

Supporting Information

Synergetic Catalysis of Cobalt Tetrapyrroldiporphyrin and Copper Phthalocyanine to Promote the Discharge Behaviors in Li/SOCl₂ Batteries

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Experimental

Preparation of blank electrodes

First, 0.242 g of acetylene black (AB) was weighed and placed in a mortar. Then, 0.213 g of polytetrafluoroethylene (PTFE) was dispersed in 11.67 g of deionized water to prepare a PTFE dispersion. Subsequently, 1.1883 g of this dispersion was added to the mortar and thoroughly ground with the AB to form a homogeneous, paste-like mixture. The mixture was dried at 180 °C for 24 h. After cooling, the dried material was soaked in ethanol for approximately 30 min to soften it, and then roll-pressed into a smooth, free-standing carbon sheet with a thickness of approximately 0.5 mm. The sheet was further dried under vacuum at 120 °C for 10 h, cooled to room temperature, and punched into multiple circular electrodes (12 mm in diameter). Each blank electrode had an average mass of approximately 9.2 mg and an apparent density of 0.16 g cm⁻³.

Preparation of electrodes containing CoTAP/CuPc/AC catalyst

The preparation procedure was similar to that of the blank electrodes, with minor modifications. First, 0.242 g of acetylene black (AB) was weighed and placed in a mortar. A PTFE dispersion was prepared by dispersing 0.213 g of polytetrafluoroethylene (PTFE) in 11.67 g of deionized water. Then, 0.0145 g of the CoTAP/CuPc/AC composite catalyst (corresponding to 6 wt.% of the AB mass) and 1.1883 g of the PTFE dispersion were weighed. The catalyst was added to the PTFE dispersion and homogenized under ultrasonication for approximately 60 min to obtain a uniform catalyst-PTFE dispersion. This dispersion was then added to the mortar containing AB, followed by thorough grinding until a homogeneous, paste-like mixture was formed. The subsequent steps—drying at 180 °C for 24 h, ethanol soaking for 30 min, roll-pressing into sheets of ~0.5 mm thickness, vacuum drying at 120 °C for 10 h, and punching into multiple circular electrodes (12 mm in diameter)—were identical to those used for the blank electrodes. Each CoTAP/CuPc/AC-containing electrode had an average mass of approximately 9.2 mg and an apparent density of 0.16 g cm⁻³.

Preparation of electrodes containing CoTAP/AC or CuPc/AC catalyst

The preparation method for electrodes containing either CoTAP/AC or CuPc/AC catalyst was identical to that of the CoTAP/CuPc/AC-containing electrode, except that the

CoTAP/CuPc/AC composite was replaced with an equivalent mass of CoTAP/AC or CuPc/AC catalyst (also 6 wt.% relative to the AB mass), respectively.

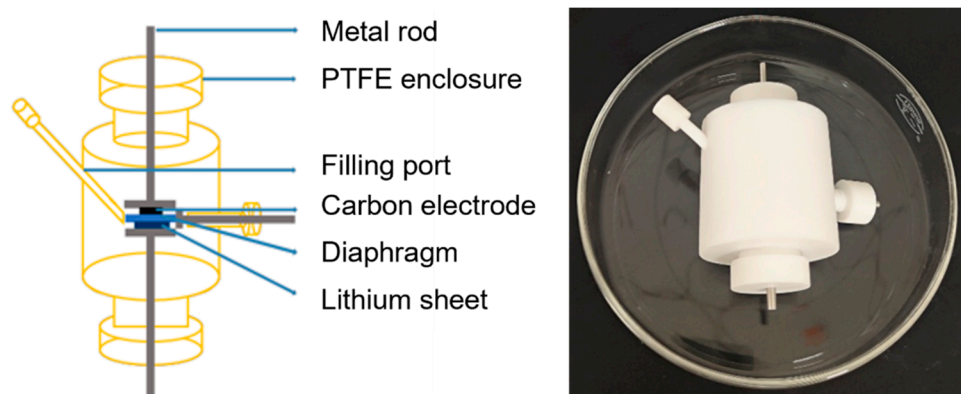


Figure S1. Mold battery schematic and mold battery photo.

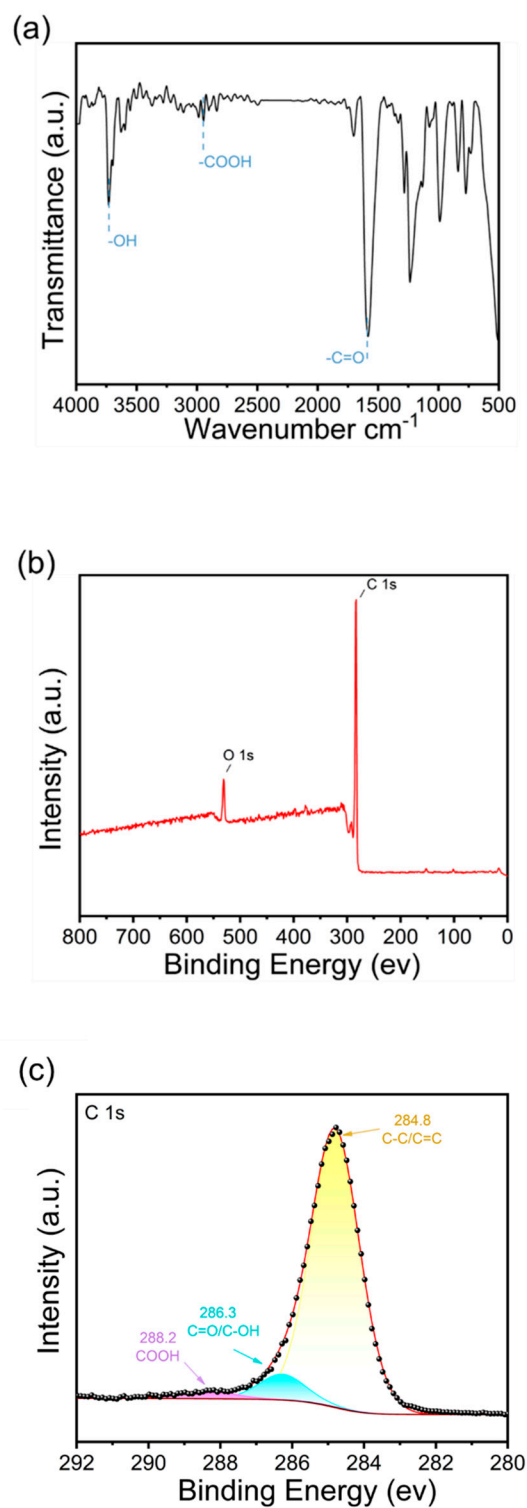


Figure S2. (a) FTIR spectra, (b) XPS spectrum, and (c) C 1s spectrum of functionalized AC.

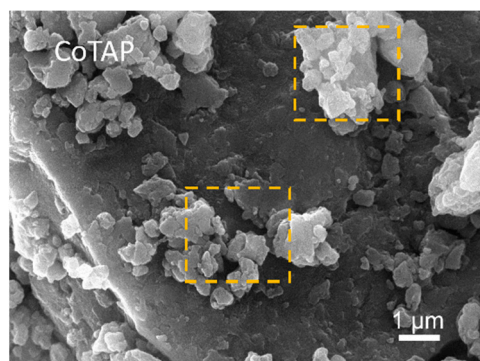


Figure S3. SEM image of the CoTAP.

Table S1. IR spectral (cm^{-1}) groups of the CoTAP/CuPc/AC, with the CoTAP, CuPc, AC as baselines.

Samples	C=O	C=N	C=C	C-H	Co-N	Cu-N	Back bone of CoTAP
AC	1690			1015			
CoTAP		1516	1385	1130	928		798,743
CuPc		1516	1385	1130		850	
CoTAP/CuPc/AC	1717	1516	1385	1130	928	850	798,743

Table S2. Raman shifts (cm^{-1}) and interpretation.

CoTAP	CuPc	CoTAP/CuPc/AC	Interpretation
593	595	610	Pyridine ring deformation
679	681	684	Macrocycle breathing
745	749	750	Macrocycle ring stretch
815	817	821	C-N aza-group stretch
868		873	C-N aza-group stretch
929	926	929	Pyridine ring stretch
1330	1330	1338	C-N pyrrole stretch
1524	1524	1532	C-N aza-group stretch

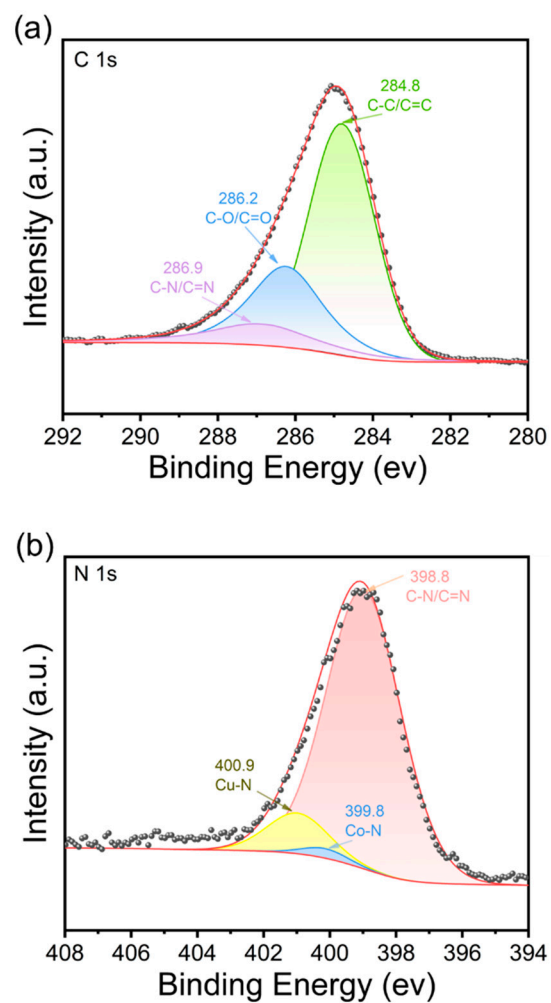


Figure S4. XPS survey of the CoTAP/CuPc/AC catalyst. (a) C 1s, and (b) N 1s spectrum of CoTAP/CuPc/AC.

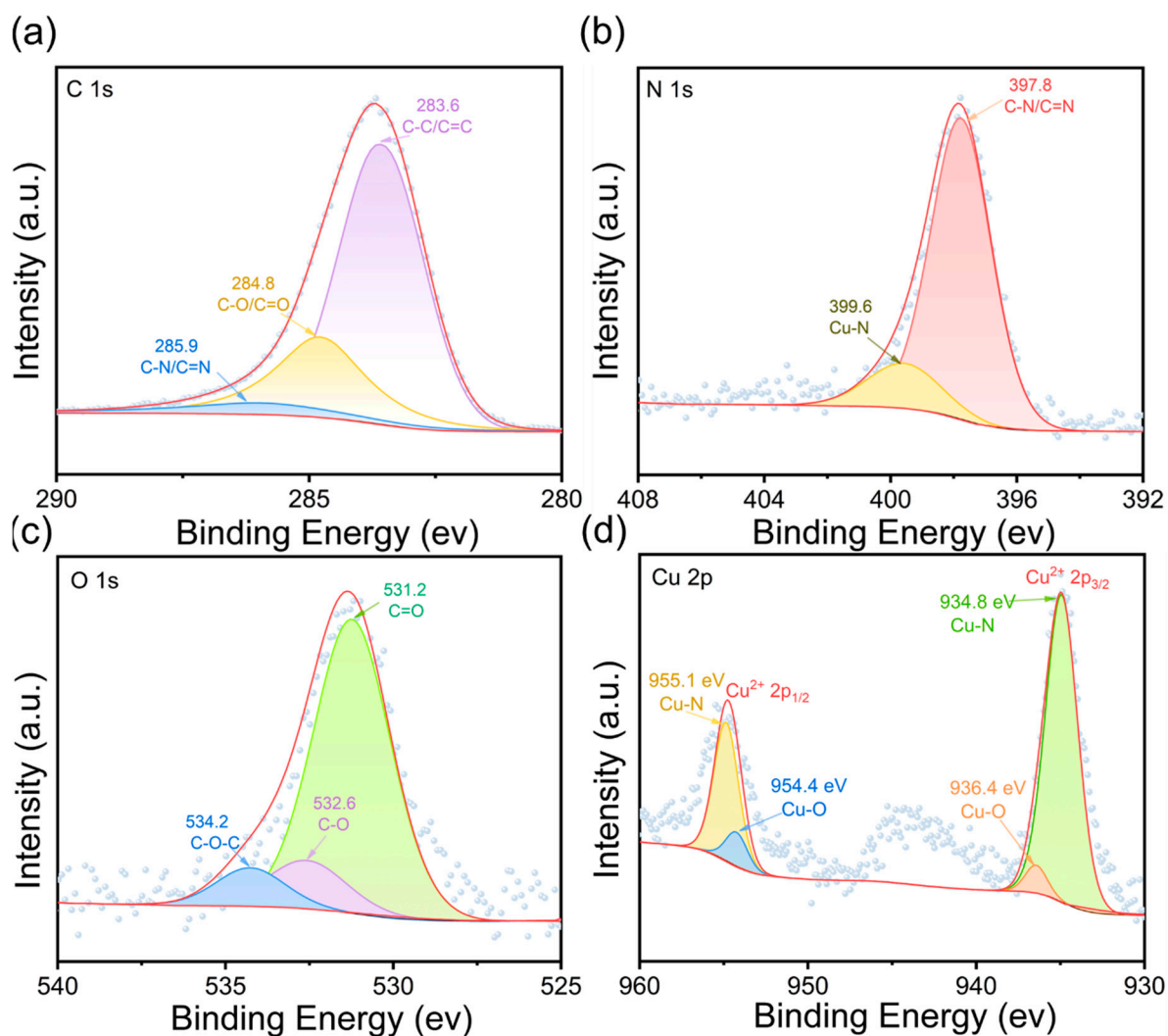


Figure S5. XPS survey of the CuPc/AC catalyst. (a) C 1s, (b) N 1s, (c) O 1s and (d) Cu 2p spectrum of CuPc/AC.

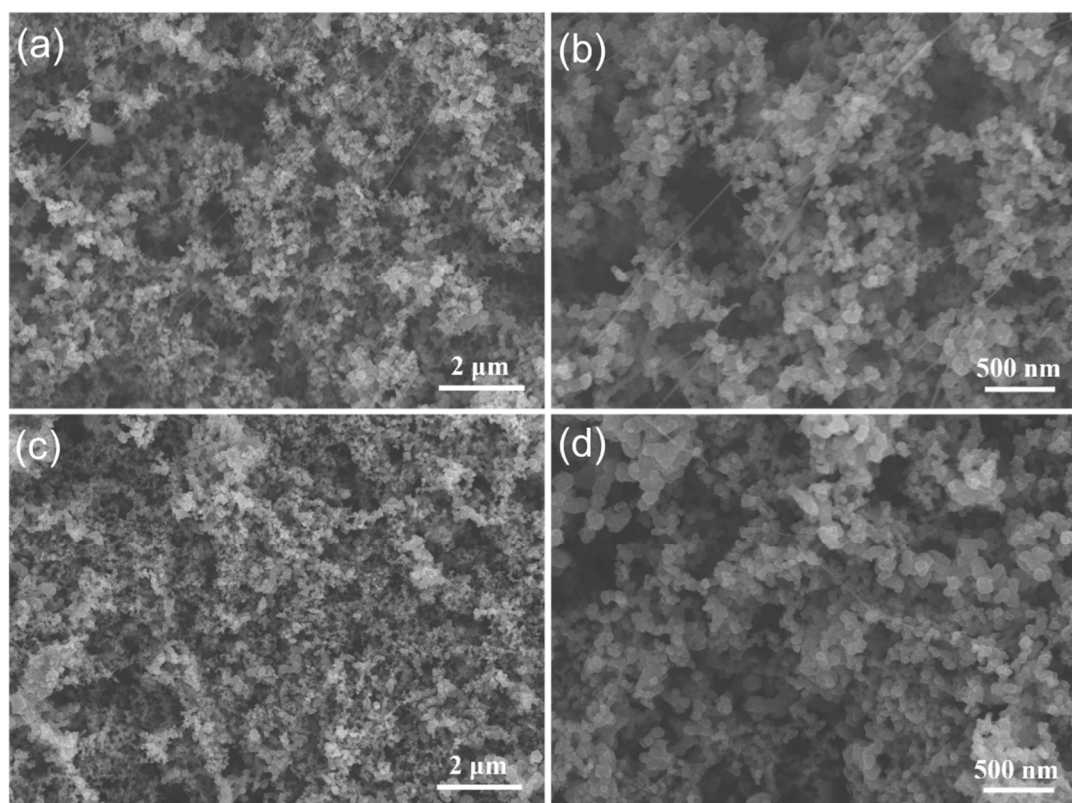


Figure S6. SEM images of (a, b) the CoTAP/CuPc/AC-catalyzed cathode and (c, d) the non-catalyzed cathode before discharge.

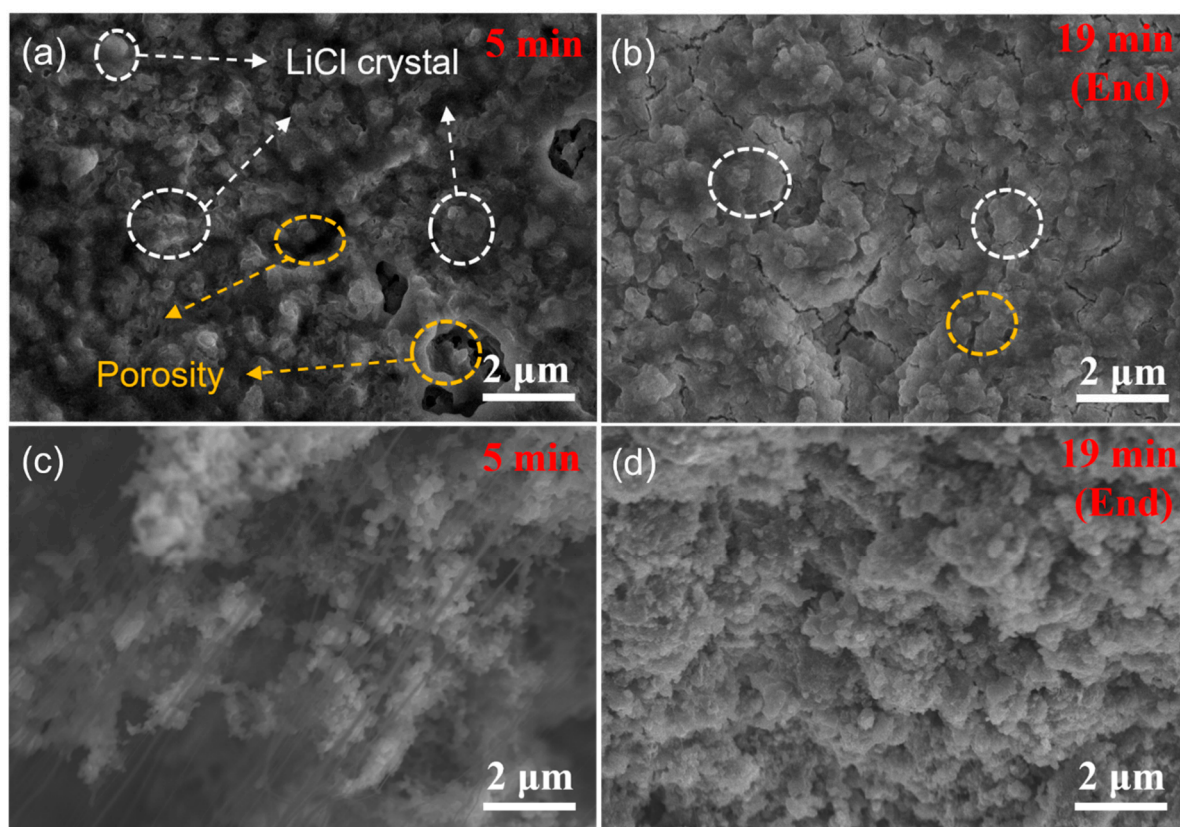


Figure S7. SEM images of the CoTAP/AC-catalyzed cathode at different discharge stages: (a, b) surface morphology and (c, d) cross-sectional morphology.

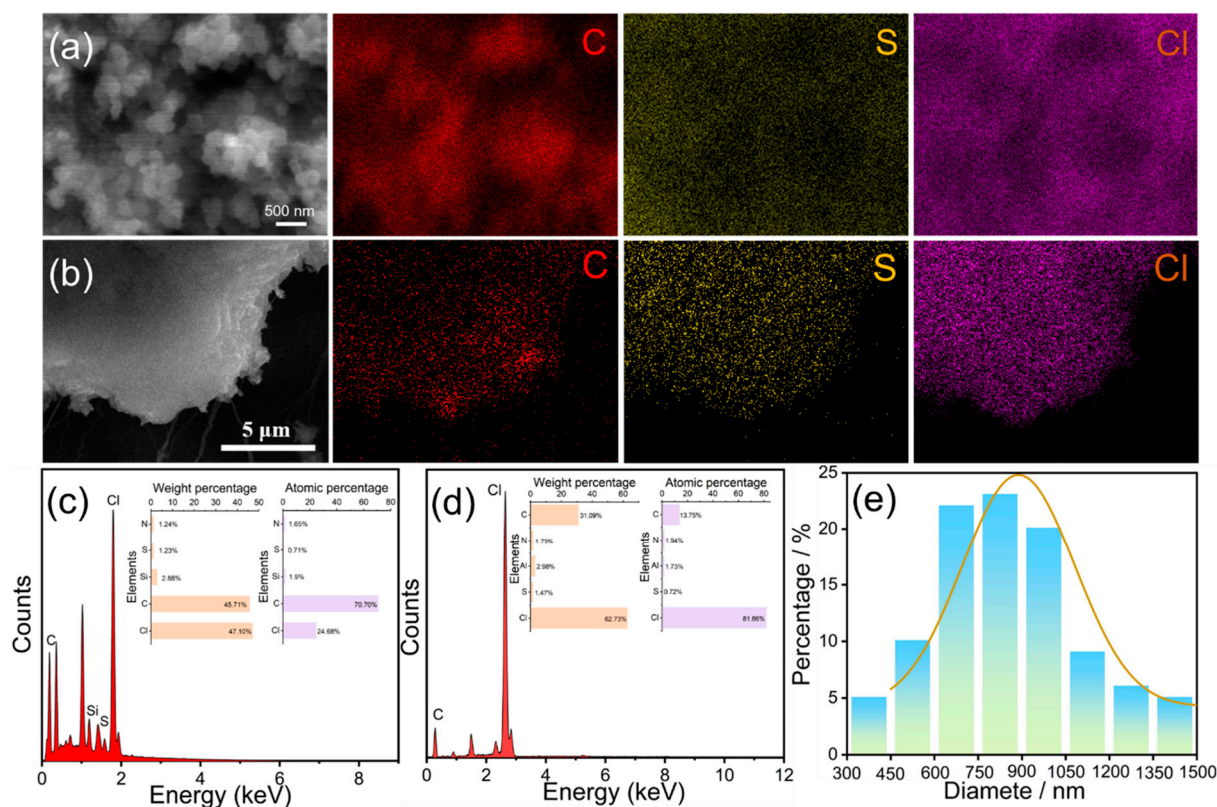


Figure S8. SEM images, corresponding EDS mappings of C, S and Cl elements, and quantitative EDS results (weight and atomic percentages) of carbon cathodes after full discharge with different catalysts, (a, c) with CoTAP/CuPc/AC catalyst, (b, d) without catalyst. (e) Particle size distribution diagram of the carbon cathode containing CoTAP/AC at 19 min of complete discharge.

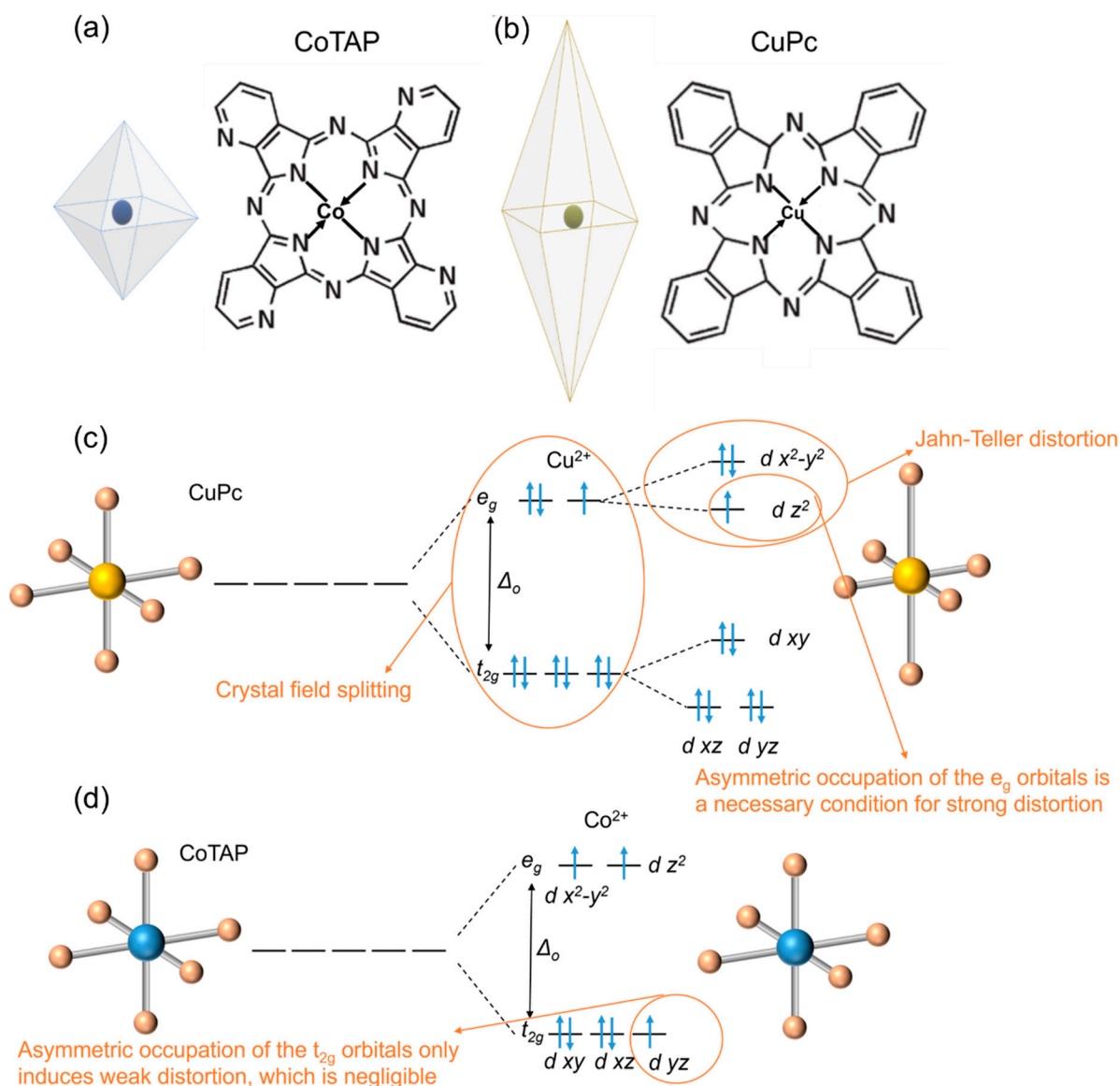


Figure S9. Octahedral spatial configuration and structural formula of (a) CoTAP, (b) CuPc. (c) Jahn-Teller distortion of the octahedral field of Cu^{2+} in CuPc caused by d-orbital splitting, leading to elongated coordination bond length along the Z-axis and shortened bond length along the X-Y axis, (d) negligible slight distortion of the octahedral field of Co^{2+} in CoTAP arising from weak asymmetric occupation of the t_{2g} orbital.

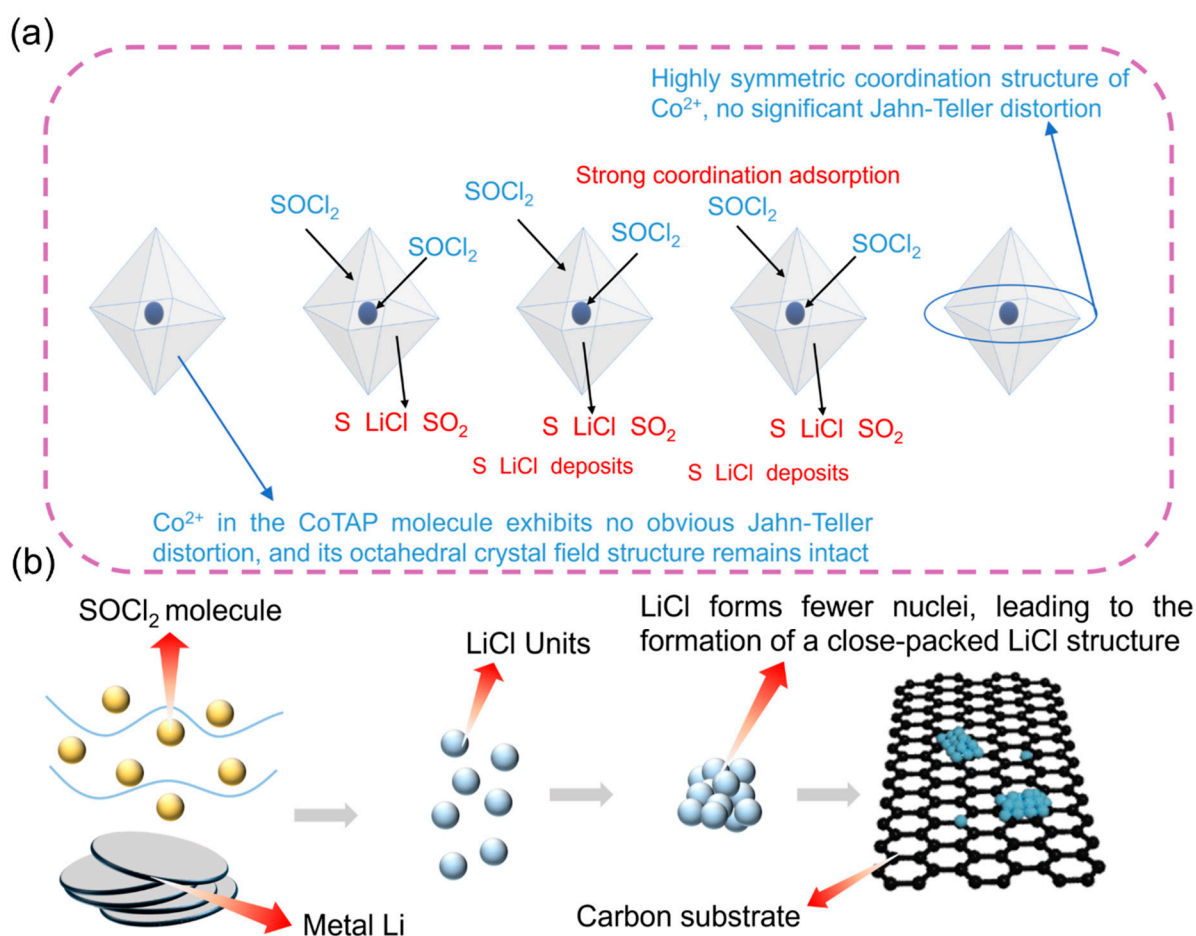


Figure S10. Schematic illustrations of (a) the strong adsorption of SOCl_2 molecules on CoTAP and (b) the limited nucleation of LiCl leading to large-sized products on the carbon cathode in the absence of catalyst.

The introduction of N atoms in the macrocyclic structures of TAP and Pc in CoTAP and CuPc modifies the ionic environment around Co^{2+} and Cu^{2+} (Figure S9a and b), which is primarily reflected in the distinct differences in the orbital occupation modes of d-level electrons. There are five degenerate d orbitals, namely d_{z^2} , $d_{x^2-y^2}$, d_{xy} , d_{yz} , and d_{xz} , whose spatial orientations correspond to the Z-axis direction, X-Y axis direction, bisector direction of the XY axial angle, bisector direction of the YZ axial angle and bisector direction of the XZ axial angle, respectively. Without the introduction of TAP and Pc systems, the five d orbitals of Co^{2+} and Cu^{2+} have the same energy level and are in a degenerate state. After the introduction of N-containing TAP and Pc systems, the atomic environment around Co^{2+} and Cu^{2+} deviates from the original spherically symmetric crystal field, and an octahedral field is formed with the N atoms in the systems. To drive the system to reach the most stable state with the lowest energy, the originally degenerate five d orbitals of Co^{2+} and Cu^{2+} undergo energy level splitting (crystal field splitting, as shown in Figure S9c and d), which is divided into the high-energy e_g orbitals (d_{z^2} , $d_{x^2-y^2}$) and the low-energy t_{2g} orbitals (d_{xy} , d_{yz} , d_{xz}). Owing to the inherent differences in the electron configurations of the two ions, Co^{2+} and Cu^{2+} exhibit completely different orbital electron filling modes and distortion behaviors, which are elaborated in detail as follows:

The crystal field splitting energy Δ_o of Co^{2+} is relatively small. Its seven 3d electrons are filled in accordance with the principle of preferential separate occupation of orbitals, and the only filling mode is $t_{2g}^5 e_g^2$, i.e., five electrons occupy the t_{2g} orbitals and two

electrons occupy the e_g orbitals (as shown in **Figure S9d**). The e_g orbitals adopt a symmetric single-electron occupation mode, where the two electrons occupy one e_g orbital each with no pairing, which completely eliminates the degeneracy of the e_g orbitals. Since the strong Jahn-Teller distortion is only induced by the asymmetric occupation of e_g orbitals, this is the fundamental reason why Co^{2+} does not undergo strong Jahn-Teller distortion. The five electrons in the t_{2g} orbitals are filled as two orbitals with paired electrons and one orbital with a single electron, which belongs to the weak asymmetric occupation of t_{2g} orbitals. However, the t_{2g} orbitals are low-energy orbitals, and such asymmetric occupation only causes negligible slight distortion, exerting no obvious influence on the coordination structure of Co^{2+} . In summary, the coordination structure of Co^{2+} is highly symmetric without significant Jahn-Teller distortion.

Cu^{2+} has nine 3d electrons. Regardless of the magnitude of the crystal field splitting energy Δ_o , the electrons are filled in accordance with Hund's rule and the Pauli exclusion principle, with the only filling mode being $t_{2g}^6e_g^3$, i.e., the t_{2g} orbitals are fully occupied and three electrons occupy the e_g orbitals (as shown in **Figure S9c**). The e_g orbitals exhibit a typical asymmetric occupation characteristic: the dx^2-y^2 orbital is fully occupied with paired electrons, while the dz^2 orbital has a single electron, which breaks the degeneracy of the e_g orbitals and renders the system in a high-energy unstable state. Based on the electron shielding principle, electrons around the atomic nucleus will partially weaken the attractive force of the nucleus on surrounding particles. The dz^2 orbital corresponds to the Z-axis direction, and the single-electron occupation of this orbital weakens the attractive force of Cu^{2+} on the N atoms along the Z-axis, which is manifested as the elongation of the coordination bond length along the Z-axis. According to the law of conservation of energy, the interaction in the X-Y plane is enhanced accordingly, and the Cu center attracts the N atoms on the plane inward, which is reflected in the shortening of the coordination bond length along the X-Y axis. The above changes in electron configuration and interatomic interactions cause the octahedral crystal field of Cu^{2+} to elongate along the Z-axis and contract along the X-Y plane, forming an elongated octahedral configuration with significant Jahn-Teller distortion. After distortion, Cu^{2+} adopts a square planar coordination structure and forms an extremely strong interaction with the four N atoms in the plane, which greatly reduces the coordination chance of the Cu center with other ligands and ultimately results in the weak coordination characteristic of Cu^{2+} .

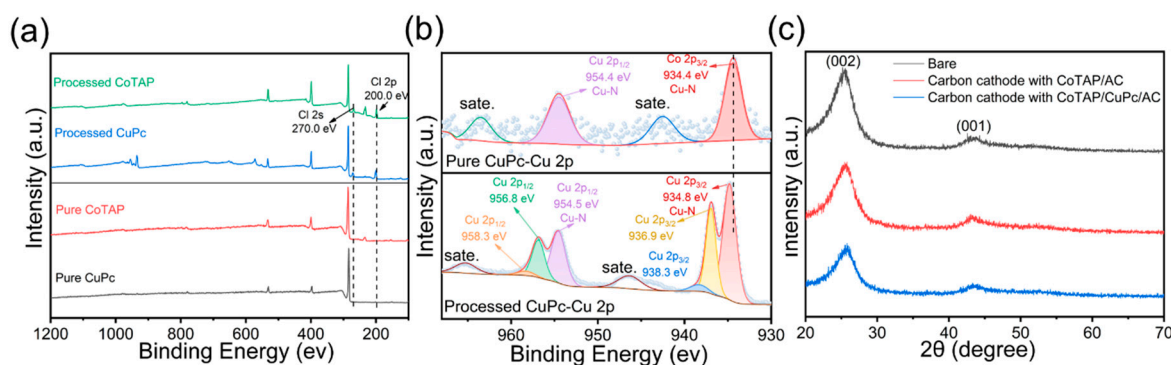


Figure S11. (a) Comparison of XPS survey spectra for pure CuPc, pure CoTAP, and their samples after SOCl₂ immersion, (b) Cu 2p XPS spectra of pure CuPc and CuPc after SOCl₂ immersion, (c) XRD patterns of the electrode surfaces of CoTAP/CuPc/AC cathode, CoTAP/AC cathode, and blank cathode before discharge.

Table S3. EIS fitting parameters of Li/SOCl₂ batteries with different catalysts.

Discharge time	Catalyst	R_e (Ω)	R_{film} (Ω)	Y_{01} ($\Omega^{-1} s^n$)	n_1	R_{ct} (Ω)	Y_{02} ($\Omega^{-1} s^n$)	n_2	χ^2
5min	Bare	3.01	3.24	3.77×10^{-5}	0.72	3.89	5.90×10^{-3}	0.76	3.36×10^{-4}
5min	CuPc/AC	3.43	3.13	3.27×10^{-5}	0.81	1.37	3.29×10^{-3}	0.98	4.12×10^{-3}
5min	CoTAP/AC	3.57	3.38	3.87×10^{-5}	0.84	2.52	3.22×10^{-3}	0.91	2.99×10^{-3}
5min	CoTAP/CuPc/AC	2.81	2.48	4.94×10^{-5}	0.82	1.16	4.47×10^{-3}	0.98	2.87×10^{-3}
18min	Bare	3.73	23.08	4.57×10^{-5}	0.69	63.95	1.21×10^{-4}	0.43	3.00×10^{-3}
19min	CoTAP/AC	3.15	7.86	1.10×10^{-5}	0.76	46.75	9.47×10^{-4}	0.54	5.74×10^{-3}
19min	CoTAP/CuPc/AC	2.94	4.30	8.41×10^{-5}	0.78	5.51	2.92×10^{-4}	0.70	1.57×10^{-3}
23.4min	CuPc/AC	3.29	2.30	6.54×10^{-5}	0.82	31.76	1.37×10^{-4}	0.60	1.00×10^{-2}
23.4min	CoTAP/CuPc/AC	3.23	3.54	1.87×10^{-5}	0.78	11.47	3.13×10^{-4}	0.68	1.27×10^{-4}
28.6min	CoTAP/CuPc/AC	7.47	3.59	1.06×10^{-5}	0.79	19.27	1.30×10^{-4}	0.65	5.54×10^{-4}

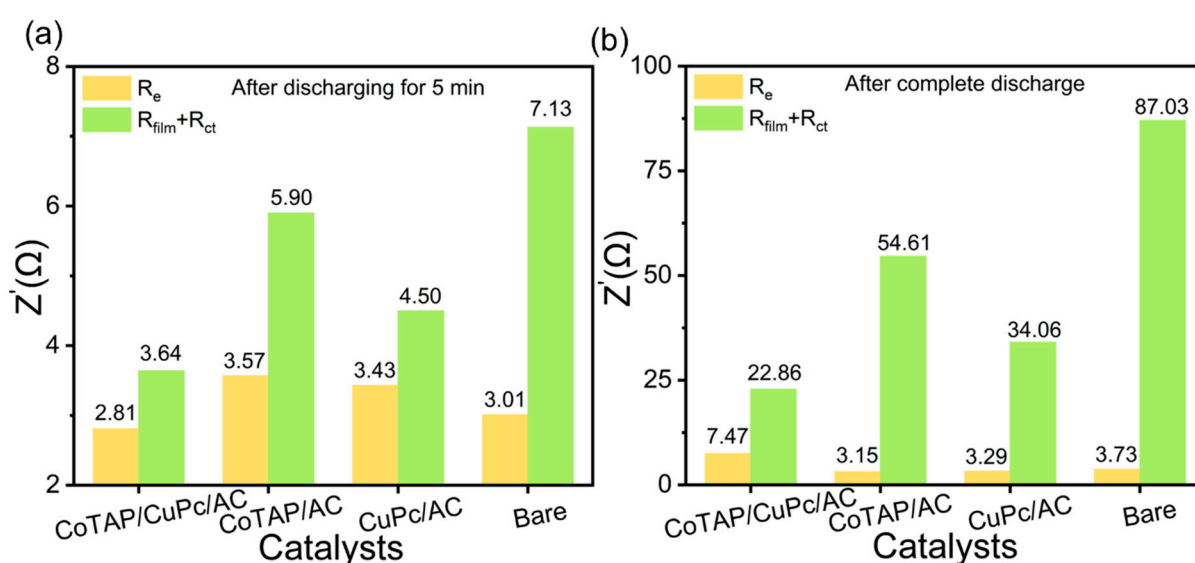


Figure S12. Impedance fitting data of Li/SOCl₂ batteries under different catalytic conditions (a) 5 min of discharge (b) full discharge.

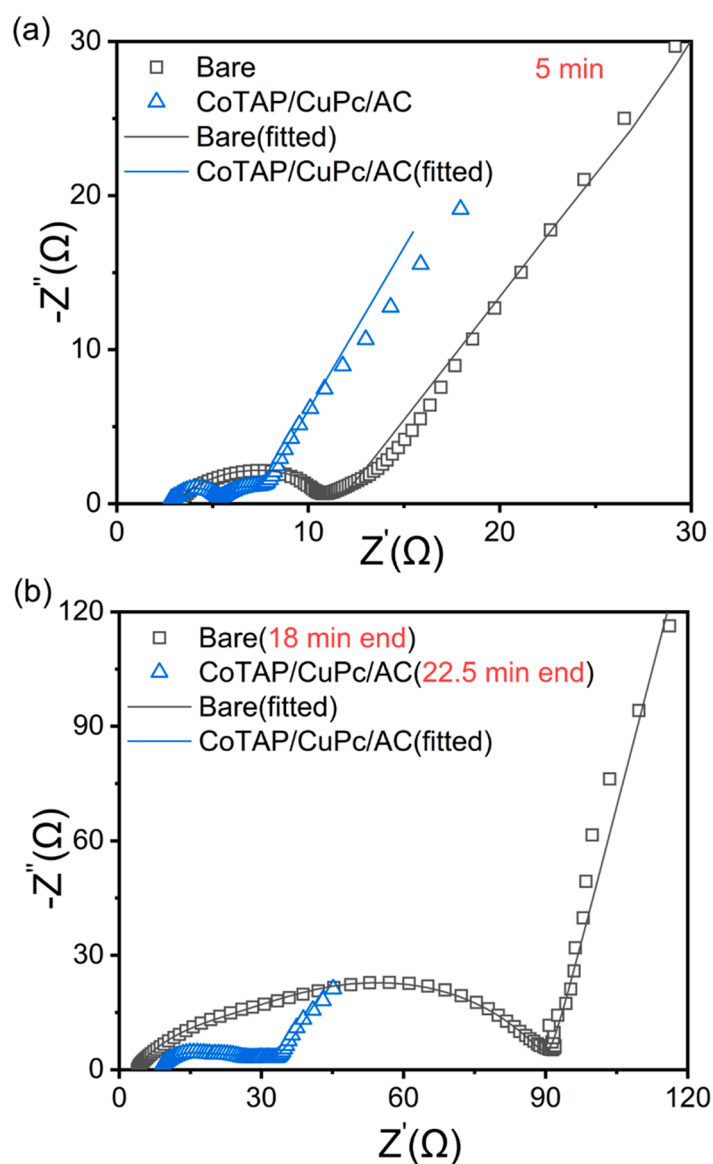


Figure S13. Nyquist plots of Li/SOCl₂ batteries with the CoTAP/CuPc/AC-catalyzed cathode and the non-catalyzed cathode after (a) 5 min and (b) complete discharge.

Table S4. Comparison of this work with other Li/SOCl₂ batteries reported in the literature.

Cathode material	Binder	Catalyst	Electrolyte	Load resistance	Current density	Cutoff voltage	Voltage plateau	Discharge capacity	Discharge time
Acetylene black	PTFE	Ref. 10 FePc/AC	1.47 mol L ⁻¹ LiAlCl ₄ ·SOCl ₂	100 Ω		2 V	3.05 V		27.5 min
Acetylene black	PTFE	Ref. 33 AC	1.47 mol L ⁻¹ LiAlCl ₄ ·SOCl ₂	80 Ω		2 V	2.96 V		18.3 min
Acetylene black	PTFE	Ref. 14 Co-N-G	1.50 mol L ⁻¹ LiAlCl ₄ ·SOCl ₂		25 mA cm ⁻²	2 V	2.92 V	1563 mAh g ⁻¹	
Acetylene black	PTFE	Ref. 7 N-G	1.50 mol L ⁻¹ LiAlCl ₄ ·SOCl ₂		25 mA cm ⁻²	2 V	2.78 V	1534 mAh g ⁻¹	
Acetylene black	PTFE	This work CoTAP/CuPc/AC	1.47 mol L ⁻¹ LiAlCl ₄ ·SOCl ₂	100 Ω	28 mA cm ⁻²	2 V	3.16 V	1639 mAh g ⁻¹	28.6 min

To facilitate a more meaningful comparison with the performance reported in Refs. 7 and 14, we have recalculated the discharge current density and specific capacity of our battery using the same evaluation approach described therein. Specifically, based on the stable discharge voltage plateau of 3.16 V observed in our system and the geometric electrode area of 1.13 cm², the corresponding discharge current density is estimated to be approximately 28 mA cm⁻². Furthermore, given that the mass of the carbon-based cathode is 9.2 mg and the total measured discharge capacity is 15.08 mAh, the specific capacity—calculated in the same manner as in Refs. 7 and 14—is 1639 mAh g⁻¹. These data allow for a relatively reasonable comparison with our results. Additionally, Ref. 33 conducted the discharge test under a load resistance of 80 Ω. Although a lower load resistance can lead to higher initial currents, the reported discharge voltage was relatively low (2.96 V), and the voltage profile exhibited noticeable instability. Moreover, the total discharge duration was only 18.3 min—significantly shorter than that of our system. In contrast, our dual-catalyst cathode delivers a stable voltage plateau and extended discharge time, suggesting more efficient utilization of SOCl₂ under practical operating conditions. These comparative results may, to some extent, reflect the potential value of the present work in advancing the performance and reliability of Li/SOCl₂ batteries.

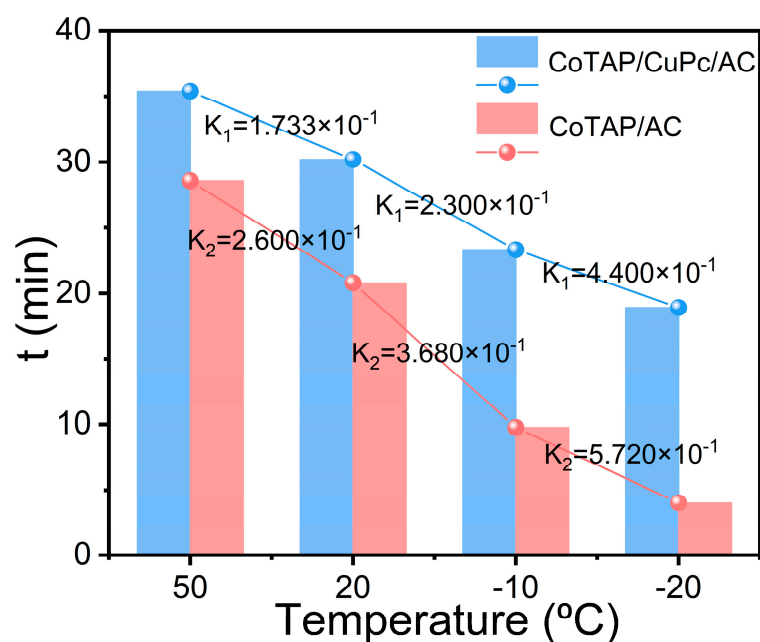


Figure S14. Discharge time comparison plots of Li/SOCl₂ batteries with different catalysts over a temperature range of 50 to -20 °C.

Table S5. EIS fitting parameters of CoTAP/CuPc/AC-catalyzed Li/SOCl₂ batteries at different temperatures.

Temperatures	R_e (Ω)	R_{film} (Ω)	Y_{01} ($\Omega^{-1} s^n$)	n_1	R_{ct} (Ω)	Y_{02} ($\Omega^{-1} s^n$)	n_2	χ^2
50 °C	2.54	2.89	2.52×10^{-4}	0.80	17.34	4.55×10^{-3}	0.73	4.09×10^{-4}
20 °C	3.10	6.97	2.33×10^{-4}	0.72	28.30	3.23×10^{-3}	0.66	2.43×10^{-4}
-10 °C	3.83	11.57	1.37×10^{-4}	0.69	38.20	2.41×10^{-3}	0.61	2.87×10^{-4}
-20 °C	4.46	17.35	7.85×10^{-4}	0.66	42.08	1.87×10^{-3}	0.54	5.57×10^{-4}

Table S6. EIS fitting parameters of CoTAP/AC-catalyzed Li/SOCl₂ batteries at different temperatures.

Temperatures	R_e (Ω)	R_{film} (Ω)	Y_{01} ($\Omega^{-1} s^n$)	n_1	R_{ct} (Ω)	Y_{02} ($\Omega^{-1} s^n$)	n_2	χ^2
50 °C	3.58	5.42	3.72×10^{-5}	0.75	24.50	4.89×10^{-3}	0.68	2.91×10^{-4}
20 °C	5.22	19.93	4.77×10^{-5}	0.64	35.67	3.47×10^{-3}	0.62	6.51×10^{-5}
-10 °C	5.74	27.74	1.42×10^{-5}	0.60	67.39	4.34×10^{-3}	0.57	3.02×10^{-4}
-20 °C	6.12	51.75	1.27×10^{-5}	0.53	78.98	9.38×10^{-3}	0.52	5.31×10^{-4}