

1 Supplementary Materials

2

3 **Stable hexaazatrinaphthylene-based covalent organic framework as high-**
4 **capacity electrodes for aqueous hybrid supercapacitors**

5

6 **Xu Li^{1,2}, Zhenhu Li^{1,3,*}, Yulin Zhang^{1,3}, Hanlin Guo⁴, Meiyong Zou^{1,3}, Haoxiang**
7 **Li^{1,3}, Yuping Liu^{1,3}, Shuangyi Liu^{1,3,*}**

8

9 ¹Research Center for Electrochemical Energy Storage Technologies, Chongqing
10 Institute of Green and Intelligent Technology, Chinese Academy of Sciences,
11 Chongqing 400714, China.

12 ²Chongqing CAS Supercap Technology Co., Ltd., Chongqing 401329, China.

13 ³Chongqing School, University of Chinese Academy of Sciences, Chongqing 400714,
14 China.

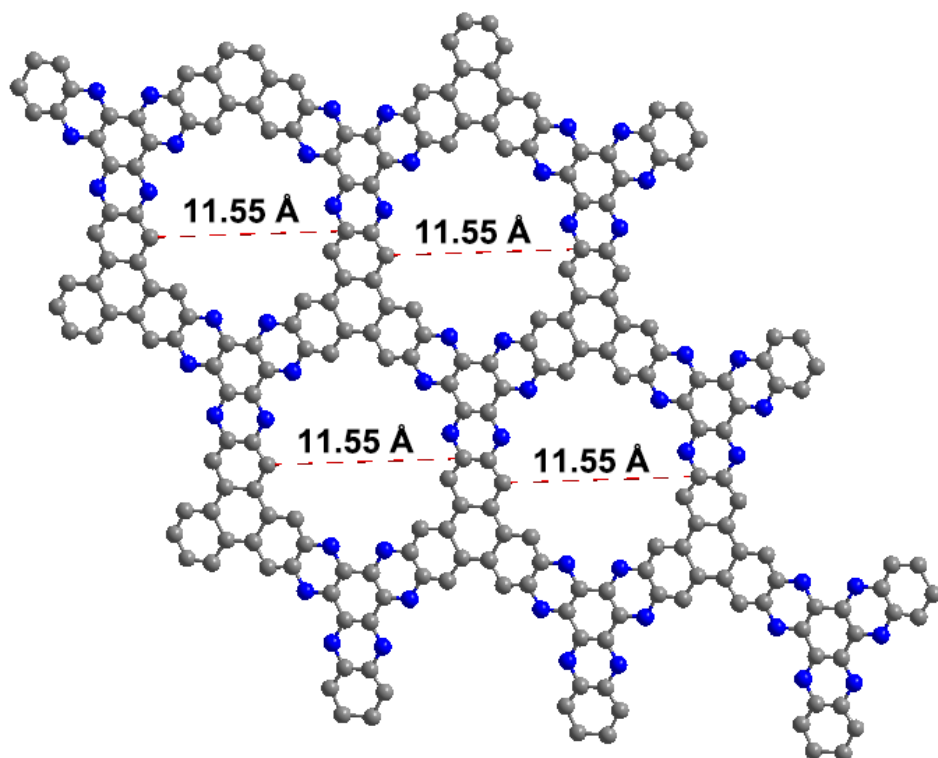
15 ⁴School of Physics and Electronic Engineering, Harbin Normal University, Harbin
16 150025, Heilongjiang, China.

17

18 ***Correspondence to:** Dr. Zhenhu Li and Prof. Shuangyi Liu, Research Center for
19 Electrochemical Energy Storage Technologies, Chongqing Institute of Green and
20 Intelligent Technology, Chinese Academy of Sciences, 266 Fangzheng Avenue,
21 Chongqing 400714, China. E-mail: lizhenhu@cigit.ac.cn; liushuangyi@cigit.ac.cn

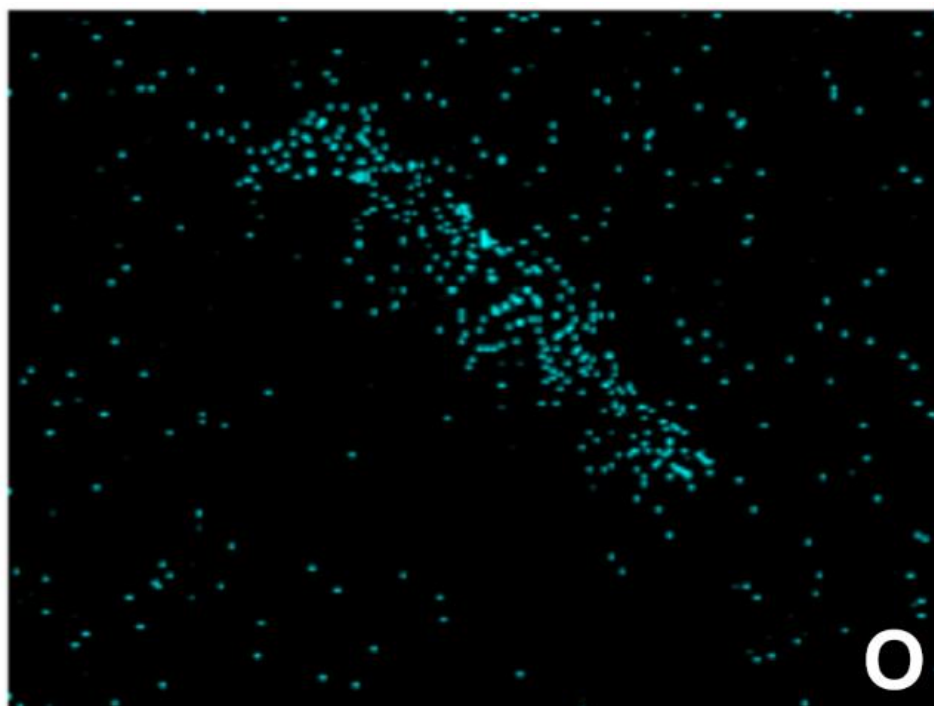
22

23



24

25

26 **Figure S1.** Simulated pore diameter of HATN-COF.

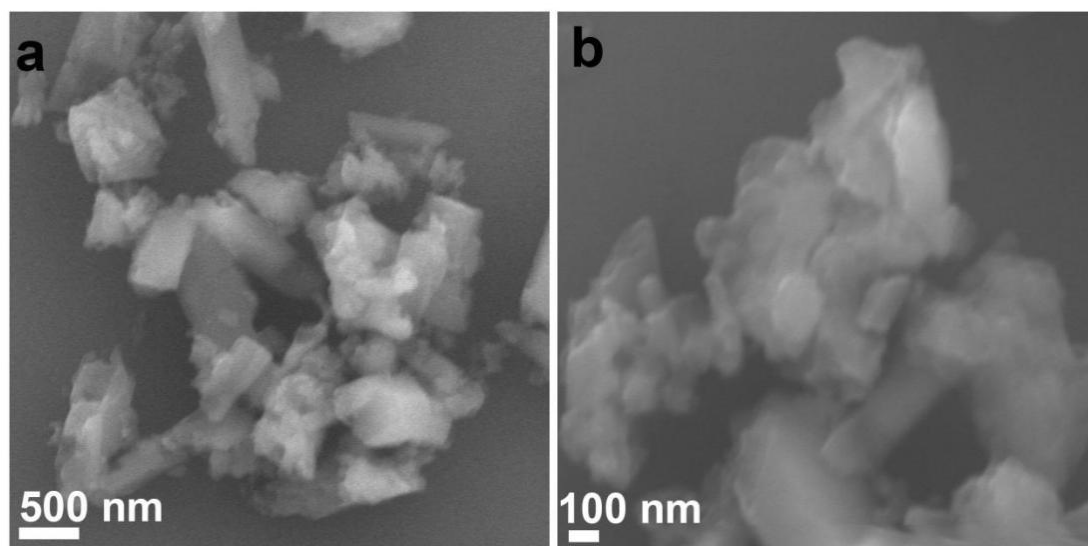
27

28 **Figure S2.** EDS elemental mapping of O element in the HATN-CO.

29 **Table S1. Elemental analysis of C and N contents of HATN-COF by a Vario EL**
30 **cube analyzer**

Element	Atomic percent (%)	Atomic ratio
C	71.5	3.4
N	20.9	1
H	7.6	-

31



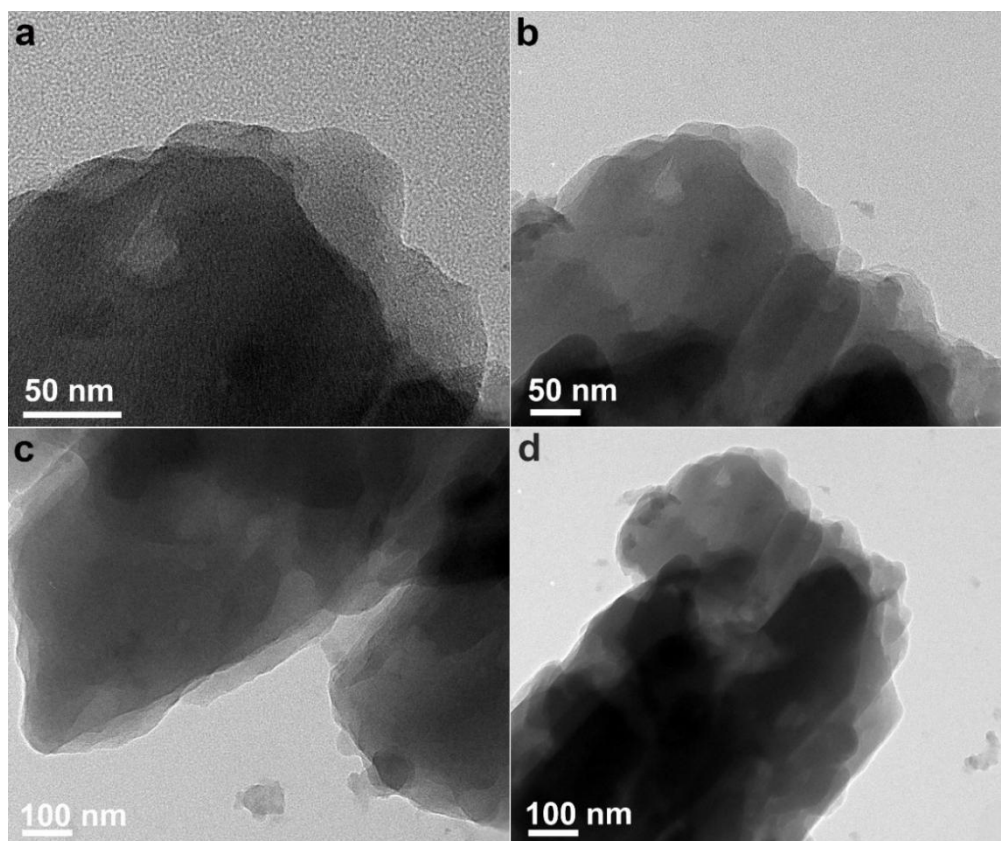
32

33

34 **Figure S3.** SEM images at different magnification after ultrasonic crushing of HATN-

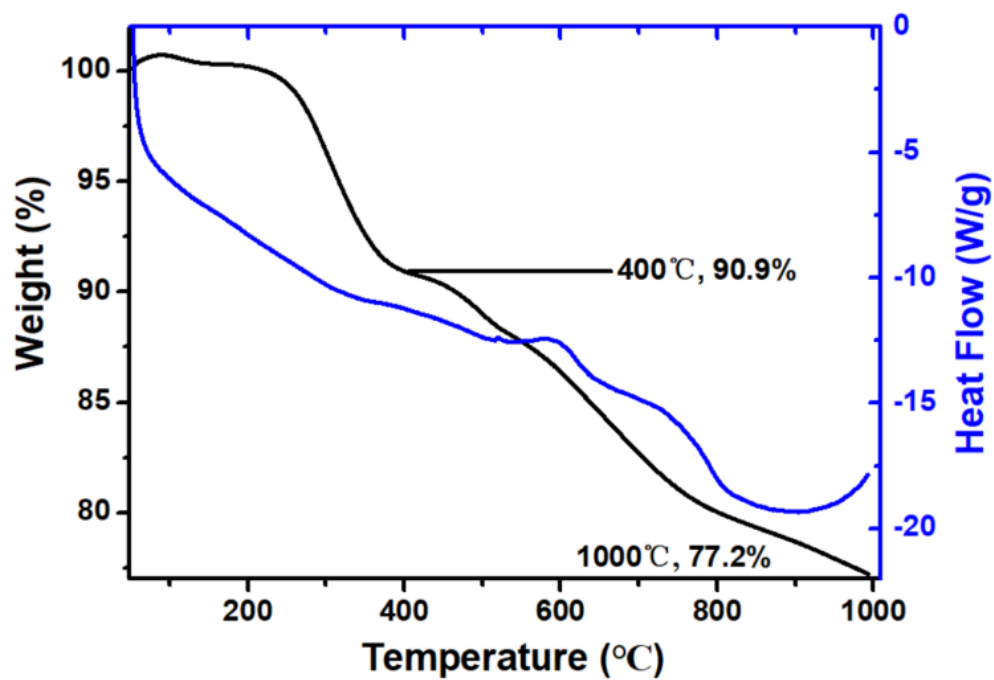
35 COF.

36



37

38 **Figure S4.** TEM images of HATN-COF.



39

40 **Figure S5.** TGA-DSC curves of HATN-COF.

41

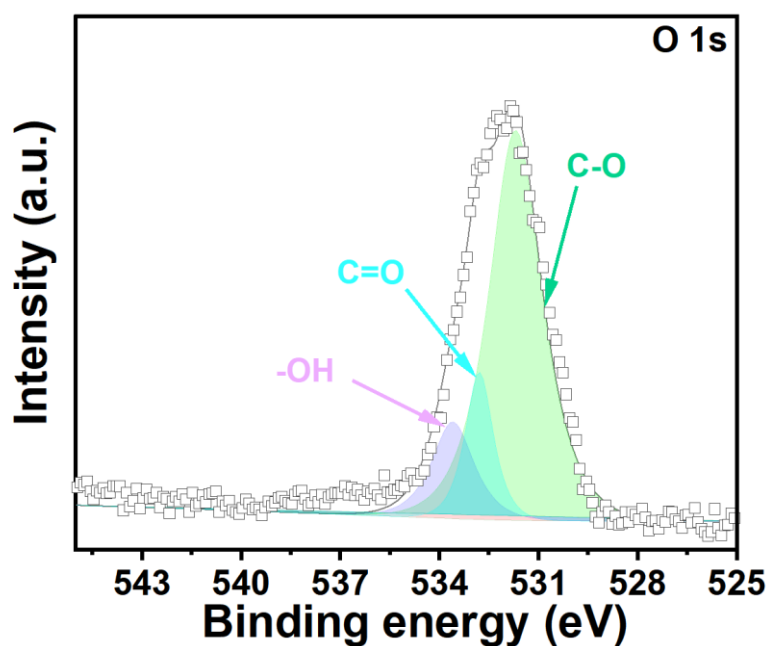
42 The thermostability of HATN-COF is estimated by using the thermogravimetric
43 analysis (TGA). The TGA curve can be divided into two stages between room
44 temperature and 1000°C. A 9.1% weight loss below 400°C resulted from the adsorbed
45 and crystalline ethanol and water molecules of the interlayer of HATN-COF.
46 Approximately 13.7% weight loss between 401 and 1000°C attributing to sectional
47 collapse of organic ligands. The result indicates that HATN-COF remains high
48 thermostability at the range from room temperature to 400°C.

49

50 **Table S2. The C, N and O contents of HATN-COF by XPS spectra**

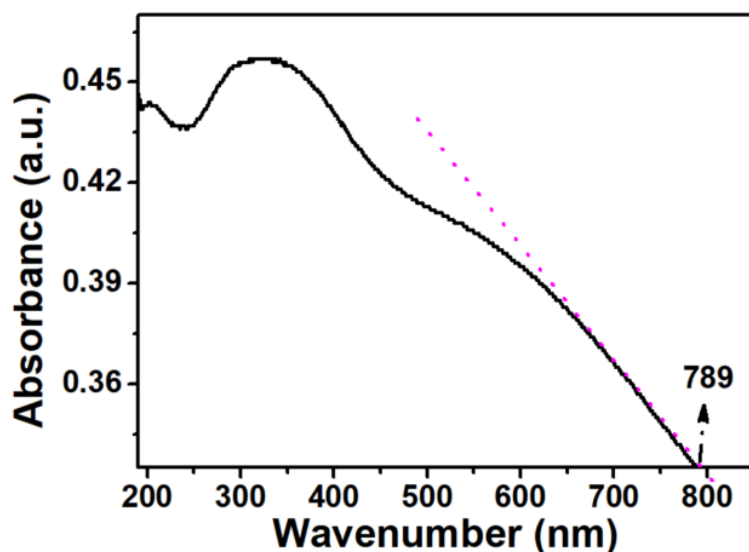
Element	Atomic percent (%)
C	74.8
N	15.7
O	9.4

51



52

53 **Figure S6.** The high resolution XPS spectrum of O 1s of HATN-COF.



54

55 **Figure S7.** The UV-Vis spectrum of HATN-COF.

56

57 The optical band gap is determined to be 1.6 eV, corresponding to a maximum
 58 absorption wavelength of 789 nm (the intersection of the purple dotted line and the X-
 59 axis in Figure. S6), indicative of semiconductor behavior^[1], according to the formula:

60

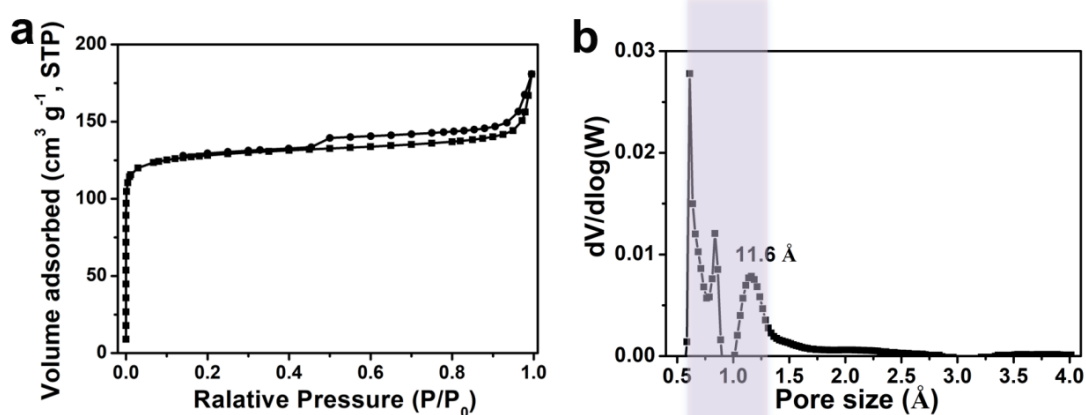
$$E_{g}^{op} = h\nu = (1240/\lambda_{abs}) \text{ eV} \quad (1)$$

61

where E_{g}^{op} is the optical band gap energy (eV), $h = 6.626196 \times 10^{-34}$ J·s, ν is the

62

frequency (Hz), and λ is the maximum absorption wavelength (nm).

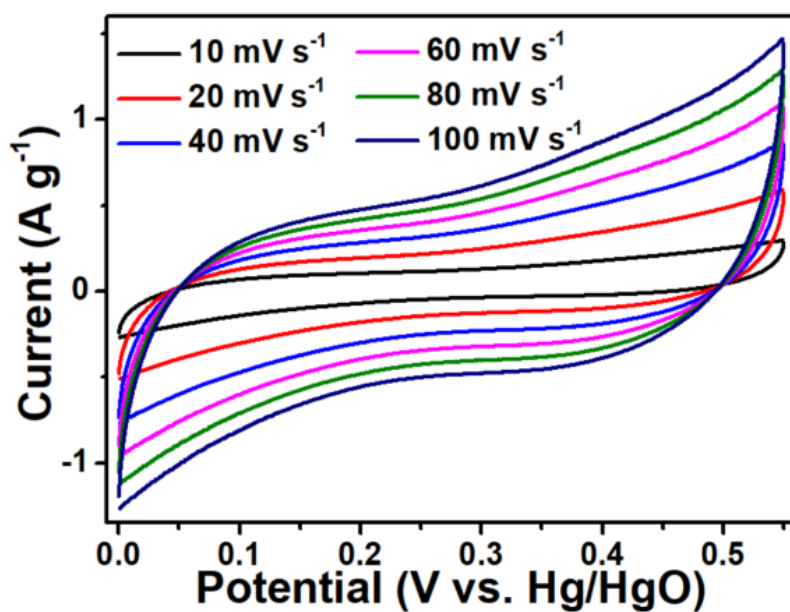


63

64 **Figure S8.** (a) Nitrogen adsorption-desorption isotherm curves and (b) pore size

65

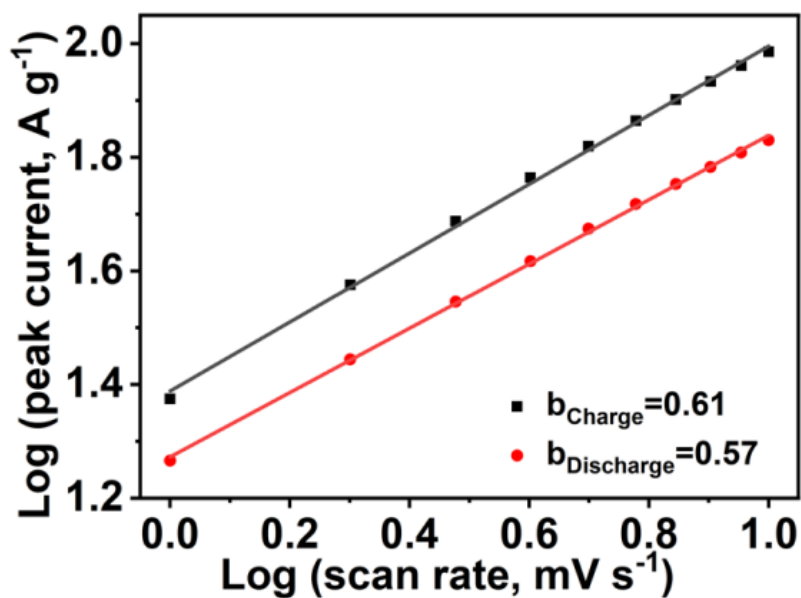
distribution curve of HATN-COF.



66
 67 **Figure S9.** CV curves of HATN-COF electrode from 10 to 100 mV s^{-1} in 1M Na_2SO_4
 68 electrolyte.

69
 70 The specific capacitance is 18.6 F g^{-1} at 10 mV s^{-1} in the neutral 1M Na_2SO_4
 71 electrolyte.

72



73
 74 **Figure S10.** Normalized peak-current plot to determine the b value for anodic process
 75 of HATN-COF electrode.

76

77 **Table S3. Specific capacity of HATN-COF electrode from 1 to 20 A g⁻¹**

Current density (A g ⁻¹)	Specific capacity (mAhg ⁻¹)
1	367.3
2	364.6
4	355.0
6	351.8
8	330.1
10	313.2
20	259.7

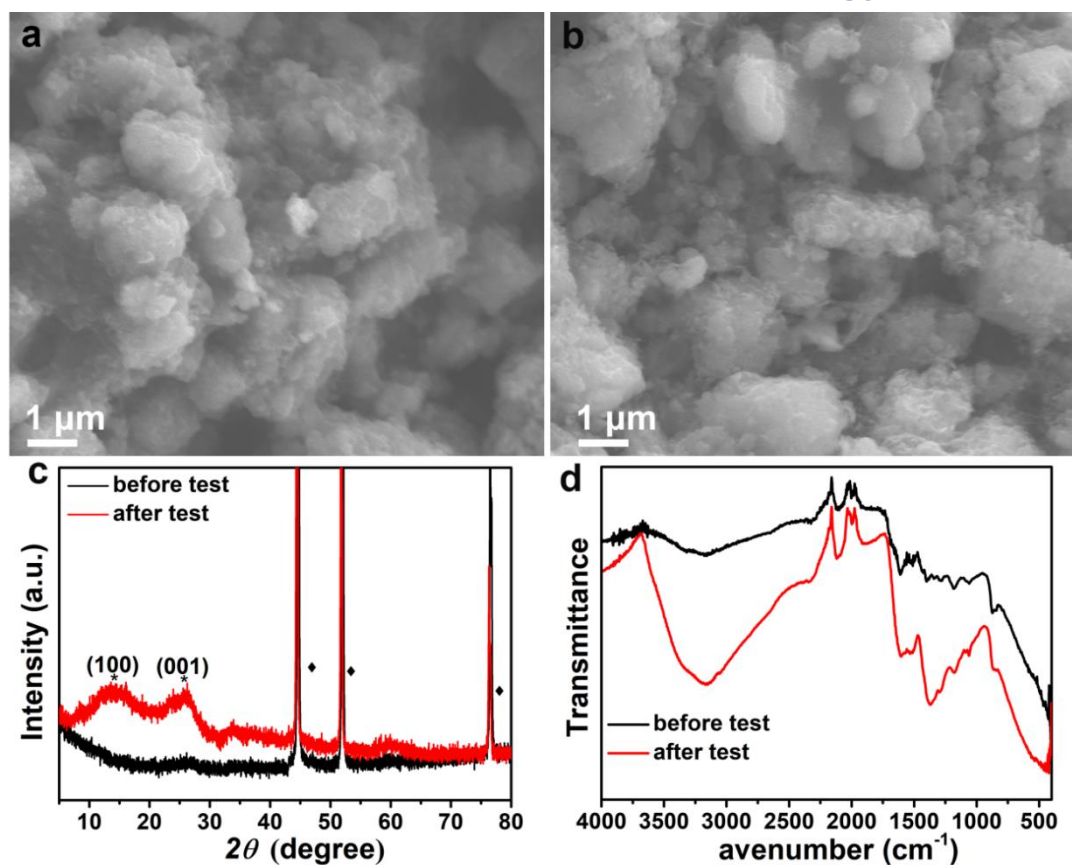
78

79 **Table S4. COF-based electrode material and their electrochemical performance**
80 **in three-electrode system reported in literature**

Electrode	Specific capacitance	Electrolyte	Retention (Cycles)	References
Ni-COF	1257 F g ⁻¹ at 1 A g ⁻¹	3 M KOH	94% (10,000)	[2]
Phos-COF-1	100 F g ⁻¹ at 1 A g ⁻¹	3 M Na ₂ SO ₄	90% (5000)	[3]
PT-COF	1443 F g ⁻¹ at 1 A g ⁻¹	0.5 M H ₂ SO ₄	91% (3000)	[4]
TpOMe-DAQ	169 F g ⁻¹ at 3.3 mA cm ⁻²	3 M H ₂ SO ₄	65% (50,000)	[5]
COF@OHP@CNTF	249 F g ⁻¹ at 30 mV s ⁻¹	1 M H ₃ PO ₄	80% (10,000)	[6]
N-PC	112 F g ⁻¹ at 1 A g ⁻¹	6 M KOH	88.4% (5000)	[7]
Ppy@COF	1983 mF g ⁻¹ at 1 A g ⁻¹	1 M PVA-H ₂ SO ₄	98% (2800)	[8]
HATN-COF	367.3 mAhg ⁻¹ (2644.5 F g ⁻¹) at 1 A g ⁻¹	6 M KOH	97.8% (20,000)	This work

81

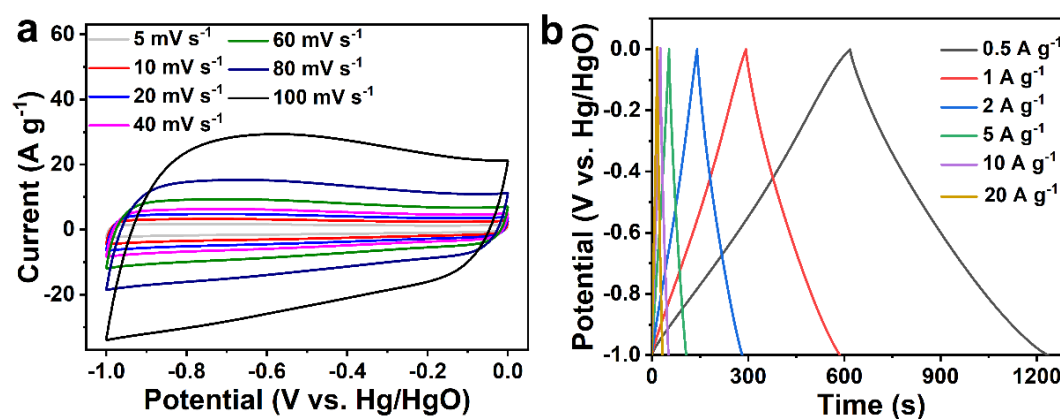
82



83

84 **Figure S11.** Structure and morphology characterizations of HATN-COF electrode.85 SEM images of (a) before and (b) after the cycling test at 6 A g^{-1} . (c) XRD patterns of86 before and after the cycling test at 6 A g^{-1} , Note that the peaks marked with * and ♦

87 originate from HATN-COF and nickel foam, respectively. (d) FTIR spectra of before

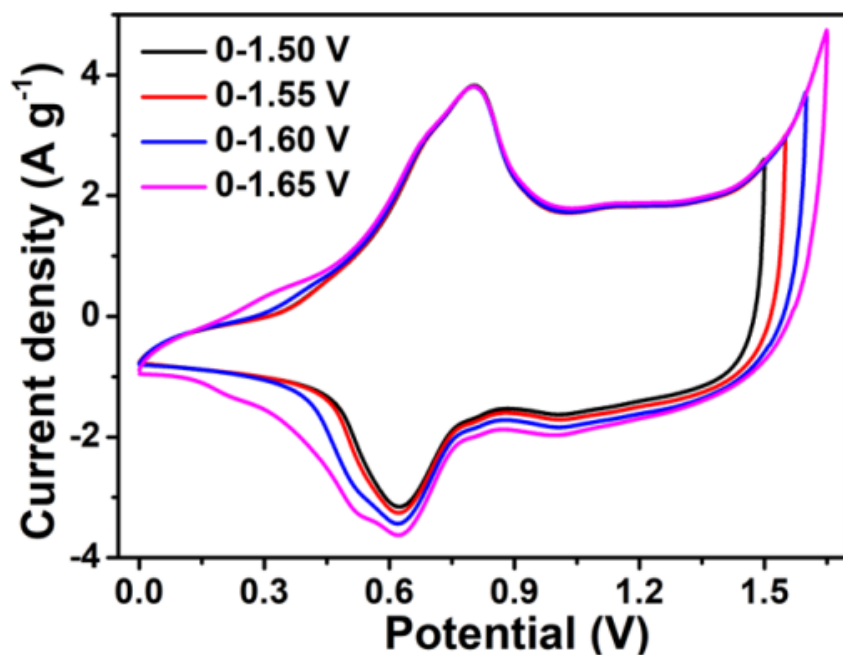
88 and after the cycling test at 6 A g^{-1} .

89

90

91 **Figure S12.** Electrochemical performances of AC electrode. (a) CV curves at different

92 scan rates. (b) GCD curves at different current densities.



93

94 **Figure S13.** CV curves of HATN-COF//AC at various voltage windows.

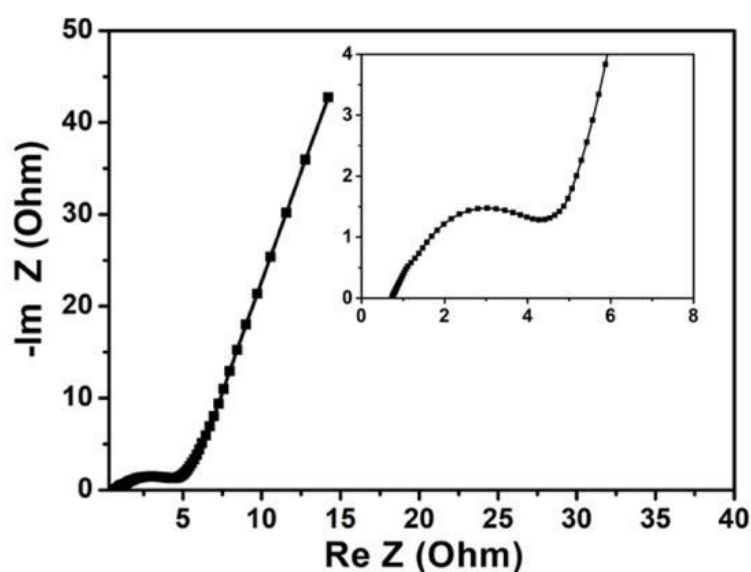
95

96 **Table S5. COF-based electrode material and their electrochemical performance**
97 **in two-electrode system reported in literature**

Electrode	Specific capacitance (F g ⁻¹)	Retention (Cycles)	Energy density at power density	References
PI-COF//PI-COF	163 F g ⁻¹ at 0.5 A g ⁻¹	84.1% (30,000)	35.7 W h kg ⁻¹ at 250 W kg ⁻¹	[9]
[C ₆₀]0.05C OF//rGO	47.6 F g ⁻¹ at 1 A g ⁻¹	99% (5000)	21.4 W h kg ⁻¹ at 900 W kg ⁻¹	[10]
FCTF//AC	148 F g ⁻¹ at 1 A g ⁻¹	98.9% (10,000)	46.3 W h kg ⁻¹ at 975 W kg ⁻¹	[11]
RuO ₂ //Hex-COF	64 F g ⁻¹ at 1 A g ⁻¹	89% (7500)	23.3 W h kg ⁻¹ at 661.2 W kg ⁻¹	[12]
TpTa-Py //TpTa-Py	102 F g ⁻¹ at 0.5 A g ⁻¹	92% (6000)	9.06 W h kg ⁻¹ at 100 W kg ⁻¹	[13]

PFM-COF1//	158 F g ⁻¹ at 0.5 A g ⁻¹	81% (2000)	28.44 W h kg ⁻¹ at 1077.72 W kg ⁻¹	[14]
PDC MA COF//AC	94 F g ⁻¹ at 1 A g ⁻¹	88% (20,000)	29.2 W h kg ⁻¹ at 750 W kg ⁻¹	[15]
HATN-COF//AC	215.4 F g ⁻¹ at 0.5 A g ⁻¹	97.3% (20,000)	67.3 W h kg ⁻¹ at 375 W kg ⁻¹	This work

98



99

100 **Figure S14.** Nyquist plots, with the inset showing the enlarged portion of HATN-
101 COF//AC.

102

103 **References**

104 1 Iqbal R, Majeed MK, Hussain A et al. Boosting the Crystallinity of Novel Two-
105 Dimensional Hexamine Dipyrazino Quinoxaline-Based Covalent Organic
106 Frameworks for Electrical Double-Layer Supercapacitors. *Micropor Mesopor Mat*
107 2023;7:2464-2474. DOI:10.1039/D3QM00169E

- 108 2 Li T, Zhang WD, Liu Y et al. A Two-Dimensional Semiconducting Covalent
109 Organic Framework with Nickel(II) Coordination for High Capacitive Performance.
110 *J Mater Chem A* 2019;7:19676-19681. DOI:10.1039/c9ta07194f
- 111 3 Sajjad M, Tao R, Qiu L. Phosphine Based Covalent Organic Framework as an
112 Advanced Electrode Material for Electrochemical Energy Storage. *J Mater Sci-mater*
113 *El* 2021;32:1602-1615. DOI:10.1007/s10854-020-04929-9
- 114 4 Patra BC, Bhattacharya S. New Covalent Organic Square Lattice Based on
115 Porphyrin and Tetraphenyl Ethylene Building Blocks toward High-Performance
116 Supercapacitive Energy Storage. *Chem Mater* 2021;33:8512-8523.
117 DOI:10.1021/acs.chemmater.1c02973
- 118 5 Halder A, Ghosh M, Khayum MA et al. Interlayer Hydrogen-Bonded Covalent
119 Organic Frameworks as High-Performance Supercapacitors. *J Am Chem Soc*
120 2018;140:10941-10945. DOI:10.1021/jacs.8b06460
- 121 6 Xu Z, Liu Y, Wu Z et al. Construction of Extensible and Flexible Supercapacitors
122 from Covalent Organic Framework Composite Membrane Electrode. *Chem Eng J*
123 2020;387:124071. DOI:10.1016/j.cej.2020.124071
- 124 7 Vargheese S, Dinesh M, Kavya KV, Pattappan D, Rajendra Kumar RT, Haldorai
125 Y. Triazine-Based 2D Covalent Organic Framework-Derived Nitrogen-Doped Porous
126 Carbon for Supercapacitor Electrode. *Carbon Lett* 2021;31:879-886.
127 DOI:10.1007/s42823-020-00190-6
- 128 8 Haldar S, Rase D, Shekhar P et al. Vaidhyanathan R, Incorporating Conducting
129 Polypyrrole into a Polyimide Cof for Carbon-Free Ultra-High Energy
130 Supercapacitor. *Adv Energy Mater* 2022;12:2200754. DOI:10.1002/aenm.202200754
- 131 9 Iqbal R, Badshah A, Ma YJ, Zhi LJ. An Electrochemically Stable 2D Covalent
132 Organic Framework for High-Performance Organic Supercapacitors. *Chinese J Polym*
133 *Sci* 2020;38:558-564. DOI:10.1007/s10118-020-2412-z
- 134 10 Zhao X, Sajjad M, Zheng Y et al. Covalent Organic Framework Templated
135 Ordered Nanoporous C₆₀ as Stable Energy Efficient Supercapacitor Electrode
136 Material. *Carbon* 2021;182:144-154. DOI:10.1016/j.carbon.2021.05.061

- 137 11 Gao Y, Zhi C, Cui P, Zhang KAI, Lv LP, Wang Y. Halogen-Functionalized
138 Triazine-Based Organic Frameworks Towards High Performance Supercapacitors.
139 *Chem Eng J* 2020;400:125967. DOI:10.1016/j.cej.2020.125967
- 140 12 Kandambeth S, Jia J, Wu H et al. Covalent Organic Frameworks as Negative
141 Electrodes for High-Performance Asymmetric Supercapacitors. *Adv Energy Mater*
142 2020;10:202001673. DOI:10.1002/aenm.202001673
- 143 13 Khattak AM, Ghazi ZA, Liang B et al. A Redox-Active 2D Covalent Organic
144 Framework with Pyridine Moieties Capable of Faradaic Energy Storage. *J Mater*
145 *Chem A* 2016;4:16312-16317. DOI:10.1039/C6TA05784E
- 146 14 Biradar MR, Rao CRK, Bhosale SV, Bhosale SV. Flame-Retardant 3D Covalent
147 Organic Framework for High-Performance Symmetric Supercapacitors. *Energy Fuels*
148 2023;37:4671-4681. DOI:10.1021/acs.energyfuels.2c04226
- 149 15 Li L, Lu F, Xue R et al. Ultrastable Triazine-Based Covalent Organic Framework
150 with an Interlayer Hydrogen Bonding for Supercapacitor Applications. *ACS Appl*
151 *Mater Interfaces* 2019;11:26355-26363. DOI:10.1021/acsami.9b06867
- 152