Supporting Information

Redox-active conjugated microporous polymers: a new organic platform for highly efficient energy storage

Fei Xu, Xiong chen, Zhiwei Tang, Dingcai Wu, Ruowen Fu, and Donglin Jiang*
Corresponding author: jiang@ims.ac.jp

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Materials and methods

Materials. Triquinoyl hydrate and 1,4-diethynylbenzene were purchased from Aldrich Chemicals. Tetrakis(triphenylphosphine)palladium(0), copper(I) iodide, *N,N*-dimethylformamide and diisopropylamine were obtained from Kanto Chemicals. 4,5-Diiodo-benzene-1,2-diamine and 2,3,8,9,14,15-hexaiododiquinoxalino[2,3-a:2',3'-c]phenazine (HIQP) was prepared according to the reported procedures.[1,2]

Analysis. ^1H nuclear magnetic resonance (NMR) spectra were recorded on JEOL models JNM-LA400 NMR spectrometers, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform infrared (IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. X-ray diffraction data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Instrument Corporation model 3Flex surface characterization analyzer. By using the non-local density functional theory (NLDFT) model, the pore volume was derived from the sorption curve. Elemental analysis was performed on a Yanako model CHN CORDER MT-6 elemental analyzer. TGA measurements were performed on a Mettler-Toledo model TGA/SDTA851^e under N_2, by heating to 800 °C at a rate of 10 °C min^{-1}.

Electrochemistry. Cathodes were prepared by mixing HATN-CMP or HATN, acetylene black (Denki Ind. Chem. Co.) and poly(vinylidene fluoride binder (PVDF; Aldrich.) (6/3/2 by wt) in *N*-methyl-2-pyrrolidinone (NMP). The obtained slurry was spreading on aluminum foil using a coater, followed by removal of NMP under vacuum. Cathode round plates with diameter of 16 mm and a total material loading of about ca. 2.5 mg were prepared. The CR2032 coin-type cells were assembled in an argon-filled glove box. The cells were composed of cathode, a separator of polyethylene membrane, lithium plate as anode and an electrolyte of 1 M LiPF6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 / 1 by wt). All cells were tested at 25 °C. Before electrochemical measurements, all electrodes were dried at 100 °C under vacuum. The cells were typically cycled galvanostatically over a voltage range of 1.5 – 4 V using an Arbin instrument.

Calculation of theoretical capacity. Theoretical capacity C_{theo} (mAh g^{-1}) was calculated by $C_{theo}=(N_Ae)/(3600(M_w/1000)$, where N_Ae is the Faraday constant (96484 C/mol), M_w is molecular weight of the repeating unit exchanging one electron in HATN-CMP.

Calculation of specific power and energy densities. Specific energy density E (Wh kg^{-1}) and specific power density P (W kg^{-1}) was calculated by $E=0.5C(\Delta V)^2/3.6$ and $P = E/(t/3600)$, where C (F g^{-1}) is the experimentally determined specific capacitance, ΔV (V) is the working voltage range and t (s) is the discharge time. C is determined by the discharge potential *vs* time curves using the equation of $C = i/[-(V/t)m]$, where V (V) represents the discharge voltage, m (g) is the mass of the active material, and I (A) is the applied current.

Synthesis of HATN-CMP. A mixture of 1,4-diethynylbenzene (50 mg, 0.4 mmol), 2,3,8,9,14,15-hexaiododiquinoxalino[2,3-a:2',3'-c]phenazine (HIQP, 100 mg, 0.088 mmol), tetrakis-(triphenylphosphine)palladium(0) (12.2 mg, 0.01 mmol) and copper(I) iodide (4 mg, 0.021 mmol) in diisopropylamine (8 mL) and *N,N*-dimethylformamide (8 mL) in a 50 mL two-necked flask was degassed by three freeze-pump-thaw cycles, filled with Ar gas and stirred at 90 °C for 3 days. The precipitate was collected by filtration, washed repetitively with THF, acetone, CH_2Cl_2, water and methanol followed by Soxhlet extraction with methanol, THF, acetone, CH_2Cl_2 and dried at 100 °C under vacuum, to yield HATN-CMP as brown solid in 96% yield.

Supporting figures

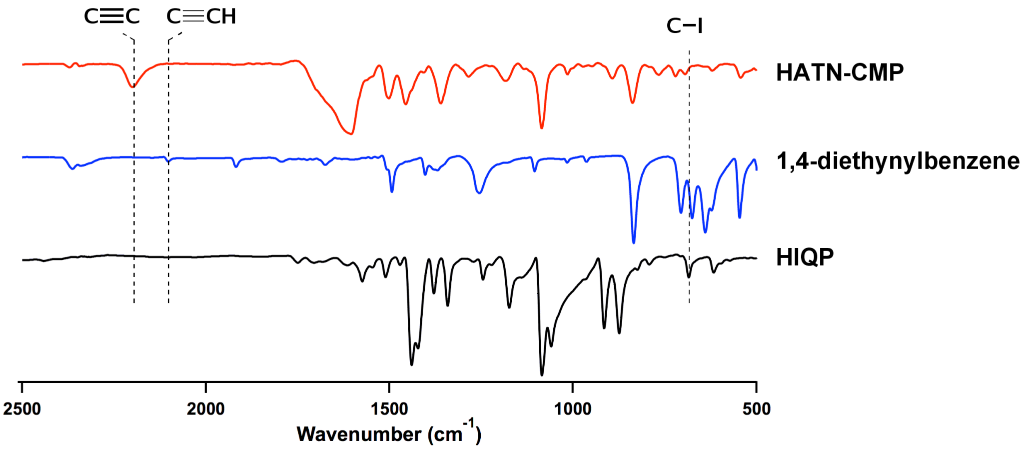

Figure S1. IR spectra of HATN-CMP and the corresponding monomers.

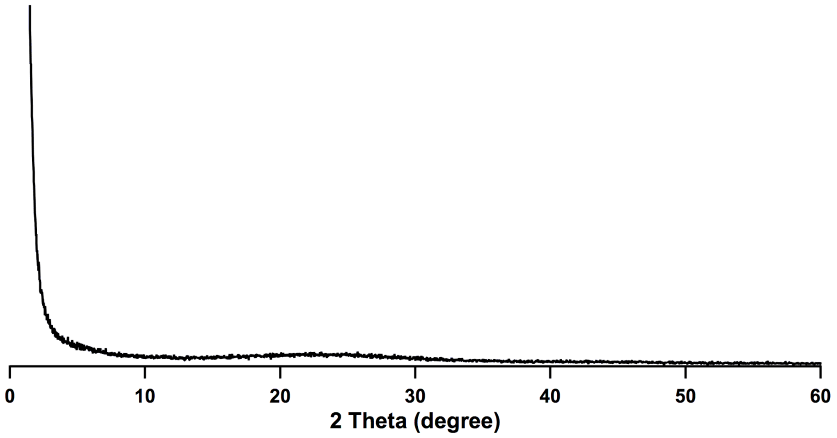

Figure S2. X-Ray powder diffraction pattern of HATN-CMP.

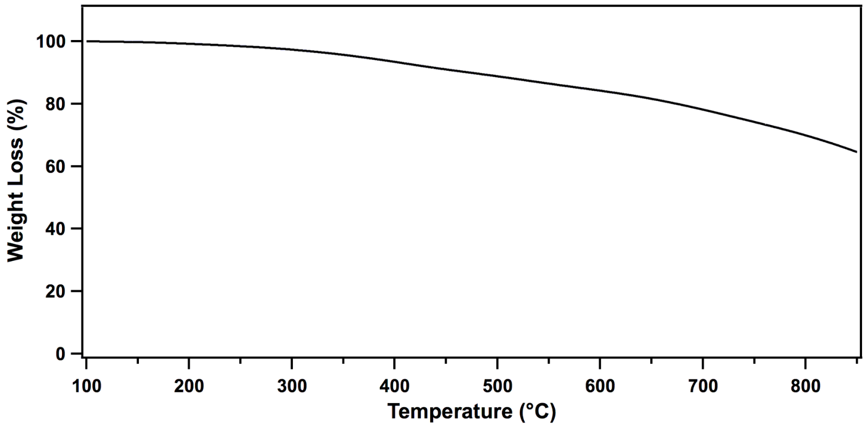

Figure S3. TGA curve of HATN-CMP.

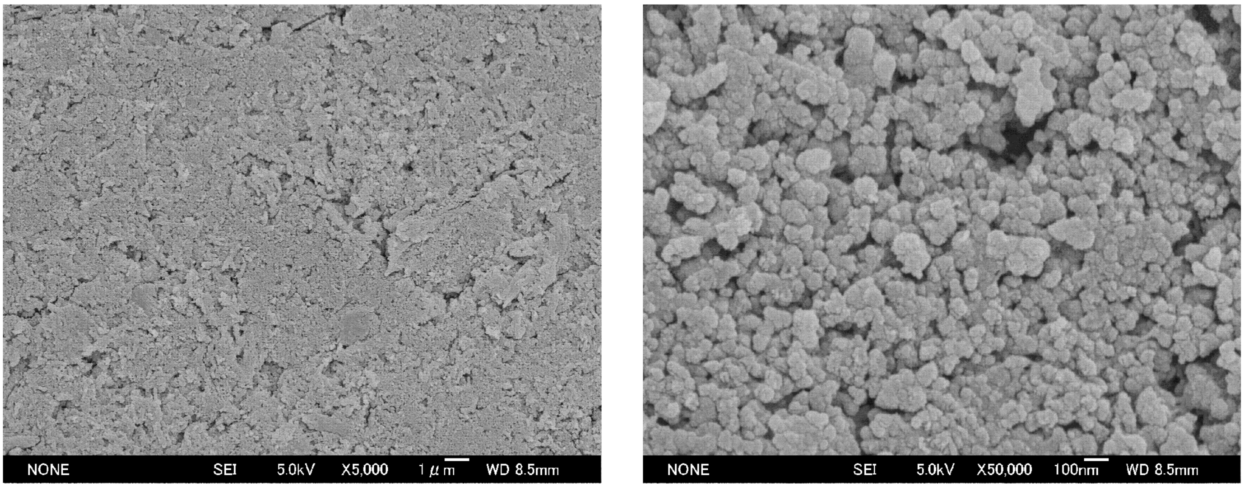

Figure S4. FE-SEM image of a typical HATN-CMP electrode at different magnifications.

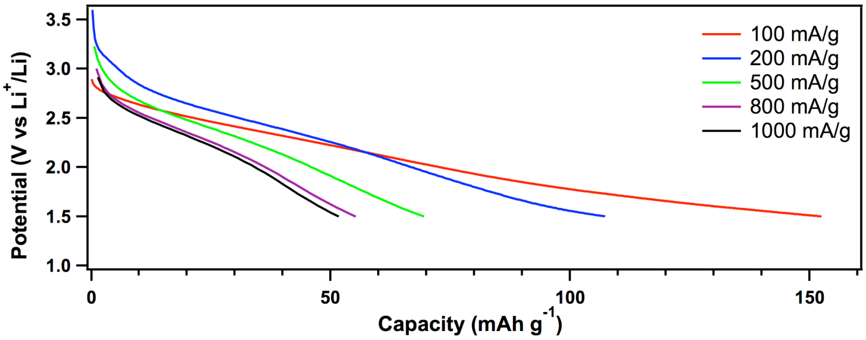

Figure S5. Discharge curves at different current densities from 100 mAg^{-1} to 1000 mAg^{-1}.

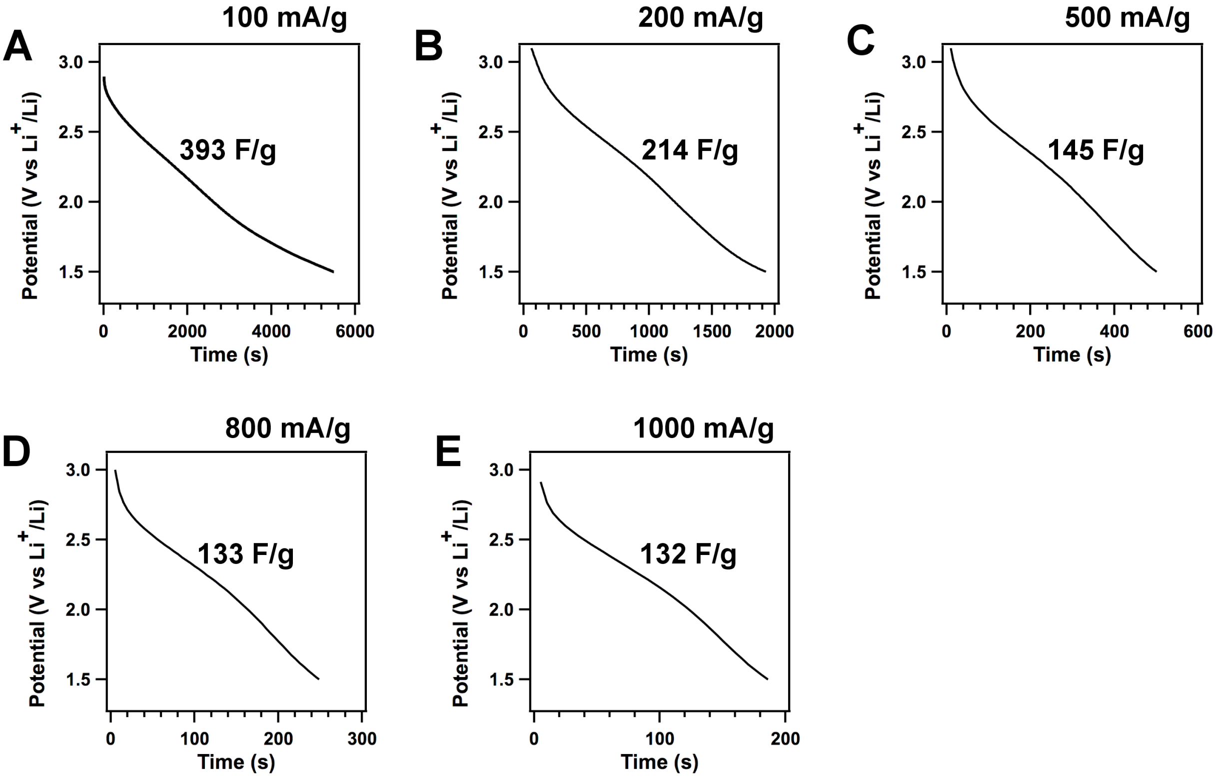

Figure S6. Potential *vs* time profiles of the HATN-CMP electrodes

Supporting references

1. W. Justin Youngblood *J. Org. Chem.,* 2006, ***71***, 3345.
2. S. Marder, Bilal Kaafarani, Steve Barlow, Bernhard Kippelen, Benoit Domercq, Qing Zhang, Takeshi Kondo, US7994423 B2, August 9, 2011.