**Dual redox groups enable organic cathode material with a high capacity for aqueous zinc-organic batteries**

Yongkang Ana, Yu Liua, Shuangshuang Tana, Fangyu Xionga, Xiaobin Liaob, and Qinyou Anac\*

*a* State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, P. R. China

*b* State Key Laboratory of Silicate Materials for Architectures, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

*c* Foshan Xianhu Laboratory of the Advanced Energy Science and Technology Guangdong Laboratory Xianhu Hydrogen Valley, Foshan 528200, Guangdong, P. R. China

\*Corresponding Author

E-mail address: anqinyou86@whut.edu.cn (Q. An)

**Experimental Section**

*Synthesis and Characterizations of TBQPH:*

TBQPH was synthesized by a simple dehydration condensation reaction with hexaketocyclohexane octahydrate (Aladdin, ≥99%) and 2,3-diaminonaphthalene-1,4-dione (Yanshen Technology Co., Ltd., ≥98%). Typically, hexaketocyclohexane octahydrate (52.2 mg) and 2,3-diaminonaphthalene-1,4-dione (94.1 mg) are dissolved in 15 ml ethanol/glacial acetic acid (volume ratio = 1:1) mixed solvent, stirred and heated to 65oC for 12 hours. The product is collected after centrifugal cleaning with acetone, ethanol and water. Finally, TBQPH was achieved by vacuum dried at 80oC (94 mg, 90% yield). 1H NMR (500 MHz, CF3COOD, δ ppm): 8.72-8.69 (m, 6H), 8.19-8.16 (m, 6H). 13C NMR (500 MHz, CF3COOD, δ ppm): 181.70, 146.75, 145.69, 137.33, 133.55, 129.23. The products are hardly soluble in solvents such as ethanol, H2O, dichloromethane (CH2Cl2), tetrahydrofuran (THF), and acetone. In addition, no self-aggregation of DND was observed under the same conditions.

Fourier transform infrared (FTIR) spectra measured on Thermo Fishe Nicolet FTIR spectrometer were used to characterize the structures of TBQPH at various states. X-ray photoelectron spectrometer (XPS, Kratos AXIS SUPRA) was adopted to examined surface element of the TBQPH powder. The microstructure of the synthesized TBQPH were characterized by the field-emission scanning electron microscopy (SEM, MIRA3 LMH). The elemental distributions were obtained from energy dispersive spectroscopy (EDS) mapping analysis. XRD data of the samples were collected with a D8 Advance Xray diffractometer with an area detector using Cu Kα radiation (λ = 1.5418 Å). EIS was recorded with a frequency range from 0.01 to 100 kHz.

*Electrochemical measurements:* The TBQPH electrode slurry were prepared by homogeneous mixing 60 wt% of TBQPH powder, 30 wt% of Ketjen black, and 10wt% polytetrafluorethylene (PTFE) binder in ethanol. Then, it was prepared into a sheet with a load of 2-3 mg cm−2 by a roller machine. The batteries were assembled into 2025 type coin cells in Air. The coin cells are composed of TBQPH as the cathode, glass fibers D as the separators, 2M ZnSO4 as the electrolyte, Zn foil as the anode.

*Computational details:* The DFT calculations were carried out using Gaussian 16 software package. The geometry of TBQPH, TBQPH-2H, TBQPH-4H, TBQPH-6H, TBQPH-8H, TBQPH-10H, and TBQPH-12H were fully optimized at B3LYP level of theory, with 6-31+G (d, p) basis set for C, H, O, and N elements.[1-3] For all of the calculations, solvent effects were incorporated employing integral equation formalism polarizable continuum model (IEFPCM) with SMD solvation model using water as solvent.[4, 5]

To further explore the energy preference of TBQPH binding to protons in water solvents, the vibrational frequencies were calculated to verify the minima of the corresponding structures. We checked the binding free energy (*∆G*) in the solution using the following formula (1):

(1)

where the G is the Gibbs free energies of the most stable water-solvated species, and n denotes the number of H atoms (n = 2, 4, 6, 8, 10, 12).

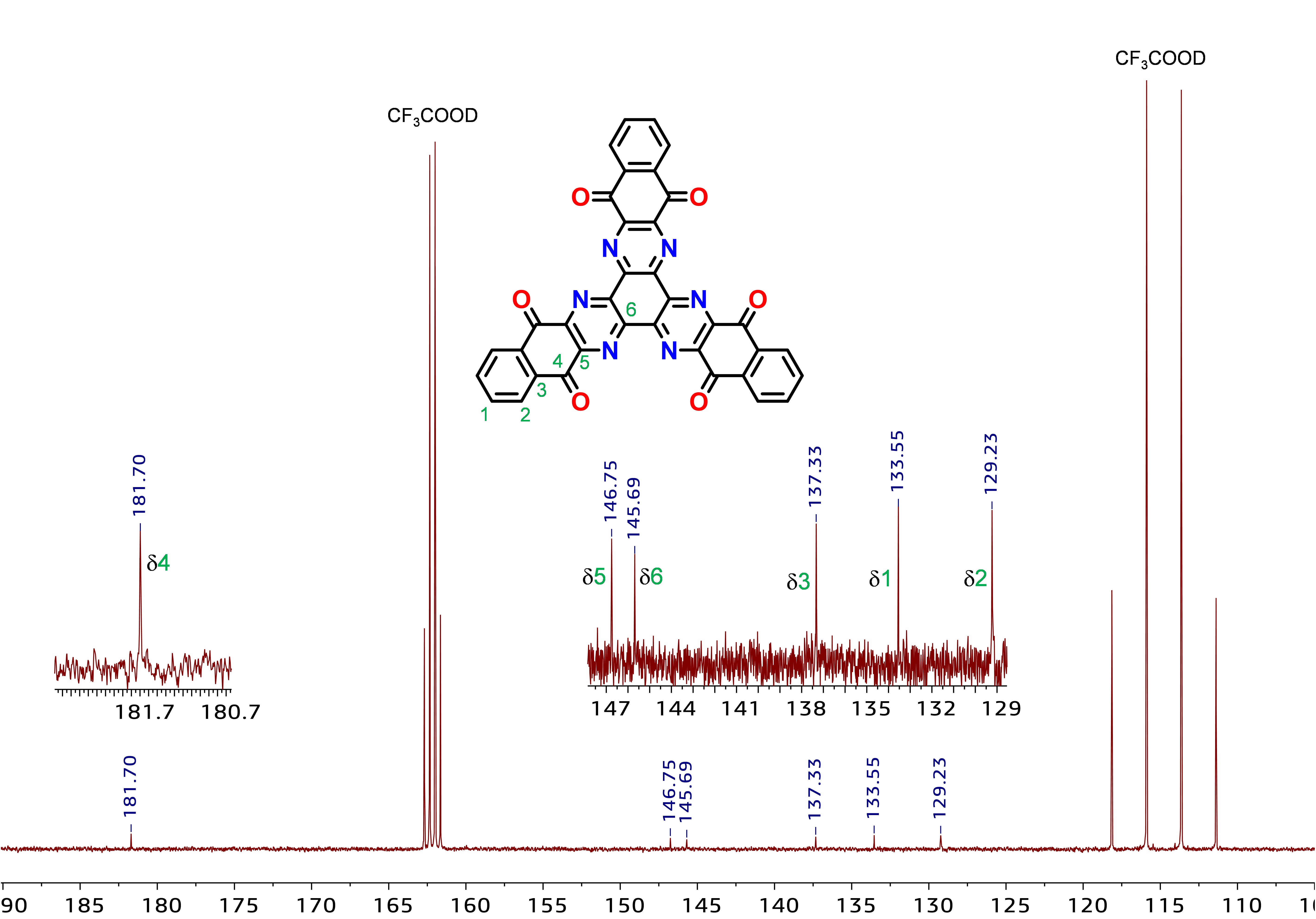
*GITT:* The calculation of ionic diffusion coefficient by GITT is employed the following formula (2), which based on Fick’s second law:

(2)

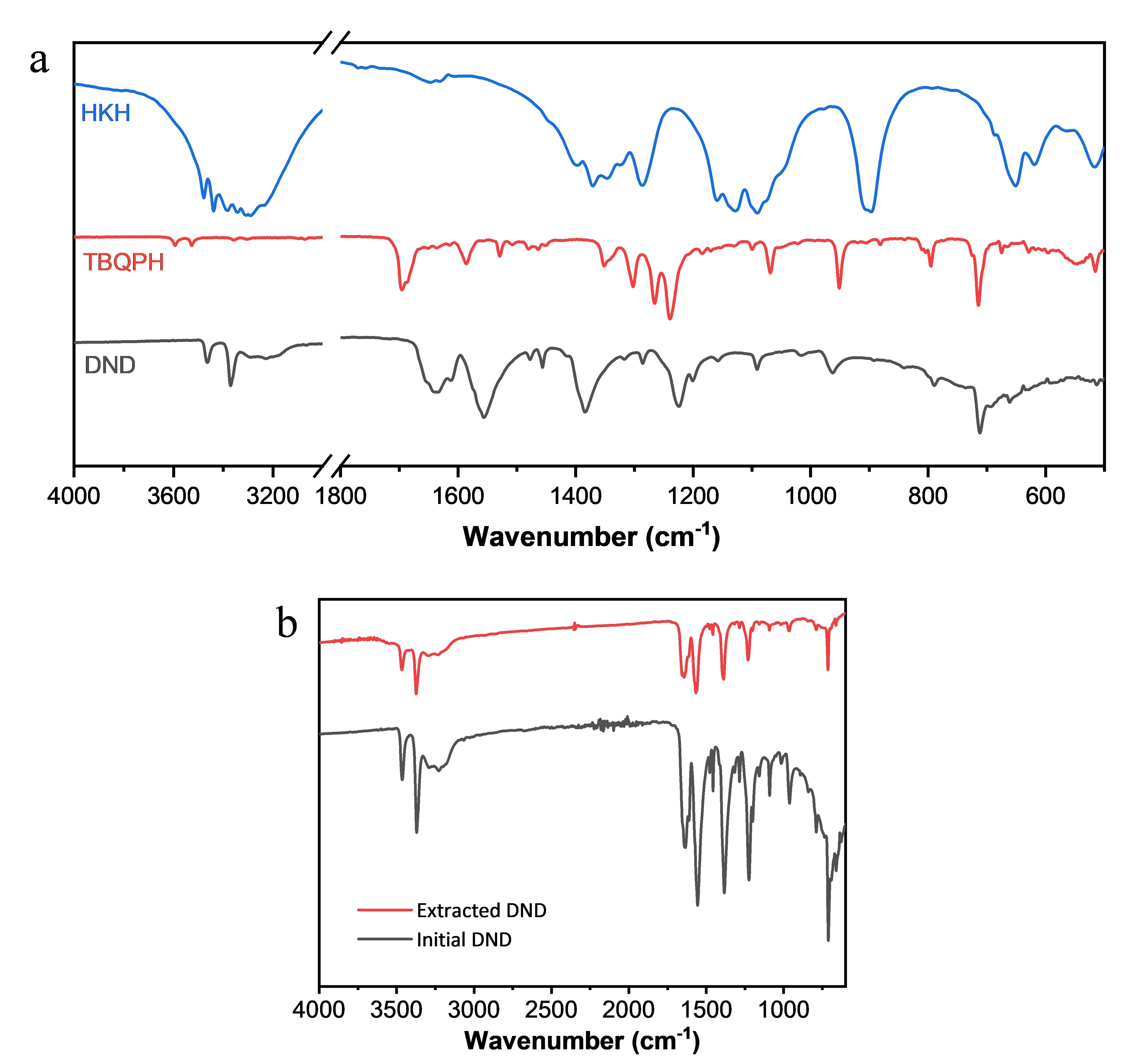
where *τ* is the duration of the current impulse; *mB* is the mass load of the electrode material; *S* represents the geometric area of the electrode; *∆ES* is the quasi-thermodynamic equilibrium potential difference between before and after the current pulse; *∆Eτ* represents the potential difference during the current pulse; *VM* is the molar volume of the material; and *MB* is the molar mass of material.

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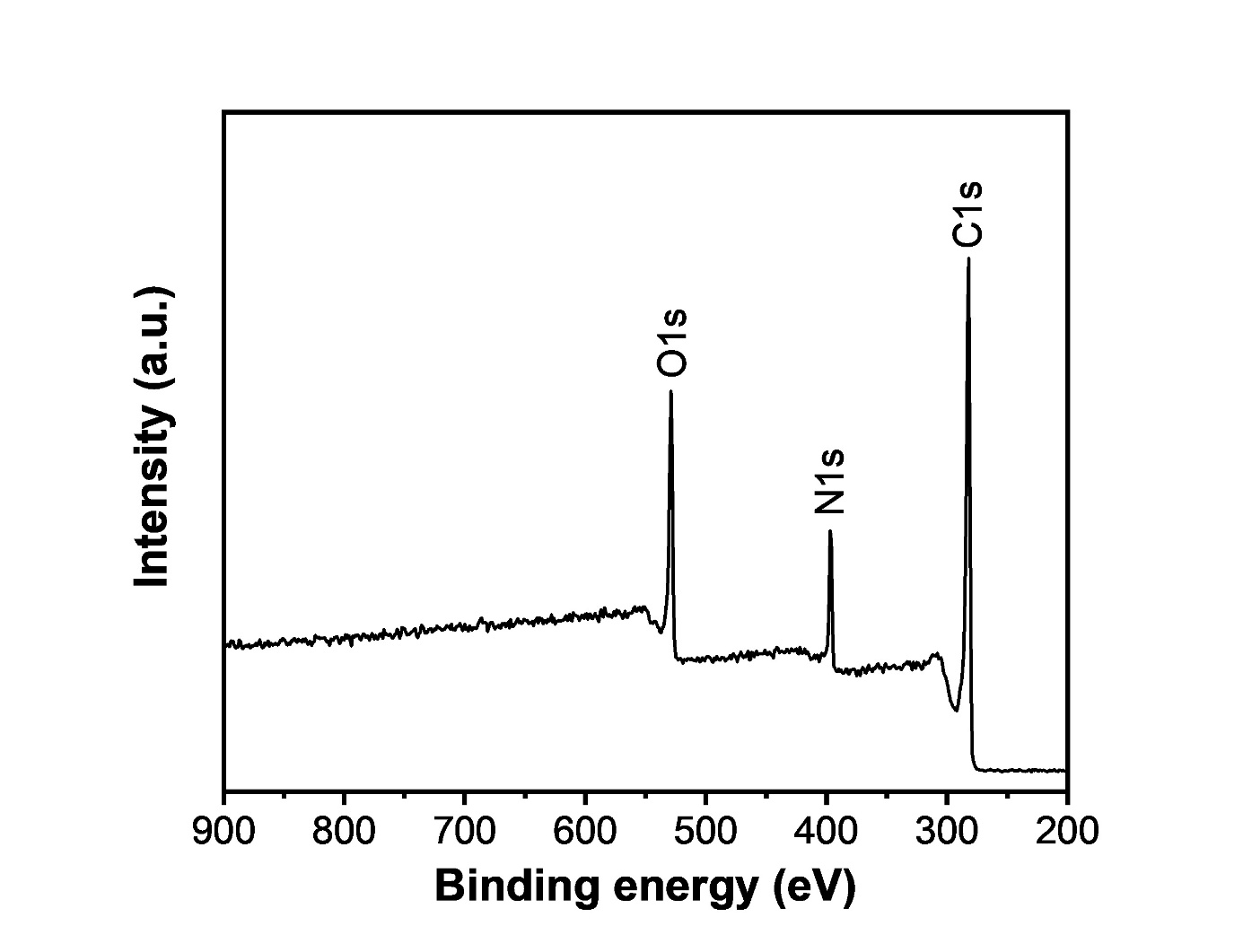
**Figure S1.** 1H-NMR spectrum of TBQPH in CF3COOD solvent.



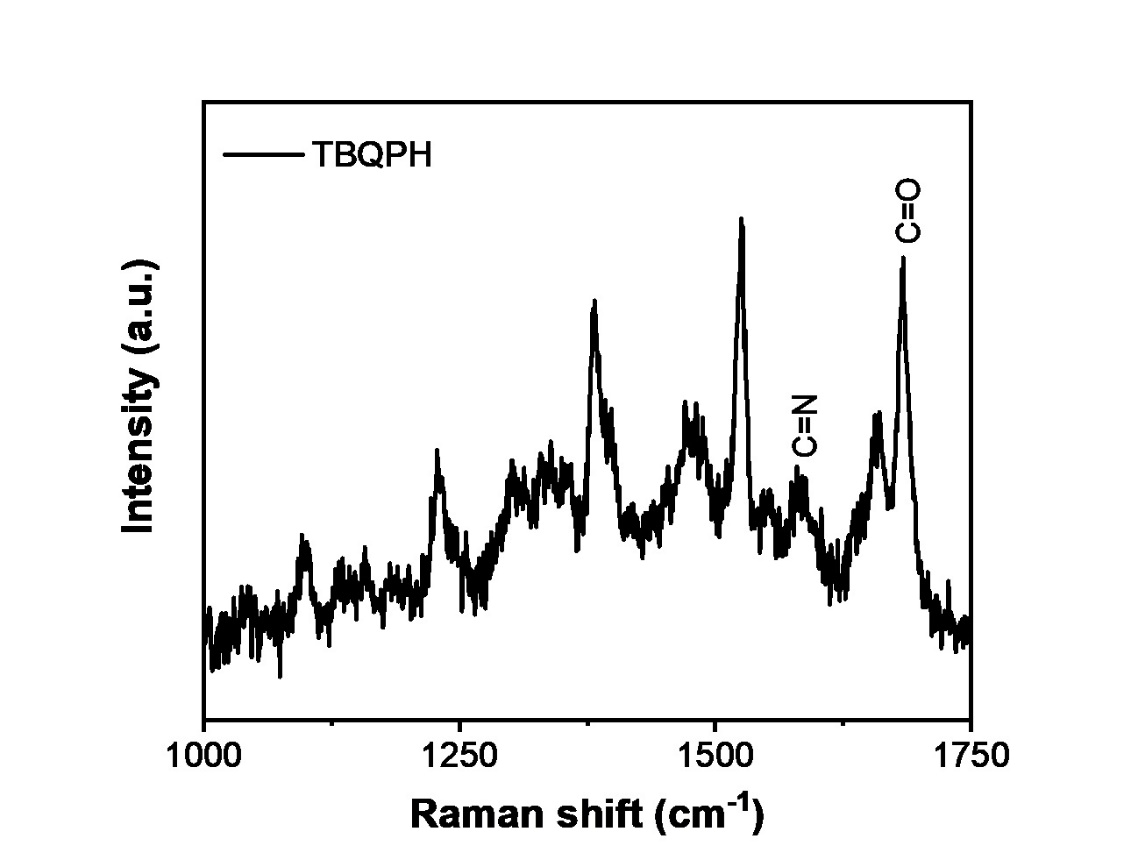
**Figure S2.** 13C-NMR spectrum of TBQPH in CF3COOD solvent.

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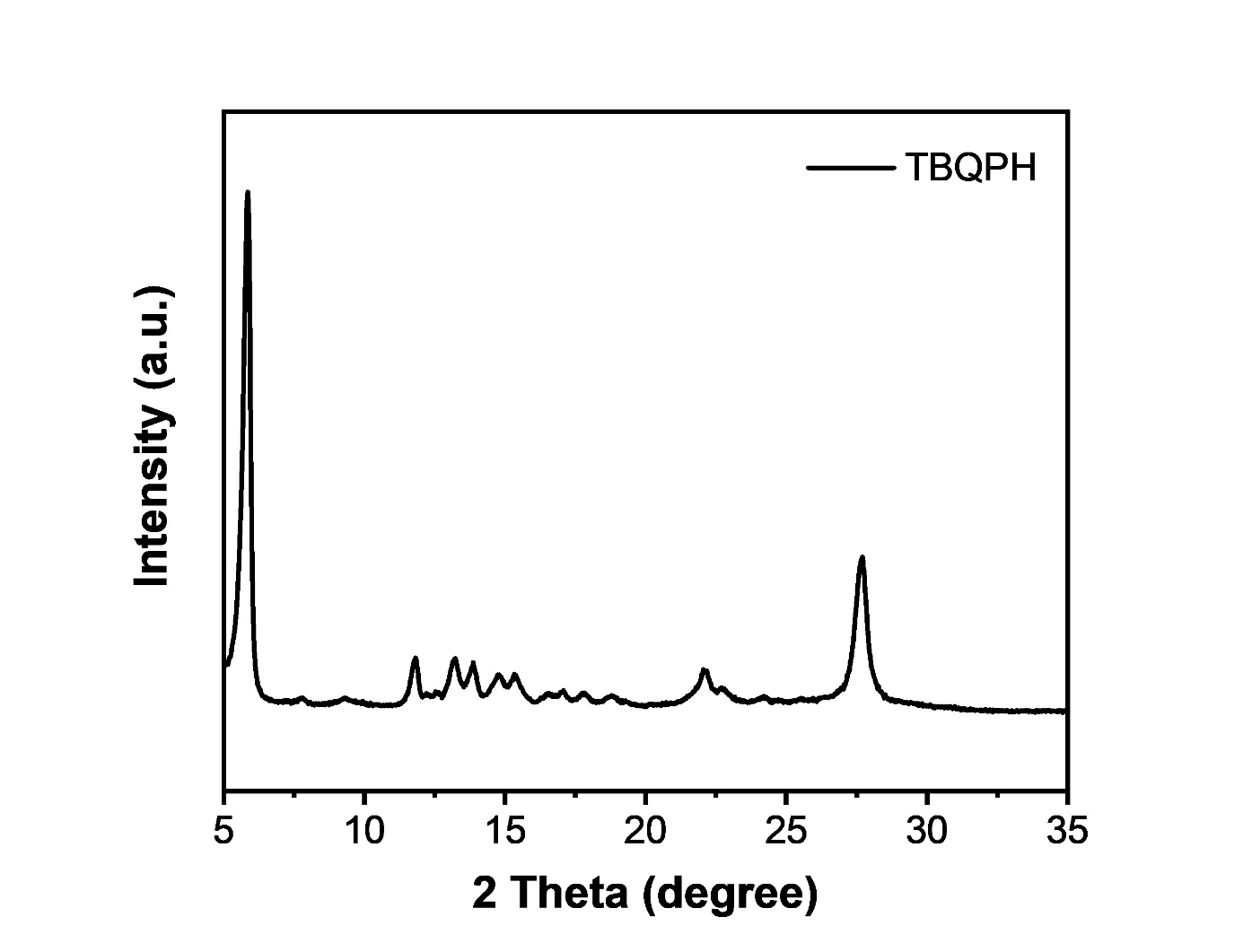
**Figure S3.** (a)FT-IR spectra of HKH (blue), TBQPH (red), and DND (black). (b) FT-IR spectra of the initial and extracted DND in the DND self-polymerization experiment.

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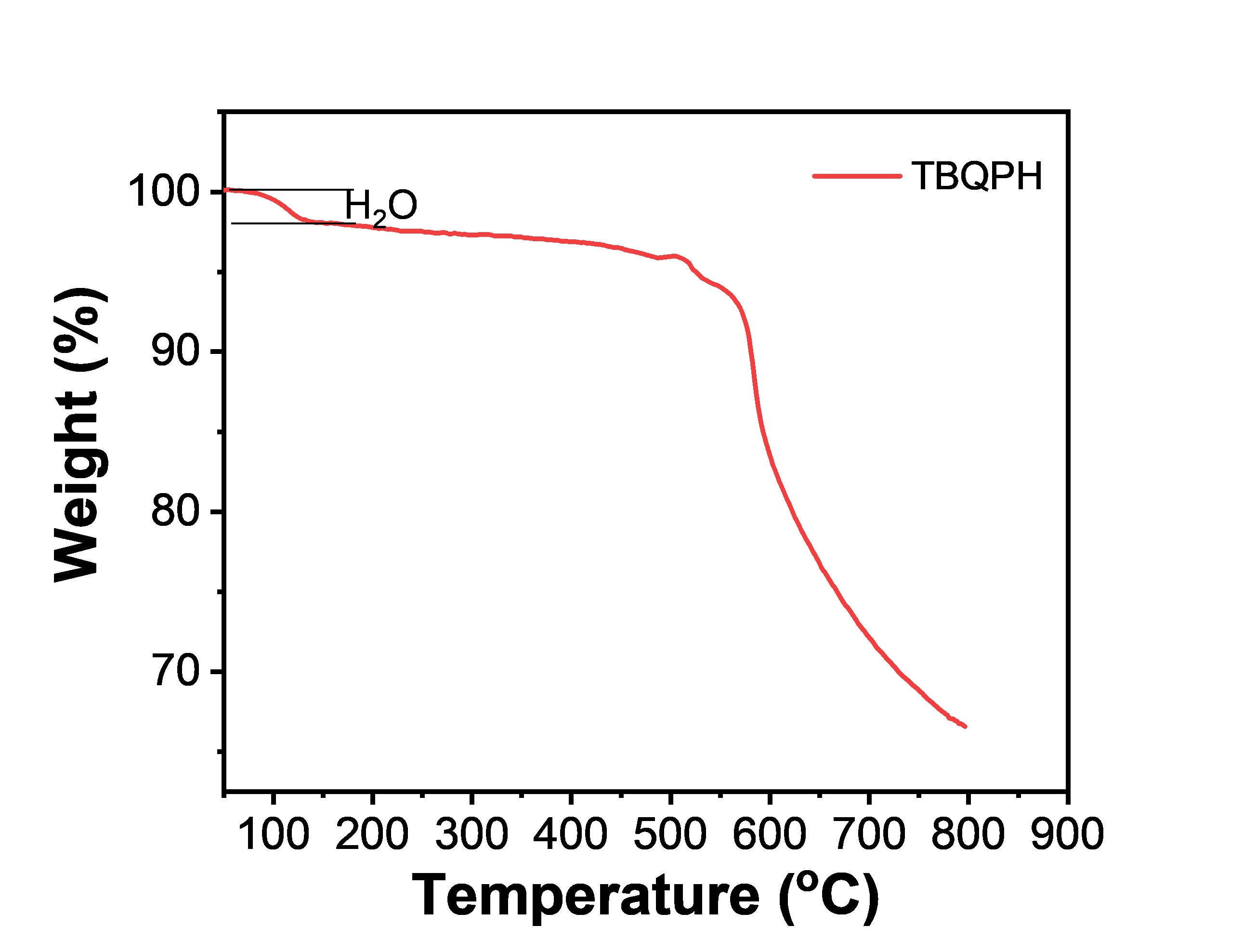
**Figure S4.** Full survey XPS spectrum of TBQPH.

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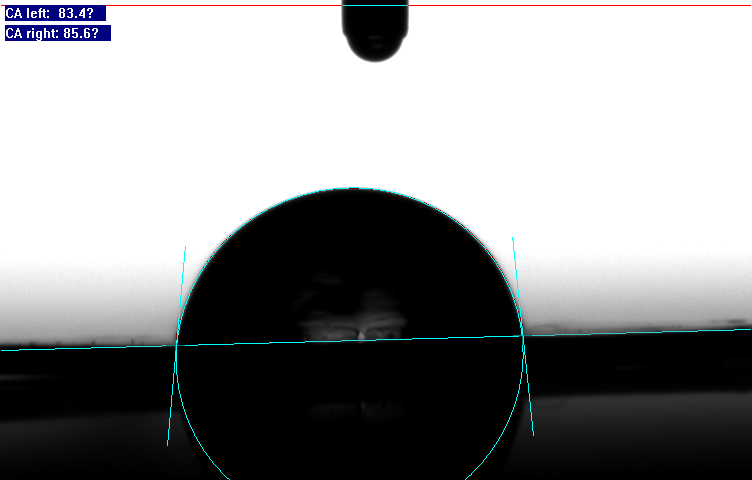
**Figure S5.** Raman spectrum of TBQPH.

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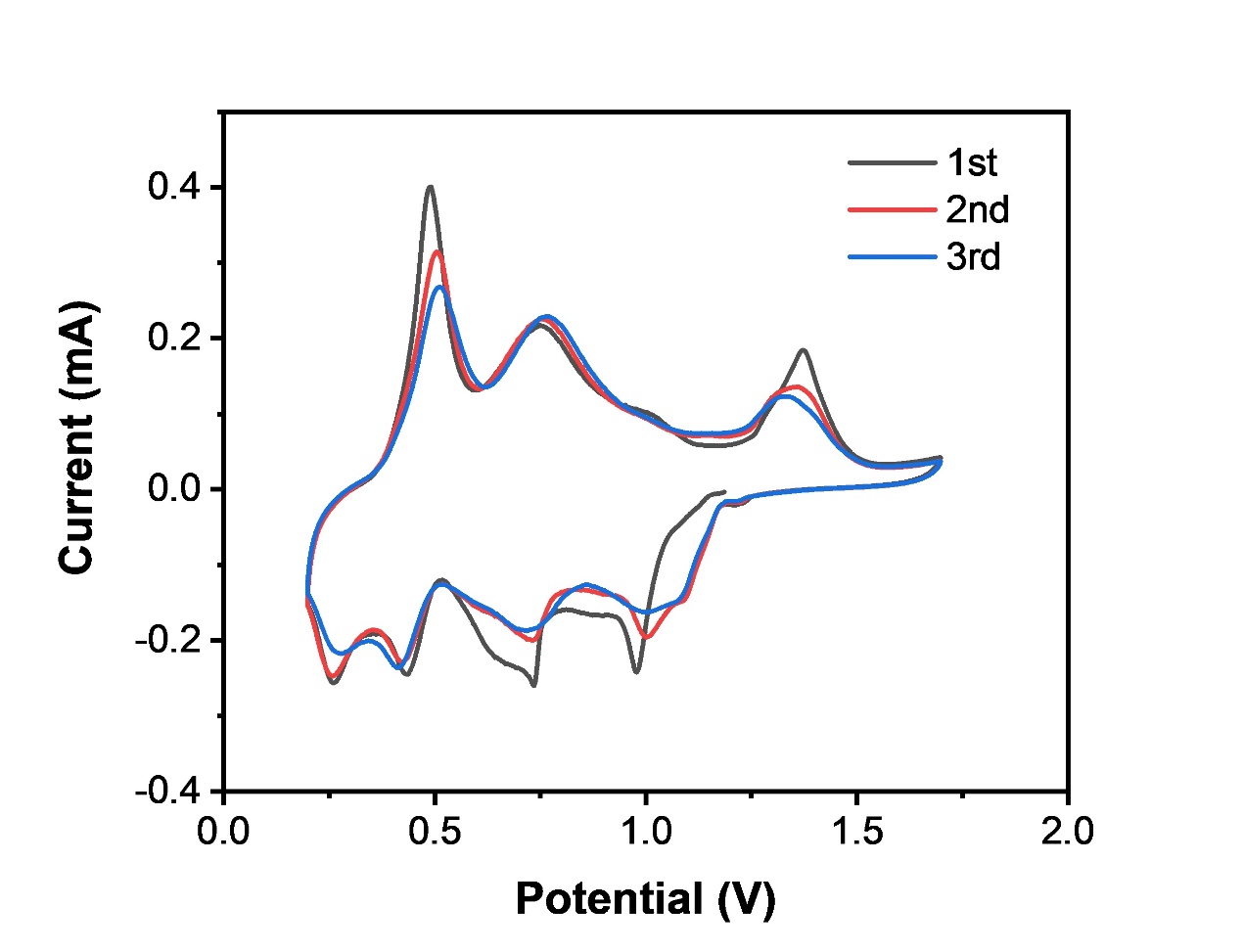
**Figure S6.** Powder XRD pattern of TBQPH.



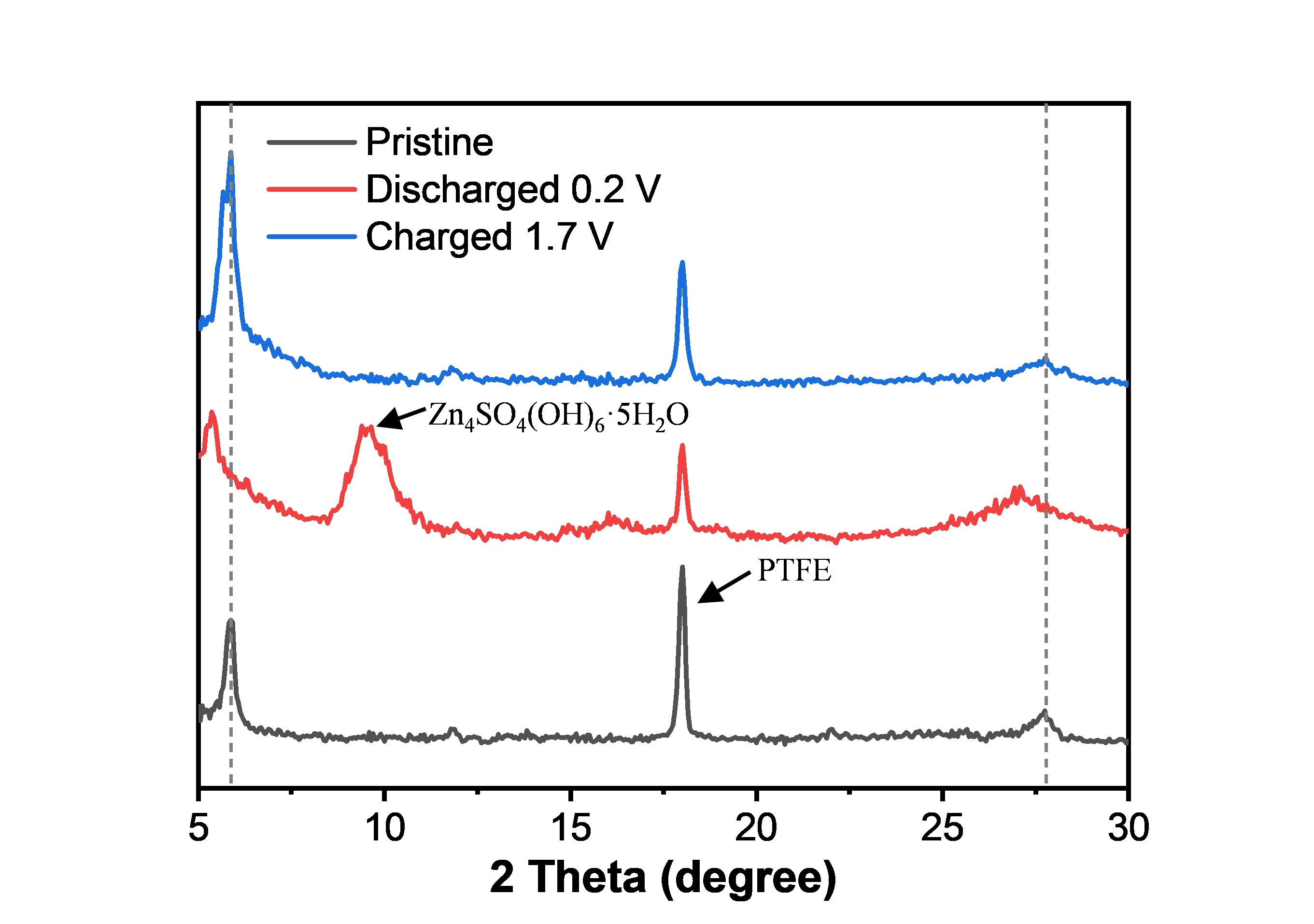
**Figure S7.** TG of TBQPH measured under argon at a heating rate of 10oC min−1.



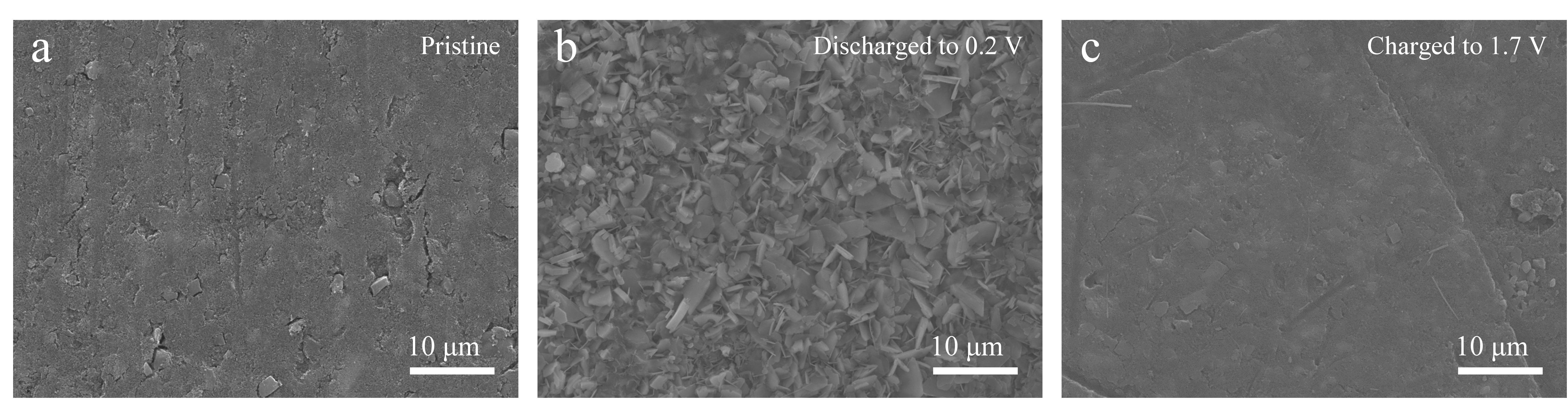
**Figure S8.** TheContact angle test of TBQPH electrode sheet.

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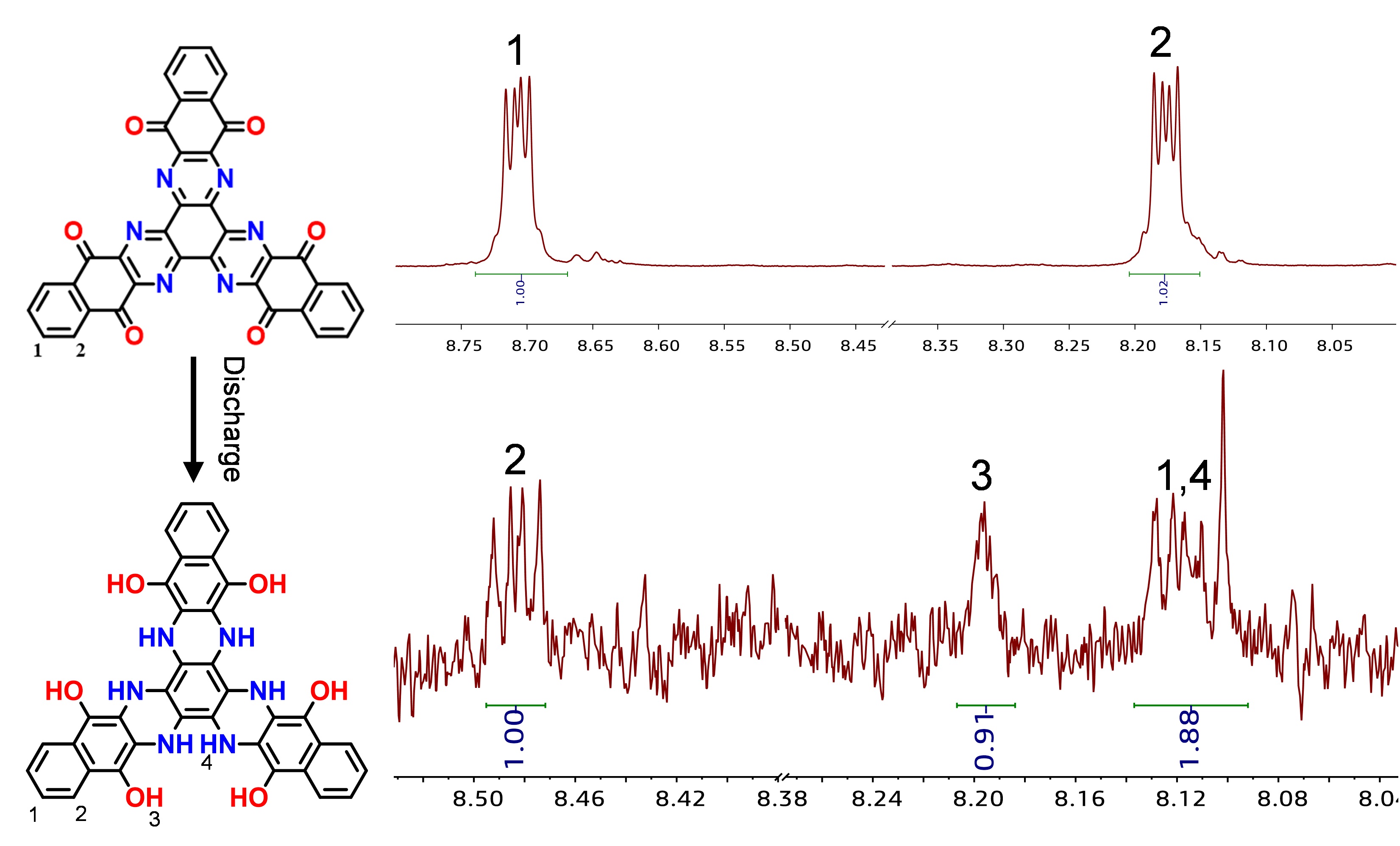
**Figure S9.** The CV curves of the first three circles of TBQPH//Zn batteries at the scan rate of 0.2 mV s−1.

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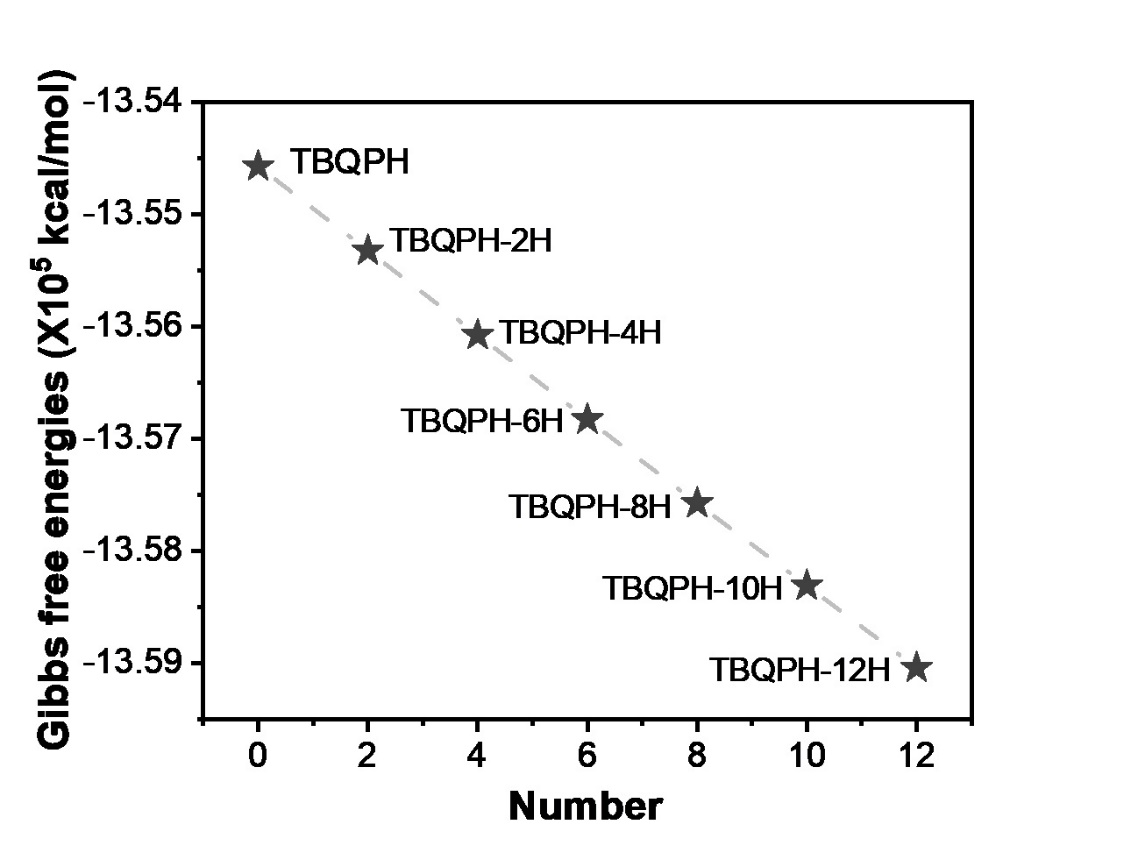
**Figure S10.** Ex-situ XRD profile of TBQPH electrode.

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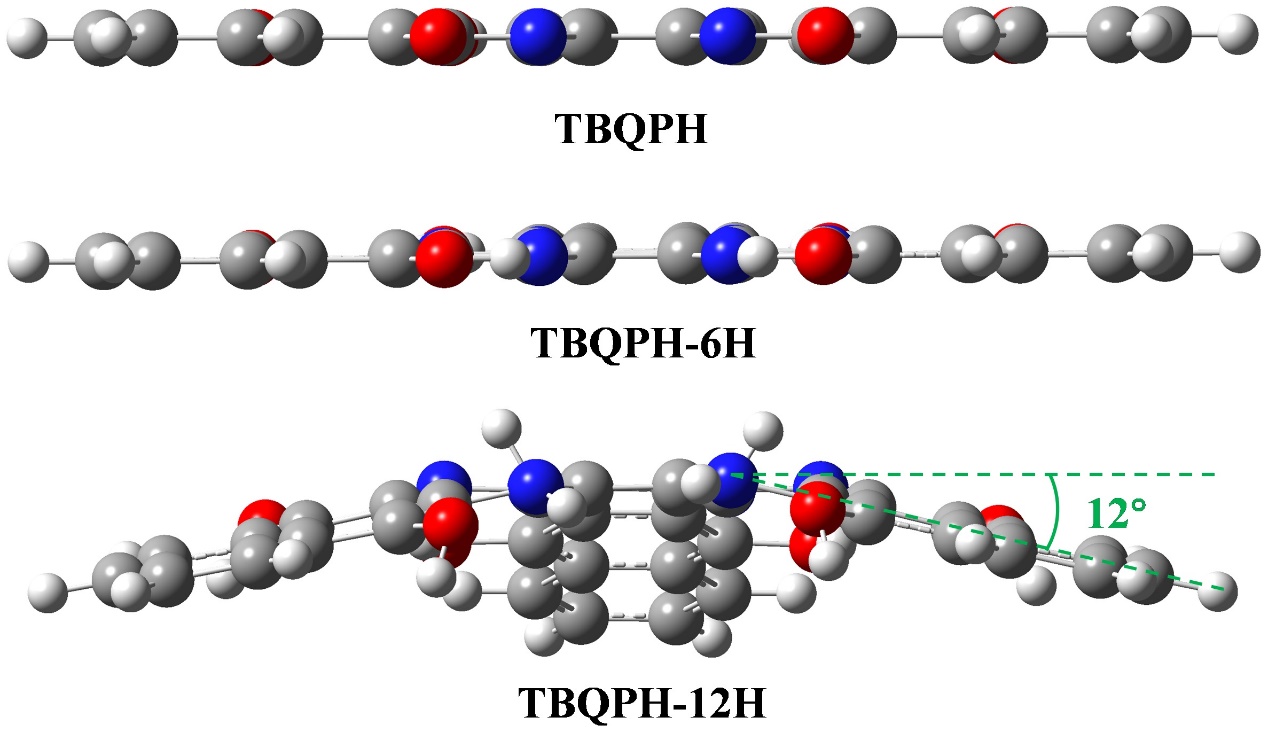
**Figure S11.** The SEM images of TBQPH cathodes at different states: (a) pristine, (b) discharged to 0.2 V, and (c) charged to 1.7 V.

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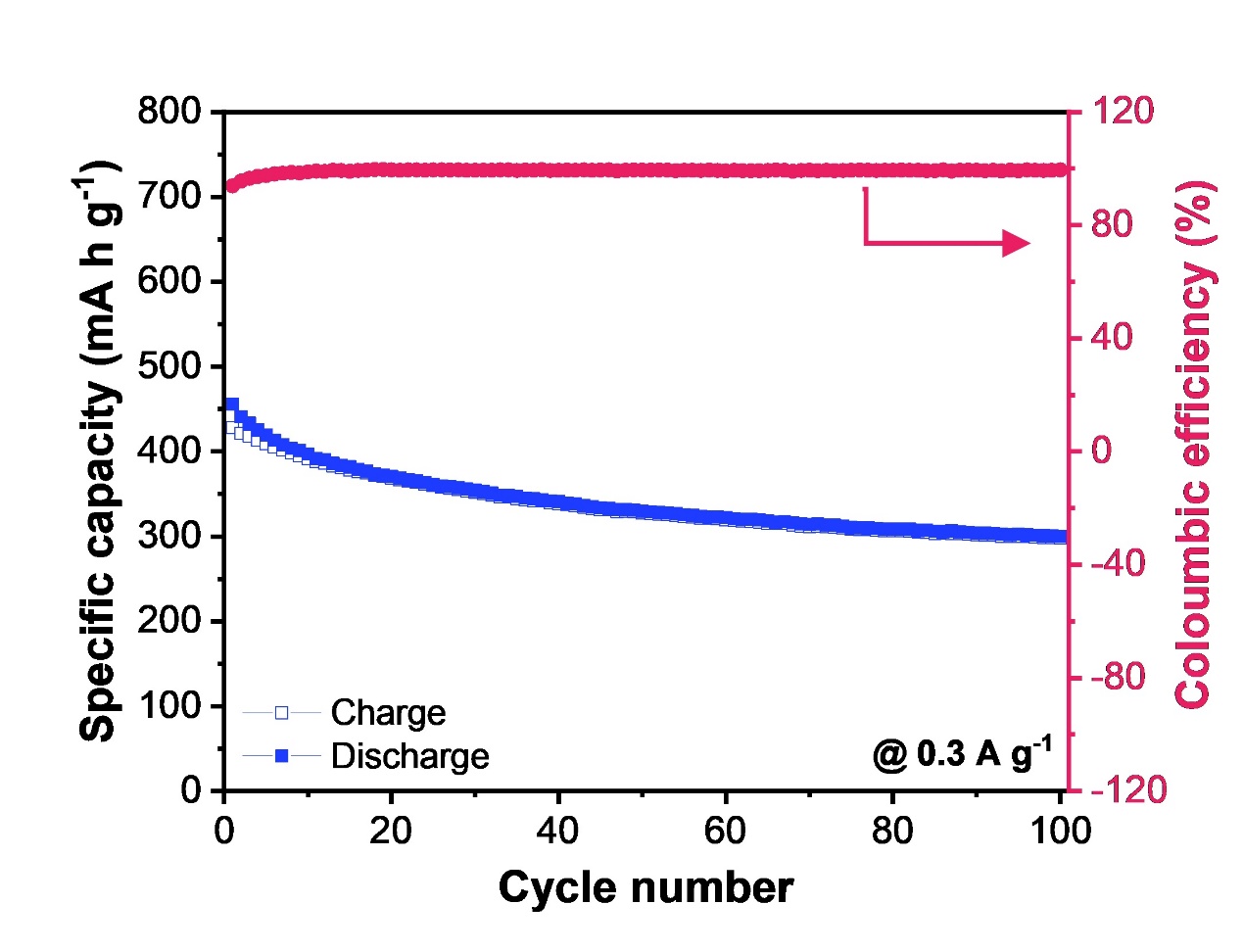
**Figure S12.** The 1H-NMR spectrum of initial state (above)was obtained in CF3COOD solvent. The 1H-NMR spectrum of discharge state (below) was obtained by dissolving a TBQPH electrode discharged to 0.2 V in DMSO-d6 solution by ultrasonic treatment.

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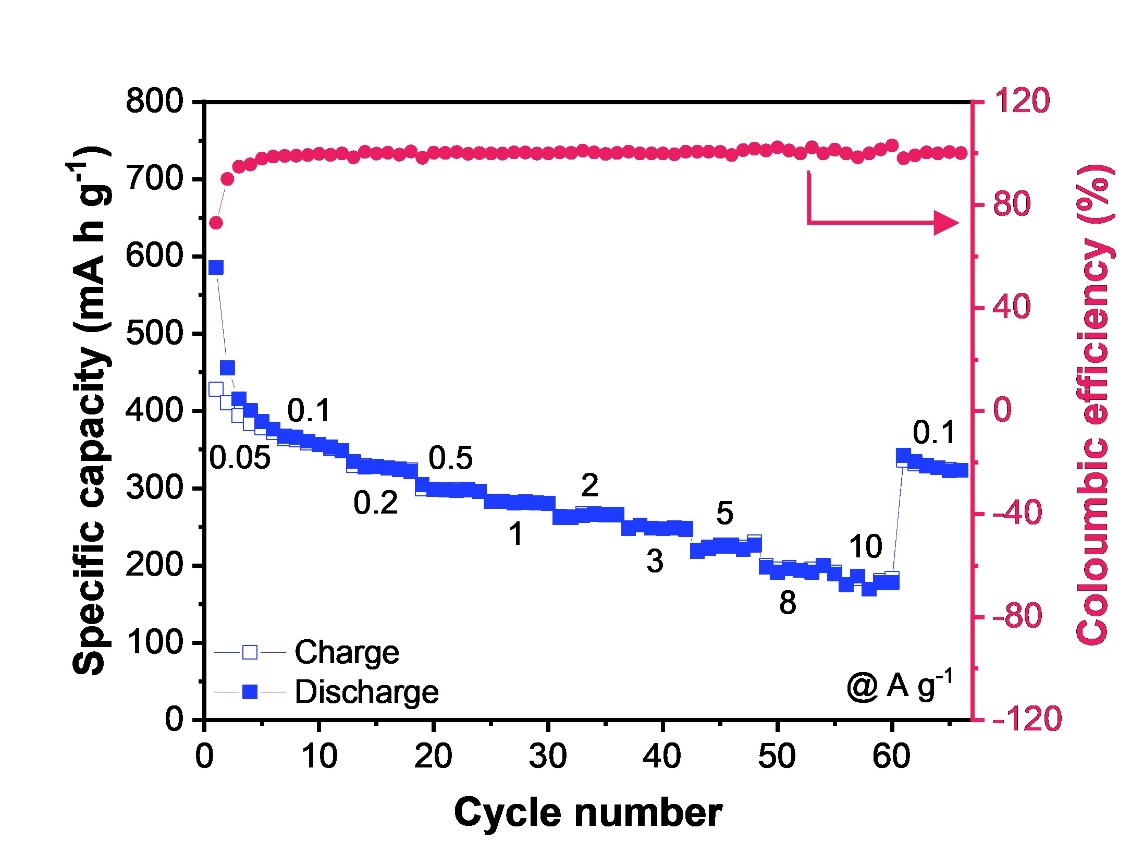
**Figure S13.** The most stable Gibbs free energies of TBQPHs in water solvent state.

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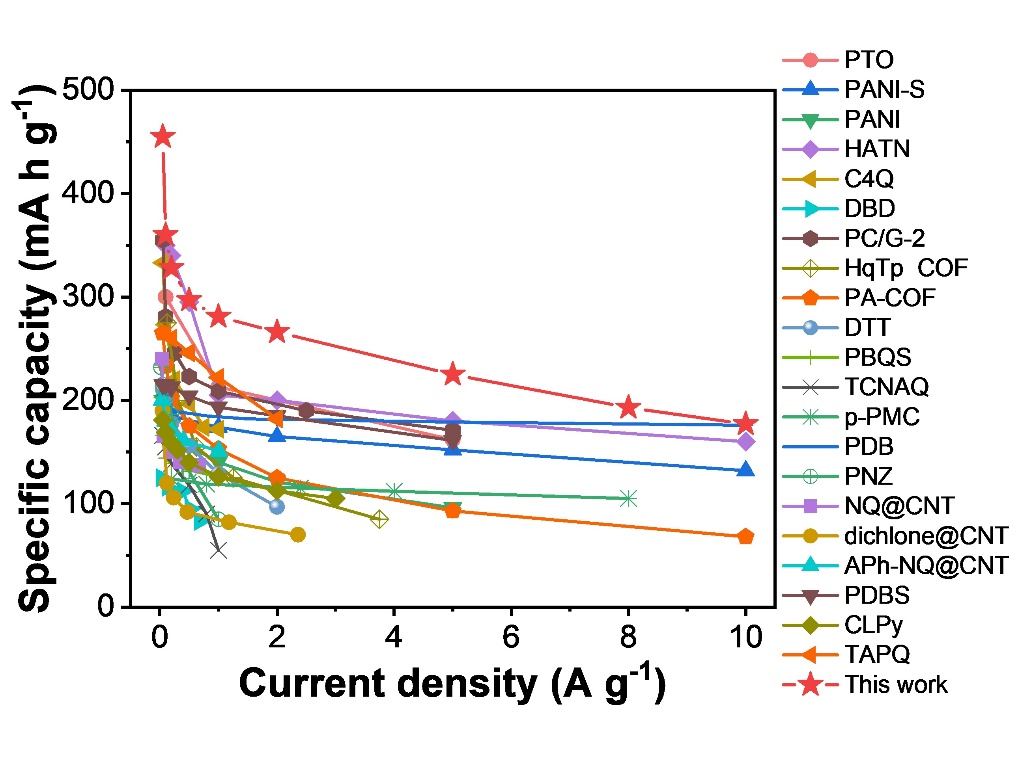
**Figure S14.** The structural transformation processes of TBQPHs.

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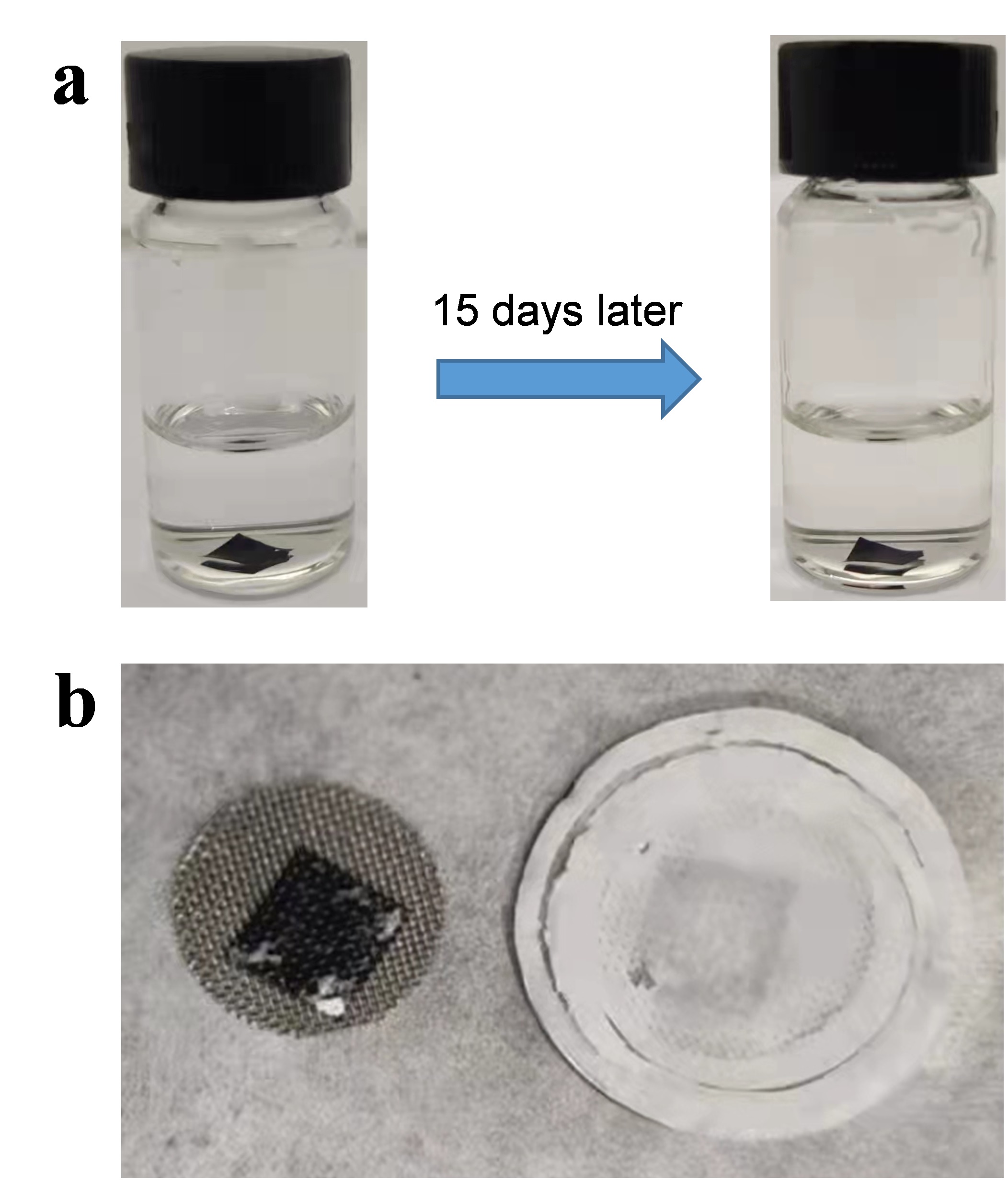
**Figure S15.** Cycling performance of TBQPH electrode at 0.3 A g−1 in 0.2-1.7 V.

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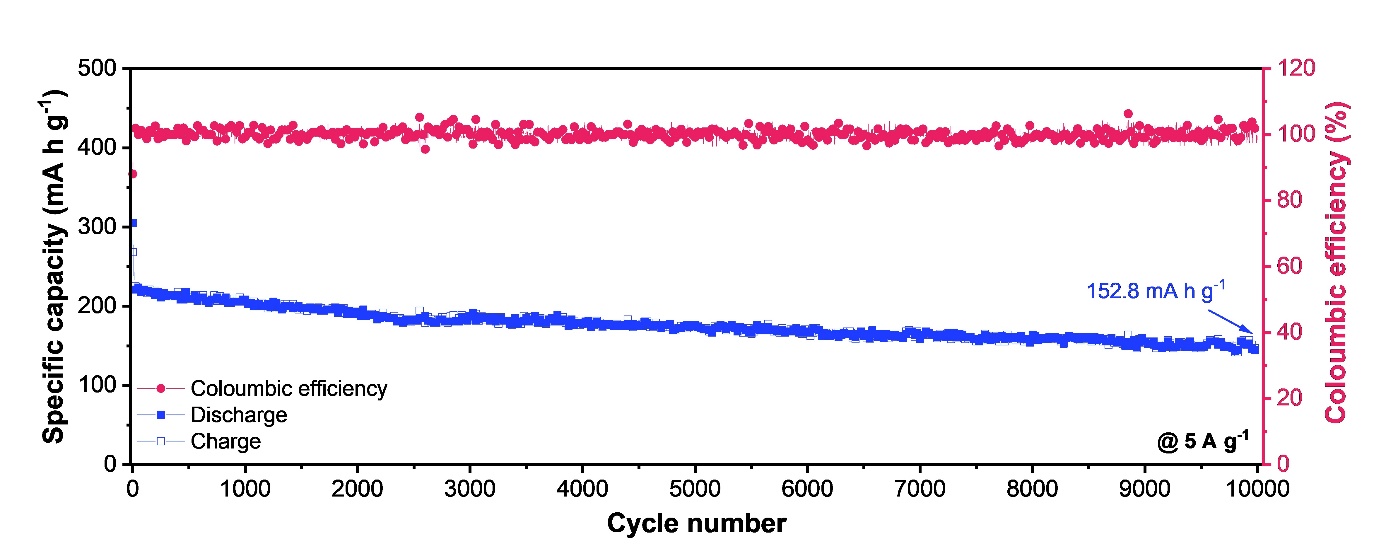
**Figure S16.** Rate performance of TBQPH electrode in 0.2-1.7 V.

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**Figure S17.** Rate capability comparison of TBQPH versus previously reported Zn-organic batteries.



**Figure S18.** TheSolubility test of TBQPH electrode. (a) The initial TBQPH electrode sheet soaked in 2M ZnSO4 aqueous solution for 15 days. (b) The state of the electrode sheet and separator when discharged to 0.2V.

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**Figure S19.** Cycling performance of TBQPH electrode at 5 A g−1.

**Table S1.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Compounds** | **Current density (A g−1)** | **Initial reversible capacity (mAh g−1)** | **Electrolyte (aqueous)** | **Refs** |
| **PTO** | **0.04** | **336** | **2 M ZnSO4** | **[6]** |
| **PANI-S** | **0.2** | **184** | **1 M ZnSO4** | **[7]** |
| **PANI** | **0.05** | **191** | **1 M Zn(CF3SO3)2** | **[8]** |
| **HATN** | **0.1** | **370** | **2 M ZnSO4** | **[9]** |
| **C4Q** | **0.05** | **337** | **3 M Zn(CF3SO3)2** | **[10]** |
| **BDB** | **0.026** | **125** | **19 M LiN(SO3CF3)2 + 1 M Zn(CF3SO3)2** | **[11]** |
| **PC/G-2** | **0.05** | **355** | **3 M ZnSO4** | **[12]** |
| **HqTp COF** | **0.125** | **275** | **3 M ZnSO4** | **[13]** |
| **DQP** | **0.1** | **392** | **1 M ZnSO4** | **[14]** |
| **PA-COF** | **0.05** | **265** | **1 M ZnSO4** | **[15]** |
| **DTT** | **0.05** | **210.9** | **2 M ZnSO4** | **[16]** |
| **PBQS** | **0.02** | **203** | **3 M Zn(CF3SO3)2** | **[17]** |
| **TCNAQ** | **0.02** | **169** | **2 M ZnSO4** | **[18]** |
| **p-PMC** | **0.2** | **122.9** | **2 M ZnCl2** | **[19]** |
| **PDB** | **0.02** | **234** | **4 M ZnSO4** | **[20]** |
| **PNZ** | **0.02** | **232** | **2 M ZnSO4** | **[21]** |
| **NQ@CNT** | **0.339** | **333.5** | **2 M Zn(CF3SO3)2** | **[22]** |
| **dichlone@CNT** | **0.118** | **210.3** | **2 M Zn(CF3SO3)2** |  |
| **APh-NQ@CNT** | **0.101** | **200.5** | **2 M Zn(CF3SO3)2** |  |
| **PDBS** | **0.05** | **225** | **2 M ZnSO4** | **[23]** |
| **CLPy** | **0.05** | **181** | **30 M ZnCl2** | **[24]** |
| **HATN-3CN** | **0.05** | **313** | **2 M ZnSO4** | **[25]** |
| **TAPQ** | **0.05** | **325** | **1 M ZnSO4** | **[26]** |
| **TBQPB** | **0.3** | **455.8** | **2 M ZnSO4** | **This work** |

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