

Supporting Information

Phenediamine bridging phthalocyanine-based covalent organic framework polymers as anode materials for lithium- ion batteries

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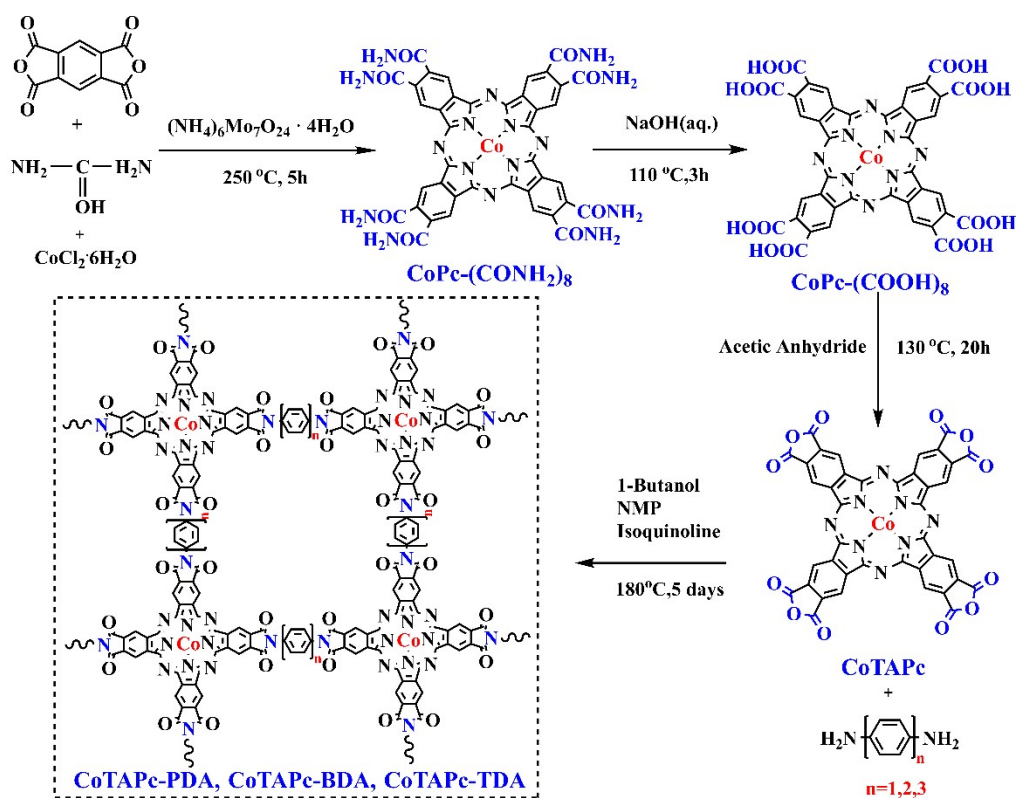


Fig. S1. Synthesis route of CoTAPc-PDA , CoTAPc-BDA and CoTAPc-TDA COFs

S1. Synthesis Synthetic procedures

S1.1 Octacarboxamide-based cobalt phthalocyanine ($\text{CoPc}-(\text{CONH}_2)_8$)

21.81 g (0.1 mol) of pyromellitic dianhydride, 60.04 g (1 mol) of urea, 9.52 g (0.04 mol) of cobalt chloride hexahydrate, and 0.39 g (2 mmol) of ammonium molybdate are placed in a mortar, ground, crushed, and mixed well to obtain a light green moist solid in a 1000 mL beaker. The beaker is heated in a high temperature oven at $250\text{ }^\circ\text{C}$ and held for 5 h. During the heating process, a large amount of pungent ammonia gas was released. After the temperature of the high-temperature oven automatically dropped to room temperature, the beaker is removed and a black-green fluffy product is obtained.

The product in the beaker is taken out, crushed and ground into powder in a mortar. Then the powder was placed in a 1000 mL beaker, and 6 M concentrated HCl solution and methanol was added, heated and stirred for 3 h at $110\text{ }^\circ\text{C}$. After that, the mixed solution is extracted and filtered, and the obtained filtrate is washed with distilled water until the filtrate flowing is colorless and transparent. After washing

once more with methanol, it was dried in a vacuum drying oven for 12 h at 90 °C, to obtain octacarboxamide-based cobalt phthalocyanine.

S1.2 Cobalt octacarboxylate phthalocyanines (CoPc-(COOH)₈)

The dried product was added to a beaker containing 200 mL of 100% sodium hydroxide solution. Heat and stir at 110 °C, when irritating ammonia overflows. Continue heating until no irritating gas overflows and stop heating and stirring. The mixed solution was adjusted with concentrated HCl solution to obtain a pH=2 and left for 12 h. After stratification, the upper clear layer is aspirated with a dropper, and the lower turbid layer is filtered. After the filtration, the residue is washed with distilled water and methanol once, respectively. The residue was then stored in an electric vacuum oven at 90 °C overnight.

The dried filtrate was put into a 500 mL three-neck flask, and 400 mL of 20% sodium hydroxide was added, the mixture was reacted at 90 °C until no ammonia gas is produced. After that, the solution was diluted 5 times, centrifuged for 5 min, and the upper layer is titrated to pH=2 with hydrochloric acid, left for several minutes, and the upper clear layer is decanted and centrifuged to obtain the solid product. The solid product was washed with acetone, anhydrous ethanol and distilled water in turn to remove impurities and dried in an vacuum oven to obtain CoPc-(COOH)₈.

S1.3 Tetra anhydride cobalt phthalocyanine (CoTAPc)

A mixture of CoPc-(COOH)₈ (2.12 g, 2.30 mmol) and acetic anhydride (45.0 mL) was heated to reflux for 10 h. After the reaction mixture was cooled, it was diluted with acetyl chloride (20 mL) and filtered. The obtained solid was washed with acetyl chloride and dried under vacuum at 80 °C, thus the product of CoTAPc was obtained.

S1.4 CoTAPc-PDA, CoTAPc-BDA and CoTAPc-TDA.

PDA or BDA or TDA (0.04 mmol), CoTAPc (17.0 mg, 0.02 mmol), NMP (0.5 mL), 1-butanol (0.5 mL) and isoquinoline (0.05 mL) were added to a three-necked flask, and the mixture is sonicated for 10 min and then heated at 180 °C for 5 days with nitrogen protection. After the reaction was cooled to room temperature, the solid was separated by centrifugation and washed sequentially with DMF, NMP and acetone, and the product was collected and dried under vacuum at 100 °C overnight to

obtained the black-green products of **CoTAPc-PDA**, **CoTAPc-BDA** and **CoTAPc-TDA**.

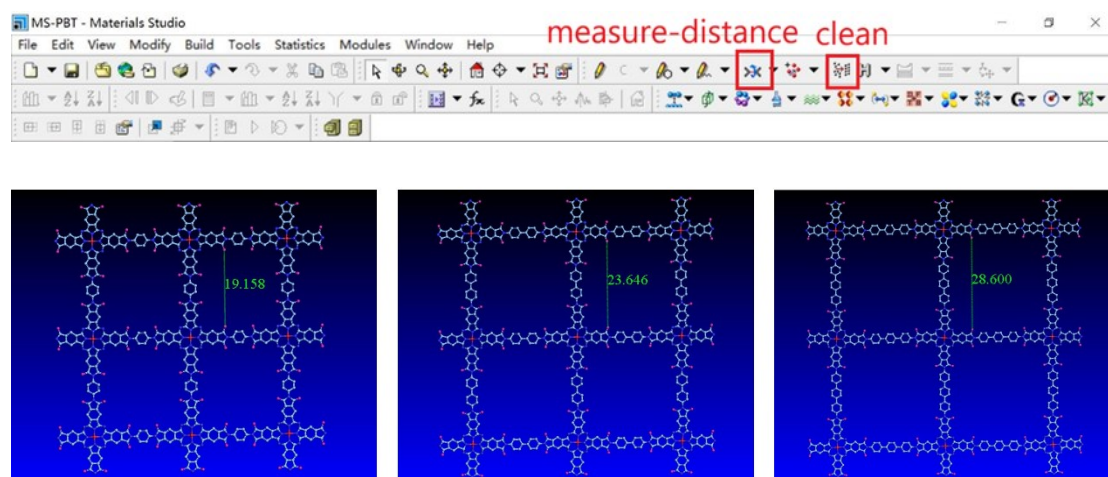


Fig. S2. Diameter diagram of CoTAPc-PDA, CoTAPc-BDA and CoTAPc-TDA COFs predicted by Material Studio (the default length unit of the MS software is Å). The values predicted by Material Studio are **1.9158nm**, **2.3646nm**, and **2.8600nm**, respectively.

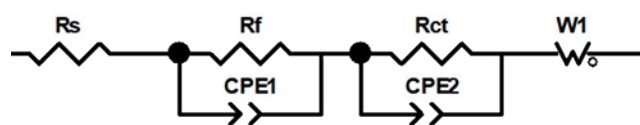


Fig. S3. Equivalent circuit models used to fit the EIS data.

Table S1. List of EIS fitting parameters for the CoTAPc-P/B/TDA electrodes

Samples	Cycle number	R_s/Ω (error/%)	R_f/Ω (error/%)	R_{ct}/Ω (error/%)	W_1/Ω (error/%)
CoTAPc-PDA	0	10.74 (4.11)	75.51 (4.91)	406.20 (4.63)	0.62 (1.53)
	50	5.03 (5.22)	15.37 (5.85)	128.30 (1.53)	0.65 (1.15)

	100	7.39 (3.74)	6.02 (8.40)	75.51 (3.26)	0.37 (0.26)
	300	6.66 (1.30)	8.25 (2.64)	72.01 (1.09)	0.63 (1.03)
	500	3.31 (4.69)	7.33 (9.69)	64.85 (2.20)	0.38 (1.41)
	0	5.61 (5.88)	44.50 (17.37)	381.70 (7.74)	0.47 (1.52)
	50	9.25 (2.46)	24.08 (2.49)	98.89 (6.22)	0.40 (7.26)
CoTAPc-BDA	100	5.88 (6.05)	28.51 (13.99)	87.52 (6.96)	0.34 (1.46)
	300	5.05 (6.15)	14.80 (5.96)	76.99 (3.40)	0.68 (0.47)
	500	6.08 (6.75)	13.78 (6.77)	60.46 (3.34)	0.34 (0.70)
	0	8.86 (5.84)	17.08 (7.74)	272.40 (1.65)	0.56 (0.37)
	50	6.63 (5.06)	15.99 (0.79)	113.30 (5.22)	0.60 (2.07)
CoTAPc-TDA	100	4.33 (3.70)	10.55 (2.44)	99.90 (2.26)	0.33 (0.76)
	300	2.05 (1.88)	6.77 (13.06)	74.05 (2.49)	0.35 (1.33)
	500	2.28 (5.84)	8.05 (12.23)	56.22 (7.53)	0.40 (0.52)

R_s is the contact and transfer impedance between the lithium ion in the electrolyte and the device such as the cell shell; R_f is the interfacial impedance caused by the solid electrolyte interface (SEI) film; R_{ct} is the charge transfer impedance during the electrochemical reaction, and W_1 denotes the Warburg impedance associated with the diffusion of Li^+ in the organic electrode

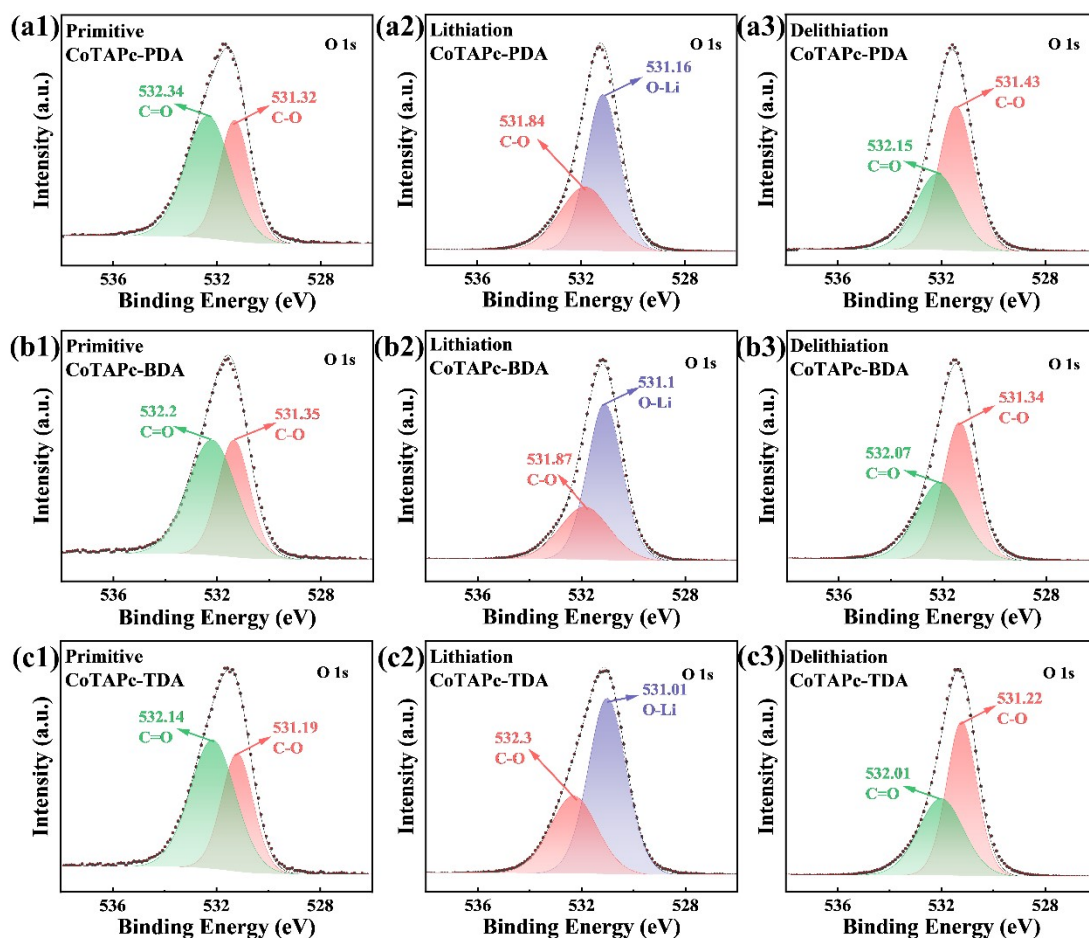


Fig. S4. The discharge (lithium insertion) and charge (lithium extraction) curves of NA-NiPc, PPDA-NiPc and DAB-NiPc electrodes at 100 mA g⁻¹ for Li-ion battery.

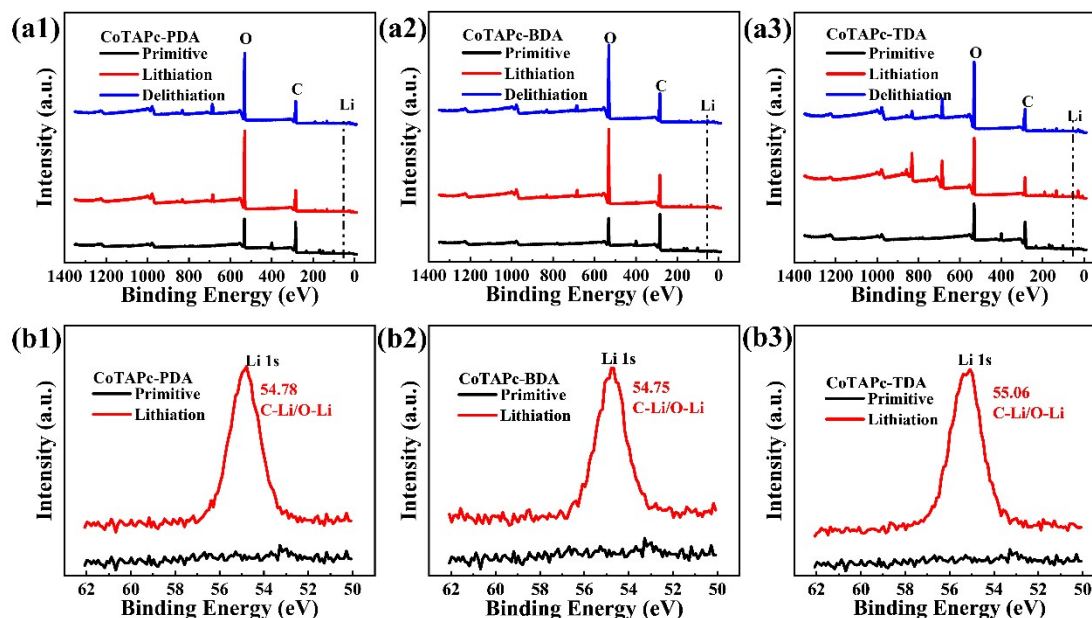


Fig. S5. (a1, a2, a3) Full XPS spectra in primitive, lithiation, and delithiation states; (b1, b2, b3) Li 1s spectra in primitive and lithiation states of CoTAPc-P/B/TDA electrodes

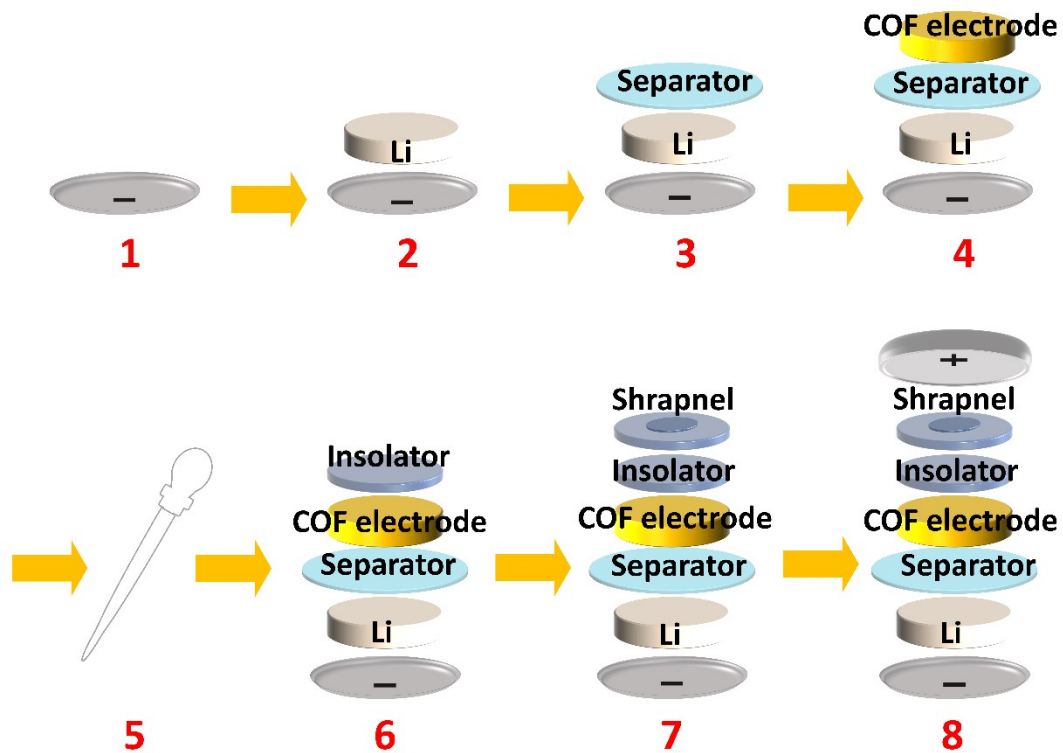


Fig. S6. The battery assembly process

Procedure description

Step 1: The negative shell opens up and lies flat on paper.

Step 2: Take the lithium sheet and put it into the negative shell.

Step 3: Clamp the diaphragm, cover the lithium sheet, Keep tiling.

Step 4: Use a glue head dropper to drop 2-3 drops of electrolyte.

Step 5: Clamp the pole piece and place it in the middle of the separator.

Step 6: Grab a insolator and place it on the electrode, strictly align.

Step 7: Clip the shrapnel and place it on the insolator, strictly align.

Step 8: Use tweezers to pick up the positive shell to cover.

Step 9: Use a sealer to seal the battery.

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