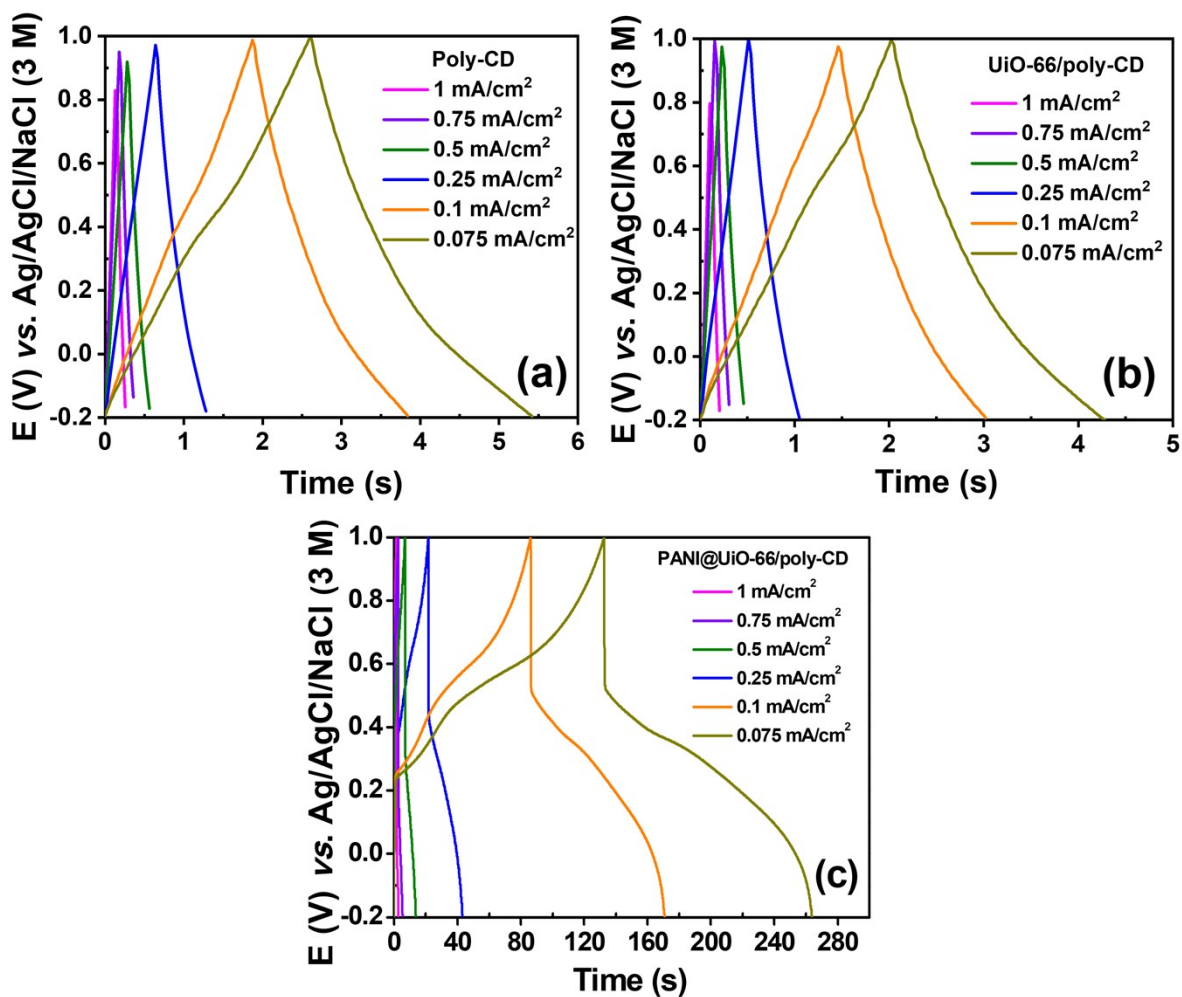


Figure S8. The magnified version of the CV curves shown in Figure 3(a) of the main text.

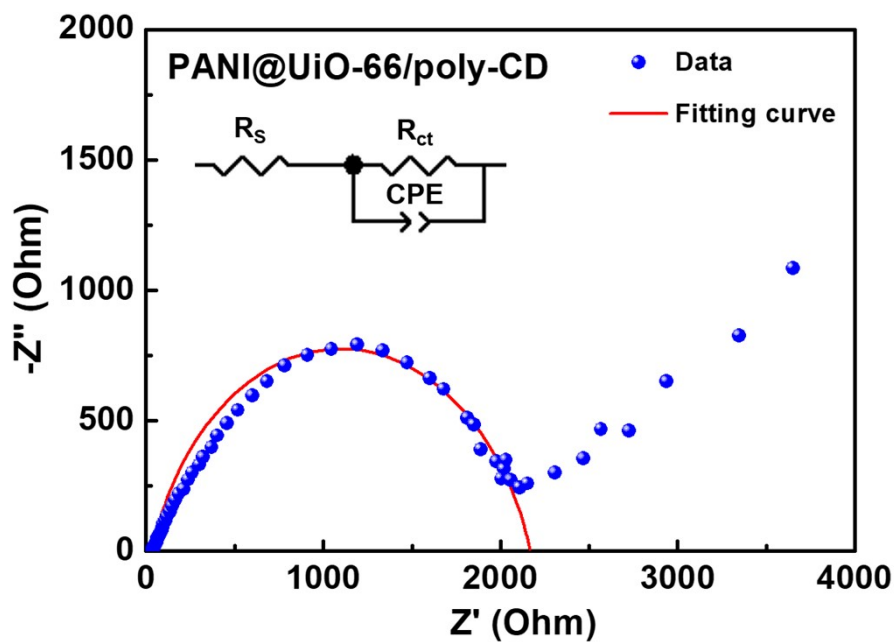


**Figure S9.** (a) CV curves of PANI@UiO-66/poly-CD collected at various scan rates ( $\nu$ ) in 0.2 M HCl (aq). Plots of (b)  $\log(\text{anodic peak current density } (J_{pa}))$  vs.  $\log(\nu)$  and (c)  $\log(|\text{cathodic peak current density } (J_{pc})|)$  vs.  $\log(\nu)$ , extracted from the data shown in (a).

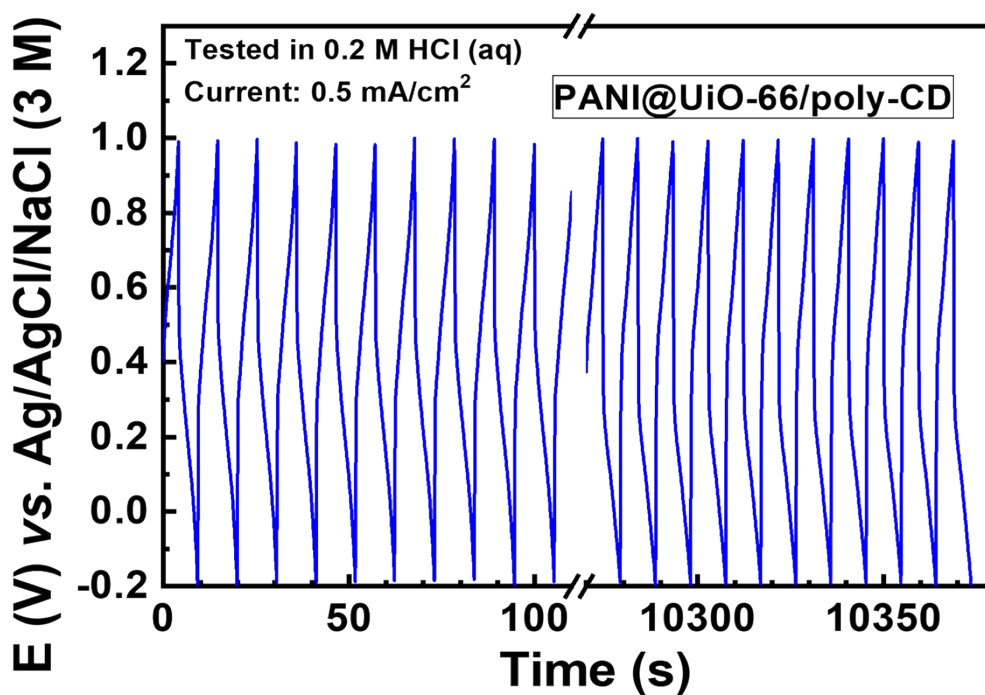


**Figure S10.** Charge-discharge curves of (a) poly-CD, (b) UiO-66/poly-CD and (c) PANI@UiO-66/poly-CD, collected at different charge-discharge current densities in the electrolyte of 0.2 M HCl (aq).

EIS measurements were also utilized to confirm the redox activity of the PANI@UiO-66/poly-CD membrane in the aqueous electrolyte containing 0.2 M of HCl. With the applied potential at the formal potential of the electrochemical reaction, the Nyquist plot shown in Figure S11 was obtained for PANI@UiO-66/poly-CD membrane. A well-defined semicircle can be observed in the data, which further confirms the Faradaic reaction occurring on the PANI@UiO-66/poly-CD membrane. The equivalent circuit containing the series resistance ( $R_s$ ), charge-transfer resistance ( $R_{ct}$ ) and constant phase element (CPE) was used to fit the EIS data within the relatively high frequency range,<sup>9, 10</sup> as shown in Figure S11. The obtained  $R_{ct}$  is 2170  $\Omega$ .



**Figure S11.** Nyquist plot of PANI@UiO-66/poly-CD measured in 0.2 M HCl (aq). The equivalent circuit used for fitting the EIS data is shown as the inset.



**Figure S12.** 1000-cycle charge-discharge curves of PANI@UiO-66/poly-CD collected at 0.5 mA/cm<sup>2</sup> in the electrolyte of 0.2 M HCl (aq).

**Table S1.** Capacitive performance of PANI@UiO-66/poly-CD compared with those of some previously reported MOF-based materials for supercapacitors.

Active material	Capacitive performance	Electrolyte	Reference
Ni <sub>3</sub> (HITP) <sub>2</sub> <sup>a</sup>	18 μF/cm <sup>2</sup> <sup>b</sup> (@0.05 A/g)	1 M TEABF <sub>4</sub> /ACN <sup>c</sup>	[11]
Polypyrrole-ZIF-67	2330 mF/cm <sup>2</sup> (@0.4 mA/cm <sup>2</sup> )	1 M Na <sub>2</sub> SO <sub>4</sub> (aq)	[12]
MOF-867 nanocrystals	5.09 mF/cm <sup>2</sup> (@0.88 mA/cm <sup>3</sup> )	1 M TEABF <sub>4</sub> /ACN <sup>c</sup>	[13]
Polyaniline-ZIF-67	35 mF/cm <sup>2</sup> (@0.05 mA/cm <sup>2</sup> )	3 M KCl (aq)	[14]
LSG/Ni-CAT MOF <sup>d</sup>	8.5 mF/cm <sup>2</sup> (@1 mA/cm <sup>2</sup> )	3 M LiCl (aq)	[15]
Mo@MOF-808	5.5 mF/cm <sup>2</sup> (@0.2 mA/cm <sup>2</sup> )	0.05 M MOPS (aq) <sup>e</sup>	[16]
Ce-MOF-808-20CNT	22.4 mF/cm <sup>2</sup> (@0.25 mA/cm <sup>2</sup> )	0.1 M Na <sub>2</sub> SO <sub>4</sub> (aq)	[17]
Mn-30CNT-UiO-66	4.9 mF/cm <sup>2</sup> (@0.05 mA/cm <sup>2</sup> )	0.1 M Na <sub>2</sub> SO <sub>4</sub> (aq)	[7]
Polyaniline/UiO-66-NH <sub>2</sub>	14 mF/cm <sup>2</sup> (@0.01 mA/cm <sup>2</sup> )	0.1 M LiBF <sub>4</sub> /propylene carbonate	[4]
PANI@UiO-66/poly-CD	8.2 mF/cm <sup>2</sup> (@0.075 mA/cm <sup>2</sup> )	0.2 M HCl (aq)	This work

<sup>a</sup> HITP = 2,3,6,7,10,11-hexaiminotriphenylene

<sup>b</sup> Normalized by BET surface area

<sup>c</sup> TEABF<sub>4</sub> = tetraethylammonium tetrafluoroborate; ACN = acetonitrile

<sup>d</sup> LSG = laser scribed graphene; CAT = catecholate

<sup>e</sup> MOPS = 3-(N-morpholino)propanesulfonic acid



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