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## **Supplementary Information**

# Bicarbozole-based redox-active covalent organic frameworks for ultrahigh-performance energy storage<sup>†</sup>

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#### **Experimental section**

#### Chemicals

Carbazole, 1,4-diaminobenzene, benzidine and other chemicals were purchased from J&K Scientific Ltd. All chemicals were used as received. 3,3'6,6'-Tetrabromo-9,9'-bicarbazole were prepared according to the previously reported methods.<sup>S1, S2</sup>

#### Synthesis of 3,6-dibromocarbazole

A solution of NBS (10.68 g, 60 mmol) in 50 mL DMF was added slowly to a suspension of carbazole (5 g, 30 mmol) in dichloromethane (300 mL). The reaction mixture was stirred at room temperature overnight. The solution was washed with water ( $3 \times 50$  mL), the organic layer was dried under magnesium sulfate and filtered. The solvent was evaporated and the residue was dissolved in acetone (50 mL) and precipitated with hexane (300 mL). The solid was collected and dried under vacuum to yield 3,6-dibromocarbazole (7.7 g, yield: 82%) of product. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) : 7.31 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2 H), 8.13 (d, J = 1.9 Hz, 2H), and 10.37 (s, 1 H).

#### Synthesis of 3,3'6,6'-tetrabromo-9,9'-bicarbazole

To a solution of 3,6-dibromocarbazole (9.75 g, 30 mmol) in 150 mL acetone, potassium permanganate (14.22 g, 90 mmol) was added at 50 °C. The solution was stirred for 2 h at 50 °C. Then the solution was hydrolyzed with 100 mL distilled water. The mixture was extracted with dichloromethane and the combined organic layers were washed with distilled water, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by using silica gel chromatography petroleum ether eluent with as to yield 3,3'6,6'-tetrabromo-9,9'-bicarbazole (6.92 g, yield: 71%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.26 (d, 4 H), 7.47 (dd, J = 10.4 Hz, 4H), 6.74 (d, J = 8.6 Hz, 4H).

#### Synthesis of 3,3',6,6'-tetraformyl-9,9'-bicarbazole.

*n*-Butyl lithium (2.4 M, 4.7 mL, 11.2 mmol) was dropwise added to a solution of 3,3'6,6'-tetrabromo-9,9'-bicarbazole (1.296 g, 2.0 mmol) in 60 mL THF at -78 °C under N<sub>2</sub> atmosphere. The mixture was stirred for 2 h at -78 °C, then 3.0 mL DMF was added to the reaction mixture, and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred overnight, hydrolyzed with 100 mL distilled water and extracted with dichloromethane. The combined organic layers were washed with distilled water, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by using silica gel chromatography with petroleum ether/ethyl acetate (4/1 by vol.) as eluent to yield 3,3',6,6'-tetraformyl-9,9'-bicarbazole (0.5 g, 56% yield) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 10.20 (s, 4 H), 8.86 (s, 4 H), 8.02 (d, J = 9.6 Hz, 4 H), 7.08 (d, J = 8.4 Hz, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 190.95 (CHO), 143.26 (C–N), 132.24 (C–CHO), 129.54 (CH), 124.17 (C), 122.41 (CH), 109.61 (CH). HRMS (ESI): Calcd. for C<sub>28</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub> (M + H)<sup>+</sup>: 445.1188; Found: 445.1173.

#### Synthesis of Cz-COF1

3,3',6,6'-Tetraformyl-9,9'-bicarbazole (111 mg, 0.25 mmol) and 1,4-diaminobenzene (54 mg, 0.5 mmol) were added into a Schlenk storage tube and dissolved in a mixture solvent (6 mL, 1,4-dioxane:mesitylene = 1:1,v/v) under a nitrogen atmosphere, and 0.6 mL aqueous acetic acid (6 M) was added into the mixture. The suspension was placed in an oven at 120 °C and left undisturbed for 72 h. The precipitates were collected by filtration and washed with chloroform, THF, methanol, and acetone thoroughly. The resulted product was dried at 80 °C in vacuum to yield Cz-COF1 as a yellow powder (124 mg, 76% yield).

#### Synthesis of Cz-COF2

Cz-COF2 was synthesized by using of 3,3',6,6'-tetraformyl-9,9'-bicarbazole (111 mg,

0.25 mmol) and benzidine (92 mg, 0.5 mmol) in a manner similar to that of Cz-COF1. Cz-COF2 was obtained as a yellow powder (135 mg, 67% yield).

#### Synthesis of amorphous Cz-CMP1

3,3',6,6'-Tetraformyl-9,9'-bicarbazole (111 mg, 0.25 mmol) and 1,4-diaminobenzene (54 mg, 0.5 mmol) were added into a Schlenk storage tube and dissolved in 5 mL dimethyl sulfoxide under a nitrogen atmosphere. The suspension was stirred at room temperature for 0.5 h. Then the temperature was raised in the heating schedule: 140 °C for 6 h, 160 °C for 30 h. After cooling down to room temperature, the precipitates were collected by filtration and washed with chloroform, THF, methanol, and acetone thoroughly. The resulted product was dried at 80 °C in vacuum to yield Cz-CMP1 as a yellow powder (131 mg, 80% yield).

#### Lithium ion batteries measurements

The working electrodes were prepared by mixing the Cz-COFs, acetylene black and sodium alginate with the mass ratio of 5:3:2. The resulting slurries were cast onto copper foil current collectors. The foils were rolled into 25 mm thin sheets, and then dried at 50 °C for 24 h. The foils were cut into disks with the diameter of 14 mm, and then dried at 110 °C under vacuum for 12 h. CR2016 coin-type cells were assembled in an argon-filled glove box with lithium foils as the counter electrodes and polypropylene macroporous films (Celgard 2400) as the separator, the batteries were aged 24 h before testing. The concentration of LiPF<sub>6</sub> was 1.0 mol L<sup>-1</sup> in a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 v/v). The galvanostatic charge and discharge tests were carried out by the NEWARE-BTS-5 V/10 mA testing instrument (Neware Co., Ltd., Shenzhen, China) in a voltage range between 0 and 3 V at the current rates of 100, 200, 500, and 1000 mA g<sup>-1</sup> at room temperature. Cyclic voltammetry (CV) measurements were carried out in the voltage range of 0-3 V with a scanning rate of 0.1 mV s<sup>-1</sup> at room temperature.

#### Characterization

Elemental analysis was performed on a EURO EA3000 Elemental Analyzer. The FT-IR spectra were collected in transmission on a Tensor 27 FT-IR spectrometer (Bruker) using KBr disks. The thermal properties of the covalent organic frameworks were evaluated using a thermogravimetric analysis (TGA) with a differential thermal analysis instrument (Q1000DSC + LNCS + FACS Q600SDT) over the temperature range from 30 to 1000 °C under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup>. Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using an ASAP 2420-4 (Micromeritics) volumetric adsorption analyzer. Samples were degassed at 120 °C for 15 h under vacuum  $(10^{-5} \text{ bar})$  before analysis. The surface areas were calculated in the relative pressure  $(P/P_{\theta})$  range from 0.05 to 0.20. Pore size distributions and pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT). Solid state <sup>1</sup>H-<sup>13</sup>C CP/MAS NMR spectra were recorded on a JEOL models JNM-LA 400 MHz NMR spectrometer. Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-8000 at an accelerating voltage of 5.0 kV. The samples were prepared by drop-casting an acetone suspension onto mica substrate and then coated with gold. High-resolution transmission electron microscopy (HR-TEM) images were obtained on a JEOL model JEM-3200 microscopy. Powder X-ray diffraction (XRD) profiles were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta = 2^{\circ}$  up to 50° with 0.02° increment.

#### **Crystalline structures**

The crystalline structures of the Cz-COFs were determined using the density-functional tight-binding (DFTB+) method including Lennard-Jones (LJ) dispersion. The calculations were carried out with the DFTB+ program package version 1.2.<sup>S3</sup> DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all-valence basis set in combination with a two-center approximation for Hamiltonian matrix elements. The Coulombic interaction between partial atomic charges was determined using the self-consistent charge (SCC) formalism. Lennard-Jones type dispersion was employed in all calculations to describe van der Waals (vdW) and  $\pi$ -stacking interactions. The lattice dimensions were optimized simultaneously with the geometry. Standard DFTB parameters for X–Y element pair (X, Y = C, O, H and N) interactions were employed from the mio-0-1 set.

The PXRD pattern simulation was performed in a software package for crystal determination from XRD pattern, implemented in MS modeling version 4.4 (Accelrys Inc.). We performed Pawley refinement to optimize the lattice parameters iteratively until the  $R_P$  and  $R_{WP}$  values converge. The pseudo-Voigt profile function was used for whole profile fitting and Berrar-Baldinozzi function was used for asymmetry correction during the refinement processes. The accessible surface areas were calculated from the Monte Carlo integration technique using a nitrogen-size probe molecule (diameter = 3.68 Å) roll over the framework surface with a grid interval of 0.25 Å.<sup>S4</sup>

# **Supporting Figures**



**Fig. S1** Thermogravimetric analysis trace of the Cz-COFs under a nitrogen atmosphere with a heating rate of 10 °C/min.



Fig. S2. FT-IR spectra for the Cz-COFs.



Fig. S3 Solid-state <sup>13</sup>C CP-MAS NMR spectra of the Cz-COFs.



**Fig. S4** FE-SEM images of (a) Cz-COF1 and (b) Cz-COF2. HR-TEM images of (c) Cz-COF1 and (d) Cz-COF2.



Fig. S5 Crystalline structure for Cz-COF1 based on the AA-stacking model.



Fig. S6 Crystalline structure for Cz-COF1 based on the AB-stacking model.



Fig. S7 Crystalline structure for Cz-COF2 based on the AA-stacking model.



Fig. S8 Crystalline structure for Cz-COF2 based on the AB-stacking model.



Fig. S9 BET plots of (a) Cz-COF1 and (b) Cz-COF2.



**Fig. S10** Cyclic voltammetry (CV) profiles of (a) Cz-COF1 and (b) Cz-COF2. The CV profiles revealed that both of the Cz-COFs have some irreversible peaks appeared at 1.5-0.25 V during the first scan, corresponding to the electrochemical decomposition of electrolyte and the formation of a solid electrolyte interface (SEI) film on the electrode surface. These peaks disappeared in the following cycles, indicating a stable SEI formed in the first cycle. A pair of asymmetric redox peaks in the low potential region of 0-0.5 V demonstrates the doping-dedoping reaction of Li<sup>+</sup> into/from the Cz-COFs skeleton.



**Fig. S11** The schematic for the charge-discharge process of dicarbazole-based COFs in the anode of lithium battery.<sup>S5-S7</sup>



**Fig. S12** Thermogravimetric analysis trace of the amorphous Cz-CMP1 under a nitrogen atmosphere with a heating rate of 10 °C/min (a) and FT-IR spectrum of Cz-CMP1 (b).



**Fig. S13** PXRD profile of the amorphous Cz-CMP1 (a) and solid-state <sup>13</sup>C CP-MAS NMR spectrum of the Cz-CMP1 (b).



**Fig. S14** Nitrogen adsorption (filled symbols) and desorption (empty symbols) isotherms of the Cz-CMP1 collected at 77.3 K (a) and pore size distribution of the Cz-CMP1 calculated by using NLDFT method (b). The BET surface area of Cz-CMP1 was found to be 485  $m^2/g$ .



**Fig. S15** Electrochemical performance of Cz-CMP1. (a) CV curves at 0.1 mV/s. (b) Discharge/charge curves at 200 mA/g. (c) cyclability at 200 mA/g. (d) Rate performance.



Fig. S16 The <sup>1</sup>H NMR spectrum of the monomer of tetraformyl bicarbazole.



Fig. S17 The <sup>13</sup>C NMR spectrum of the monomer of tetraformyl bicarbazole.



Fig. S18 The FT-IR spectrum of the monomer of tetraformyl bicarbazole.

# **Supporting Tables**

Sample	Expected	Expected	Expected	Found	Found	Found
Sumple	C%	Н%	N%	C%	Н%	N%
Cz-COF1	81.61	4.11	14.28	81.63	4.08	14.29
Cz-COF2	84.30	4.35	11.34	84.32	4.32	11.35

 Table S1. Elemental analysis of the Cz-COFs

Atom	x/a	у/b	z/c
C1	0.2597	0.29965	0.8034
C2	0.21096	0.28379	0.7979
C3	0.20231	0.2335	0.80474
C4	0.13332	0.39424	0.6865
C5	0.14334	0.44214	0.59367
C6	0.10518	0.47492	0.55051
C7	0.05588	0.4606	0.59136
C8	0.04596	0.41339	0.70614
С9	0.08436	0.38124	0.75033
C10	0.17422	0.35958	0.70113
N11	0.16962	0.31487	0.80012
H12	0.00877	0.40149	0.75826
H13	0.07663	0.34416	0.83334
H14	0.26818	0.33847	0.81135
H15	0.16462	0.22042	0.80726
H16	0.18098	0.45379	0.54944
H17	0.20982	0.37463	0.6099
N18	0.02589	0.5	0.5

**Table S2.** Atomistic coordinates for the refined unit cell parameters for Cz-COF1 via Pawley refinement (Space group: C222;a = 27.0673Å, b = 27.7347Å, and c = 3.9927Å)

Atom	x/a	<i>y/b</i>	z/c
C1	0.10825	0.41255	0.25745
C2	0.11745	0.45199	0.37053
C3	0.08627	0.47925	0.43842
C4	0.04562	0.46729	0.39744
C5	0.03639	0.42804	0.27572
C6	0.06771	0.40137	0.2077
C7	0.14094	0.38309	0.20666
N8	0.13436	0.34605	0.10051
C9	0.16785	0.31952	0.06996
C10	0.16212	0.27765	0.13436
C11	0.19417	0.25064	0.11694
C12	0.23271	0.26436	0.03029
C13	0.23786	0.30598	-0.04717
C14	0.206	0.33325	-0.02915
H15	0.14876	0.46123	0.40913
H16	0.00535	0.41824	0.23967
H17	0.06124	0.37038	0.1166
H18	0.13241	0.2667	0.21028
H19	0.18943	0.21824	0.17845
H20	0.26741	0.31717	-0.12587
H21	0.21065	0.36551	-0.09588
H22	0.17172	0.60589	0.72286
N23	0.0212	0.5	0.5

**Table S3.** Atomistic coordinates for the refined unit cell parameters for Cz-COF2 via Pawley refinement (Space group: *C222;a* = 33.2737Å, *b* = 32.22 Å, and *c* = 3.9763 Å)

Atom	x/a	у/b	z/c
C1	0.2597	0.29965	0.8034
C2	0.21096	0.28379	0.7979
C3	0.20231	0.2335	0.80474
C4	0.13332	0.39424	0.6865
C5	0.14334	0.44214	0.59367
C6	0.10518	0.47492	0.55051
C7	0.05588	0.4606	0.59136
C8	0.04596	0.41339	0.70614
С9	0.08436	0.38124	0.75033
C10	0.17422	0.35958	0.70113
N11	0.16962	0.31487	0.80012
H12	0.00877	0.40149	0.75826
H13	0.07663	0.34416	0.83334
H14	0.26818	0.33847	0.81135
H15	0.16462	0.22042	0.80726
H16	0.18098	0.45379	0.54944
H17	0.20982	0.37463	0.6099
N18	0.02589	0.5	0.5

**Table S4.** Atomistic coordinates for the AA-stacking model of Cz-COF1 optimized by using DFTB+ method (Space group: *C222;a* = 27.3616 Å, *b* = 27.4776 Å, and *c* = 3.9778 Å)

Atom	x/a	<i>y/b</i>	z/c
C1	0.51079	0.54926	0.34095
C2	0.46083	0.53393	0.3425
C3	0.45096	0.48415	0.34114
C4	0.38421	0.64551	0.33491
C5	0.39538	0.69306	0.29984
C6	0.35662	0.72568	0.28204
C7	0.30637	0.71143	0.29956
C8	0.29533	0.66506	0.34827
С9	0.33429	0.63268	0.36308
C10	0.42546	0.61103	0.33519
N11	0.41893	0.56485	0.34948
H12	0.25723	0.6543	0.37309
H13	0.32651	0.59579	0.39637
H14	0.52033	0.58763	0.34289
H15	0.41221	0.47186	0.34218
H16	0.43399	0.70398	0.28131
H17	0.46279	0.62754	0.31548
N18	0.27619	0.75011	0.25971
C19	0.98945	0.4507	-0.1591
C20	1.03934	0.46625	-0.159
C21	1.04897	0.51607	-0.15889
C22	1.11625	0.3551	-0.18198
C23	1.10493	0.30785	-0.21981
C24	1.14352	0.27509	-0.23829
C25	1.19384	0.28896	-0.21991
C26	1.20507	0.33507	-0.16961
C27	1.16623	0.3675	-0.1531
C28	1.0751	0.38972	-0.17946
N29	1.08128	0.4353	-0.15395
H30	1.24322	0.34557	-0.14457
H31	1.17419	0.40413	-0.11799
H32	0.9802	0.41226	-0.156
H33	1.08766	0.52851	-0.15753
H34	1.06627	0.29716	-0.23882
H35	1.03809	0.374	-0.20713

**Table S5.** Atomistic coordinates for the AB-stacking model of Cz-COF1 optimized by using DFTB+ method (Space group: *C222;a* = 26.7661 Å, *b* = 27.6369 Å, and *c* = 9.9556 Å)

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Atom	x/a	y/b	<i>z/c</i>
C1	0.10825	0.41255	0.25745
C2	0.11745	0.45199	0.37053
C3	0.08627	0.47925	0.43842
C4	0.04562	0.46729	0.39744
C5	0.03639	0.42804	0.27572
C6	0.06771	0.40137	0.2077
C7	0.14094	0.38309	0.20666
N8	0.13436	0.34605	0.10051
C9	0.16785	0.31952	0.06996
C10	0.16212	0.27765	0.13436
C11	0.19417	0.25064	0.11694
C12	0.23271	0.26436	0.03029
C13	0.23786	0.30598	-0.04717
C14	0.206	0.33325	-0.02915
H15	0.14876	0.46123	0.40913
H16	0.00535	0.41824	0.23967
H17	0.06124	0.37038	0.1166
H18	0.13241	0.2667	0.21028
H19	0.18943	0.21824	0.17845
H20	0.26741	0.31717	-0.12587
H21	0.21065	0.36551	-0.09588
H22	0.17172	0.60589	0.72286
N23	0.0212	0.5	0.5

**Table S6.** Atomistic coordinates for the AA-stacking model of Cz-COF2 optimized by using DFTB+ method (Space group: C222;a = 33.1865 Å, b = 32.485 Å, and c = 3.9868 Å)

Atom	x/a	y/b	<i>z/c</i>
C1	0.10693	1.16908	0.17127
C2	0.11712	1.20794	0.2073
C3	0.0862	1.23552	0.2289
C4	0.04526	1.22391	0.21519
C5	0.03485	1.18586	0.17416
C6	0.06606	1.15888	0.153
C7	0.1394	1.139	0.1588
N8	0.13276	1.10173	0.12835
С9	0.16671	1.07514	0.12446
C10	0.16072	1.03297	0.1418
C11	0.19332	1.00614	0.14193
C12	0.23265	1.02039	0.12356
C13	0.23818	1.06245	0.10371
C14	0.20578	1.08951	0.1035
H15	0.14884	1.21607	0.22025
H16	0.0033	1.17761	0.16016
H17	0.05937	1.12845	0.12275
H18	0.13028	1.02163	0.15797
H19	0.18818	0.97346	0.15794
H20	0.26843	1.07418	0.08692
H21	0.21078	1.12204	0.08568
H22	0.17004	1.36266	0.31507
C23	0.89306	1.34292	0.17301
C24	0.88288	1.30411	0.20938
C25	0.91379	1.27643	0.23043
C26	0.95471	1.28791	0.2159
C27	0.9651	1.3259	0.17455
C28	0.9339	1.35297	0.1539
C29	0.86063	1.37307	0.16083
N30	0.86725	1.4102	0.12946
C31	0.83334	1.43684	0.12547
C32	0.83948	1.47912	0.14107
C33	0.80693	0.50603	0.14079
C34	0.76752	1.49174	0.1237
C35	0.76183	1.44956	0.1056
C36	0.79418	1.42243	0.10581
H37	0.85118	1.29609	0.22295
H38	0.99663	1.33404	0.15991

**Table S7.** Atomistic coordinates for the AB-stacking model of Cz-COF2 optimized by using DFTB+ method (Space group: *C2221; a* = 32.9367 Å, *b* = 32.272 Å, and *c* = 13.9736 Å)

H39	0.94057	1.38335	0.12339
H40	0.87	1.49052	0.15614
H41	0.8122	0.53882	0.1554
H42	0.73152	1.43778	0.08963
H43	0.78903	1.38979	0.08931
H44	0.82986	1.14956	0.31794
N45	0.02115	1.25586	0.24993

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