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Supporting Information

An azobenzene-modified redox-active ionic liquid electrolyte for supercapacitors

Yuhua Zhao,[a] Yujuan Chen,[a] Kelei Zhuo,*[a] Quanzhou Du,[a] Dong Sun,[a] Zhiyong Li,[a] Huiyong Wang,[a] Changling Yan[a] and Jianji Wang*[a]

[a] Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, PR China

E-mail addresses: kzhuo@htu.edu.cn, jwang@htu.edu.cn

ORCID: **0000-0002-8773-8694**

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S1 Synthesis and characterization of the redox IL

S1.1 Chemicals and Materials

4-(Phenylazo)phenol (98%), 1-methylimidazole (99%), 1,2-dibromoethane (99%), 18-crown-6 (99%), hydroquinone (99%)， and potassium carbonate (99%) were purchased from Shanghai Macklin. Petroleum ether (b.p. 60–90 °C), acetonitrile (99.9%), dichloromethane (99.9%) and anhydrous ethanol were commercial products from Shanghai Aladdin. 1-Ethyl-3-methylimidazolium tetrafluoroborate (≥98%) was purchased from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences), and was dried under vacuum before use.

Graphite (325 mesh, 44 μm) and polytetrafluoroethylene (PTFE, 60%) were purchased from Aladdin Industrial Co., China.

S1.2 Characterization of [ABEMIM][BF_4]

NMR analyses were carried out with Bruker 600 MHz and 400 MHz instruments, and the appropriate deuterated solvents were chosen according to the properties of compounds at room temperature. Time-of-flight mass spectrometry analysis was carried out on an Autoflex speed MALDLTOF/TOF. Mass spectra were recorded between 100 and 1500 Da. DSC thermograms were recorded using a differential scanning calorimeter at a heating rate of 10 °C min^{-1} from room temperature to 300 °C under nitrogen atmosphere.

S1.3 Synthesis of the redox IL

1-(4-(2-Bromoethoxy)phenyl)-2-phenyldiazene (AzoC$_2$Br). First, 4-(phenylazo)phenol (2.3 g, 0.011 mol) and 1,2-dibromoethane (10.33 g, 0.055 mol) were added into acetonitrile (100 mL) under magnetic stirring. Then, K_2CO_3 (3.1 g, 0.022 mol) and 18-crown-6 (0.05 g) were added into the mixture under magnetic stirring and refluxing for 24 h[1]. The mixture after the completion of the reaction was poured into water, then was extracted with dichloromethane. The organic phase was collected, and the solvent was removed by rotary evaporation to obtain a crude product. The crude product was purified by silica gel column chromatography eluting with dichloromethane/petroleum ether (1:3) as the mobile phase, and then the solvent was removed by rotary evaporation to obtain an orange-yellow powder product (1-(4-(2-bromoethoxy)phenyl)-2-phenyldiazene (AzoC$_2$Br)) with a yield of about 70%.

(2-(4-(Phenyldiazenyl)phenoxy)ethyl)-1-methyl-imidazolium bromide ([ABEMIM]Br). Excess 1-methylimidazole was added into the acetonitrile solution of AzoC$_2$Br and their reaction was kept at 75 °C for 24 h under nitrogen protection. After removal of the acetonitrile and 1-methylimidazole via evaporation, the resulting yellow solid was dissolved in a small amount of dichloromethane, and the solution added dropwise to an excess of petroleum ether under magnetic stirring. The resulting yellow solid was collected by filtration and dried under vacuum overnight to obtain the target product with a yield of about 90%.

(2-(4-(Phenyldiazenyl)phenoxy)ethyl)-1-methyl-imidazolium tetrafluoroborate ([ABEMIM][BF$_4$]). Lastly, excess sodium tetrafluoroborate and moderate [ABEMIM]Br were dissolved in water and stirred for 48 h, and then left to stand, the upper layer is an aqueous solution containing high concentration of sodium bromide and the lower layer contained [ABEMIM][BF$_4$] ionic liquid[2, 3]. The reaction solution was separated using a separatory funnel, and extracted with dichloromethane. Finally, it was washed with a small amount of deionized water several times to remove Na$^+$ and Br$^-$, until bromide ions in the aqueous phase could not be detected with aqueous silver nitrate solution. The crude product was spin-dried and placed in a vacuum drying oven at 70 °C for 48 h to obtain an orange-yellow solid (i.e. [ABEMIM][BF$_4$]). The structures of the ionic liquids and related compounds were characterized by NMR spectroscopy.

NMR spectra

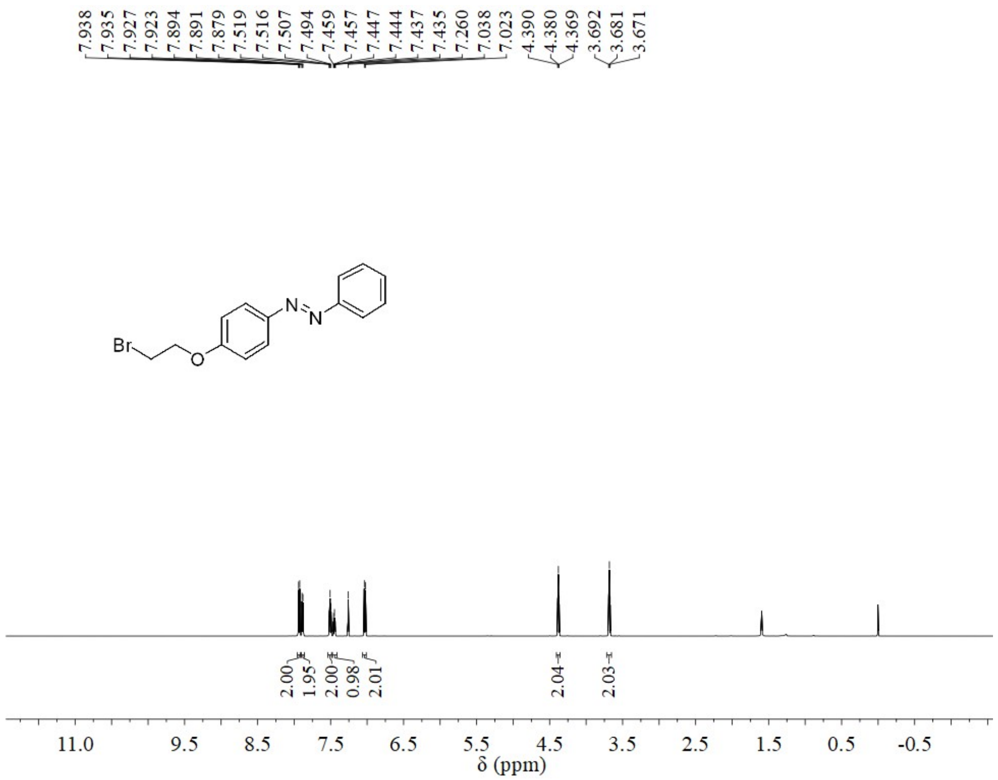

Fig. S1 ^{1}H NMR spectrum of [AzoC$_2$]Br.

[AzoC$_2$]Br:^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.90 – 7.88 (m, 2H), 7.52– 7.49 (m, 2H), 7.46– 7.44 (m, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.38 (t, *J* = 6.3 Hz, 2H), 3.68 (t, *J* = 6.3 Hz, 2H).

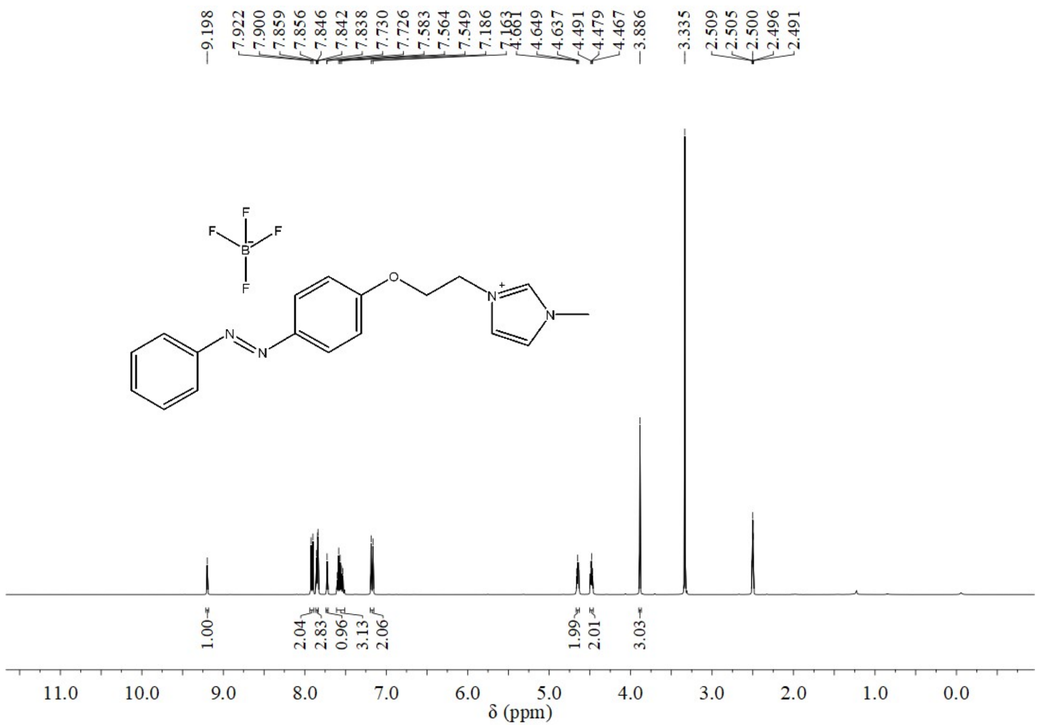

Fig. S2 ^{1}H NMR spectrum of [ABEMIM][BF$_4$] in DMSO-d6.

[ABEMIM][BF$_4$]: ^{1}H NMR (400 MHz, DMSO-d6) δ 9.20 (s, 1H), 7.92 – 7.90 (m, 2H), 7.86 – 7.84 (m, 3H), 7.73 (t, J = 1.7 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.19 – 7.16 (m, 2H), 4.66 – 4.64 (m, 2H), 4.48 (t, J = 4.9 Hz, 2H), 3.89 (s, 3H).

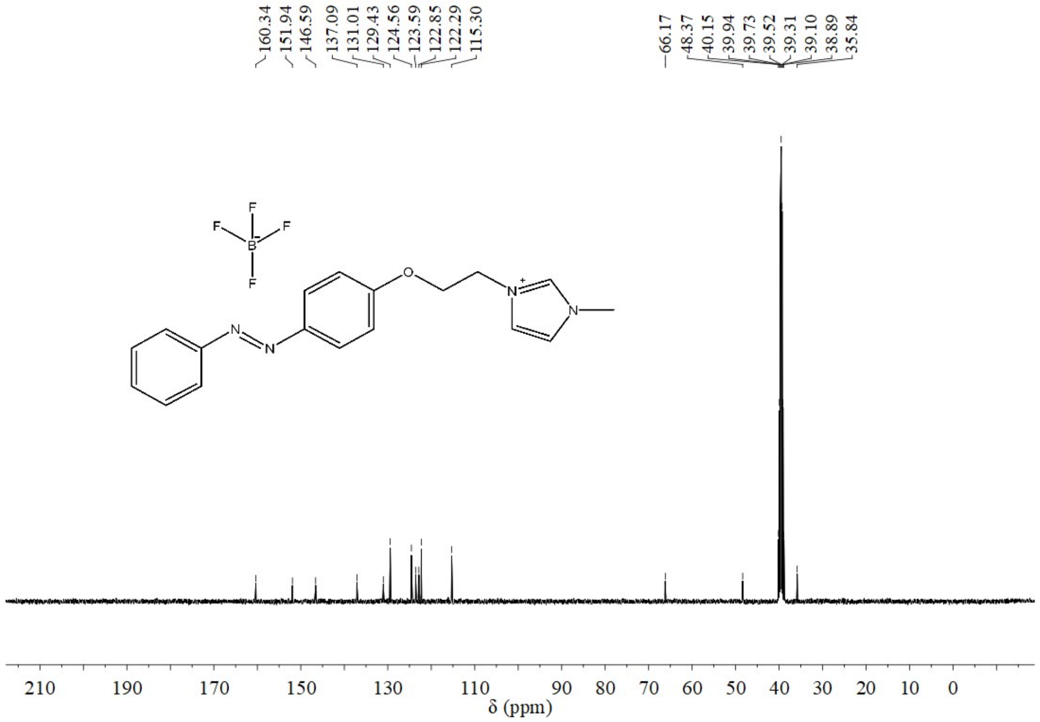

Fig. S3 ^{13}C NMR spectrum of [ABEMIM][BF$_4$].

[ABEMIM][BF$_4$]: ^{13}C NMR (100 MHz, DMSO-d6): *δ* 160.3, 151.9, 146.6, 137.1, 131.0, 129.4, 124.6, 123.6, 122.9, 122.3, 115.3, 66.2, 44.4, 35.8.

TOF mass spectrometry

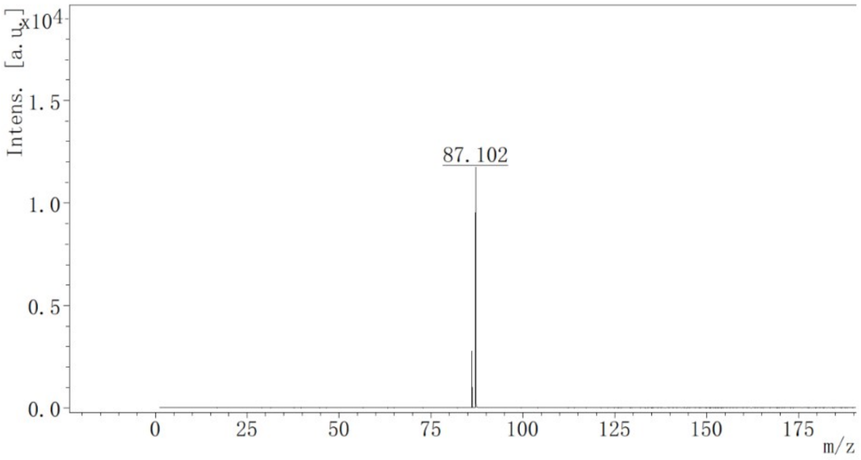

Fig. S4. TOF mass spectrometry of $[BF_4]^+$.

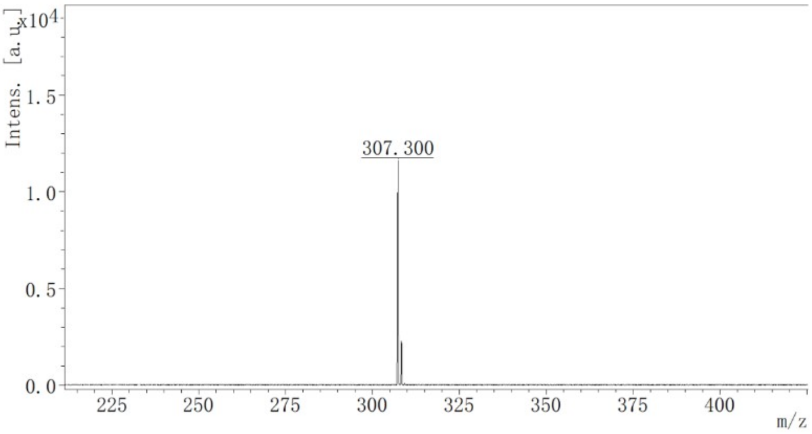

Fig. S5 TOF mass spectrum of [ABEMIM]⁻.

TOF MS ES⁻: m/z = 87.102 and 86.007, theoretical mass for $[BF_4]^-$: 87.102 g mol^{-1}.

TOF MS ES⁺: m/z = 307.300 and 308.158, theoretical mass for [ABEMIM]⁺: 307.300 g mol^{-1}.

The spectrum shows the expected peaks corresponding to the molecular weights of cations and anions in positive and negative ion modes, respectively.

DSC

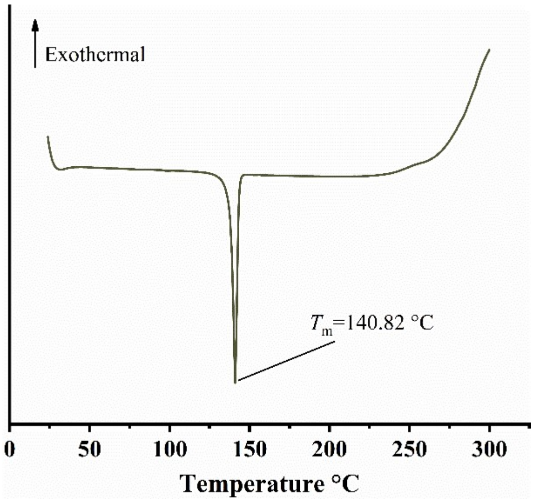

Fig. S6 Differential scanning calorimetry (DSC) in the heating mode.

The melting point temperature T_m = 140.82 °C was measured by DSC in heating mode.

S2 Preparation of electrode and electrolyte

S2.1 Synthesis of reduced graphene oxide (rGO)

Graphite powder (325 mesh) was oxidized into oxide graphene (GO) by the improved Hummers method[4, 5]. 60 mg of GO powder was dispersed into 60 mL deionized water, stirred and sonicated for 1 h to form a homogeneous GO dispersion (1 mg mL^{-1}). 60 mL of GO dispersion was transferred to a 100 mL Teflon-lined autoclave, hydrothermally treated at 180 °C for 12 h, and then cooled to ambient temperature. Subsequently, the obtained hydrogels were washed with water and finally freeze-dried to obtain solid reduced graphene oxide (rGO).

S2.2 Electrode preparation

RGO, acetylene black and polytetrafluoroethylene were mixed with ethanol in a small weighing bottle at a mass ratio of 85:10:5, followed by ultrasonically treated for 1 h to obtain a slurry. Then the slurry was pasted on the foamed nickel and dried in a vacuum at 110 °C for 6 h, and then pressed with a tablet press at 10 Mpa for 1 min. The obtained electrodes were weighed for later use. The mass loading of rGO is 2.0 − 2.5 mg cm^{-2}.

S2.3 Electrolyte preparation and Characterization

S2.3.1 Preparation of [ABEMIM][BF_4]-[EMIM][BF_4]

Due to the solubility limitation of [ABEMIM][BF_4] in 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), [ABEMIM][BF_4] was dissolved in [EMIM][BF_4] in the glove box to prepare 25, 50, or 75 mM [ABEMIM][BF_4] in [EMIM][BF_4] mixed IL electrolytes.

S2.3.2 Characterization of [ABEMIM][BF$_4$]-[EMIM][BF$_4$]

Measurement of conductivity

Conductivity measurements of the electrolytes were performed using a conductivity meter (Mettler Toledo-S320) with an electrode (Inlab-751) at 25 °C. Measured conductivity values for [EMIM][BF$_4$] and 50 mM [ABEMIM][BF$_4$]-[EMIM][BF$_4$] are 1.562 S m^{-1} (1.553 S m^{-1} reported in the literature[6]) and 1.455 S m^{-1}, respectively. These two values are very close because the amount of [ABEMIM][BF$_4$] in the binary IL mixture is relatively small.

Measurement of water content

The water content in [ABEMIM][BF$_4$]-[EMIM][BF$_4$] was determined using the Karl Fischer method to be less than 100 ppm.

Measurements of impurities in ionic liquids

The Br$^-$ content in [ABEMIM][BF$_4$] and [EMIM][BF$_4$] was determined by means of electroanalytical method using a Br$^-$ selective electrode (Shanghai Precision & Scientific Instrument Co. Ltd) coupled with a double salt bridge electrode (Shanghai Precision & Scientific Instrument Co. Ltd). Results show that the Br$^-$ content in [ABEMIM][BF$_4$] and [EMIM][BF$_4$] was 0.073 wt% and 0.055 wt%, respectively.

Based on the method described by Santosh et al.,[7] the purity of [ABEMIM][BF$_4$] and [EMIM][BF$_4$] was determined by ^{1}H NMR spectroscopy using ^{1}H peak area of hydroquinone as internal standard. The equation

$$P_X = \frac{I_X}{I_{\mathrm{std}}} \cdot \frac{I_{std}}{I_X} \cdot \frac{M_X}{M_{\mathrm{std}}} \cdot \frac{W_{std}}{W_X} \cdot P_{\mathrm{std}}$$

was applied for purity quantification of [ABEMIM][BF$_4$] and [EMIM][BF$_4$] by qNMR (where, *I*, *N*, *M*, *W* and *P* are integral area, number of nuclei, molar mass, gravimetric weight and purity of the analyte (X) and standard (STD), respectively). Taking [ABEMIM][BF$_4$] as an example, the internal standard hydroquinone (3.0 mg) and [ABEMIM][BF$_4$] (10.5 mg, $m_{[\mathrm{ABEMIM}]^+} = 8.18$ mg) were carefully weighed in a centrifuge tube, and then 1 mL DMSO-d6 was added, shaken well, and transferred into a nuclear magnetic tube for measurements. ^{1}H peak area of hydroquinone at 6.55 ppm is 1.0. At the same time, the ^{1}H peak area of the CH$_3$ in [ABEMIM]$^+$ anion (at 3.89 ppm) is 0.73.

Therefore, the purity of [ABEMIM][BF_4] can be estimated to be 98.6%. Similarly, the purity of [EMIM][BF_4] can be estimated to be 98.9%. In summary, these two IL electrolytes have high purity.

S3. Electrochemical measurements

S3.1 Assembly of the split test cell for three-electrode measurement and coin-type supercapacitors

A split test cell is constructed using rGO, YP-50F and silver wire as the working electrode, counter electrode and reference electrode, respectively, and [EMIM][BF_4] or its mixtures with [ABEMIM][BF_4] ionic liquid as the electrolyte. The three-electrode system was assembled in an argon-filled glove box (H_2O, $O_2 < 0.1$ ppm). The open circuit voltage was measured to be about 0.2 V.

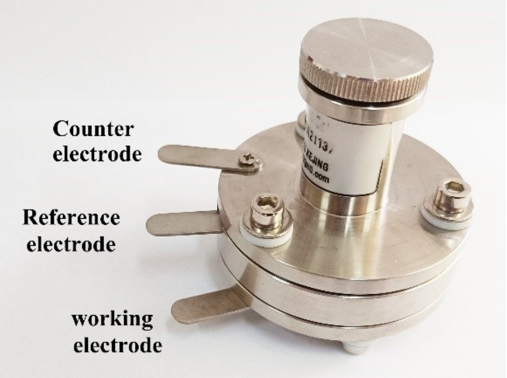

Fig. S7 Split test cell for three-electrode measurements.

Two-electrode supercapacitors (coin type CR2032) were assembled with [ABEMIM][BF_4]-[EMIM][BF_4] or [EMIM][BF_4] ionic liquids as the electrolyte, rGO as the working electrode, and cellulosic NKK TF 4030 as the separator in an argon-filled glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm).

S3.2 Electrochemical characterization

The electrochemical characterizations including cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) were conducted on an electrochemical workstation (CHI660D, Shanghai Chenhua Instrument Co., Ltd., China).

S3.2.1 Measurements of Split test cells as three-electrode systems

The open circuit potential in this work is about 0.2 V, with a little change at different cases. The potential range of the negative electrode was -0.18 − 0.2 V, and the potential range of the positive electrode was 0.2 − 1.8 V. The CV scan rates were: 5.0 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1} and 100 mV s^{-1}.

The potential range of the galvanostatic charge/discharge at the negative electrodes was set as -0.18 − 0.2 V, and the current density was set based on the quality of the active material at the negative electrode. When the electrode was used as the positive electrode, the potential range of galvanostatic charge/discharge was set as 0.2 − 2.0 V. The current densities were set as: 1.0 A g^{-1}, 2.0 A g^{-1}, 3.0 A g^{-1}, 5.0 A g^{-1} and 10 A g^{-1}.

S3.2.2 Measurements of CR2032 coin-type supercapacitors

The voltage range of the supercapacitor devices was set as 0~3.6 V, and the scan rates of the CVs were: 5.0 mV s^{-1}, 10 mV s^{-1}, 20 mV s^{-1}, 50 mV s^{-1} and 100 mV s^{-1}. In the GCD tests, the current density was based on the total mass of the active material at the two electrodes, and were set as: 1.0 A g^{-1}, 2.0 A g^{-1}, 3.0 A g^{-1}, 5.0 A g^{-1} and 10 A g^{-1}. EIS tests were performed at open circuit potential with a frequency range of 10^5 Hz to 10^{-2} Hz and an amplitude of 5.0 mV.

S3.3 Calculations

The specific capacitances of the three electrode systems were calculated by:

$$C_{\mathrm{s}}(\mathrm{F\ g^{-1}}) = \frac{I\Delta t}{m \times \Delta V} \tag{S1}$$

For the two electrode devices:

$$C_{\mathrm{s,cell}}(\mathrm{F\ g^{-1}}) = \frac{I\Delta t}{M \times \Delta V} \tag{S2}$$

$$E_{\mathrm{cell}}(\mathrm{Wh\ kg^{-1}}) = \frac{1}{7.2} C_{s,cell} \Delta V^2 \tag{S3}$$

$$P_{\mathrm{cell}}(\mathrm{W\ kg^{-1}}) = \frac{3600 \times E_{\mathrm{cell}}}{t_d} \tag{S4}$$

In the above formula: I (A) is the discharge current, m is the loading mass of the active material on the working electrode, Δt (s) is the discharge time, ΔV (V) is the operating voltage, m (g) is the mass of the active material on the working electrode. M (g) refers to the total mass of the active materials on two electrodes. t_{d} (s) is the discharging time.

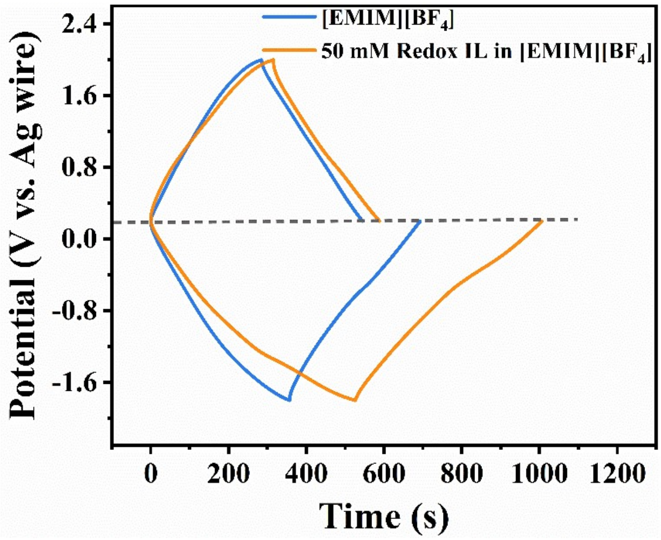

Fig. S8 Comparison of the GCD curves in [EMIM][BF$_4$] electrolyte and in 50 mM [ABEMIM][BF$_4$]-[EMIM][BF$_4$] mixed electrolyte using rGO as the electrode material at 1.0 A g^{-1}.

S4. IR measurements

IR spectra were recorded on a Spectrum 400 spectrometer (PerkinElmer).

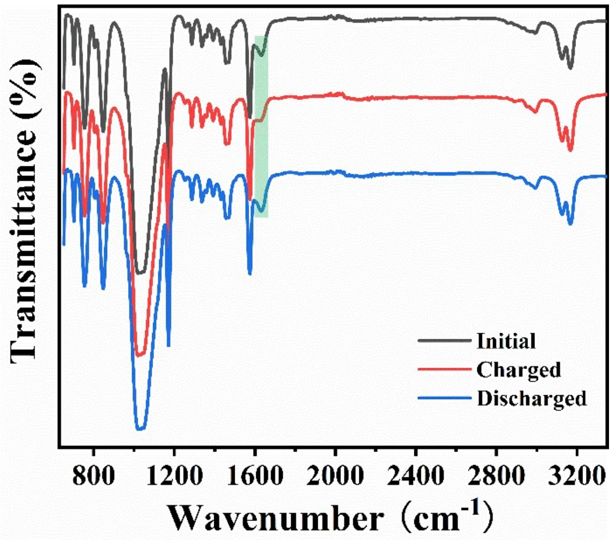

Fig. S9 IR spectra of 50 mM [ABEMIM][BF_4]-[EMIM][BF_4] in different states.

References

1. Z. Li, X. Yuan, Y. Feng, Y. Chen, Y. Zhao, H. Wang, Q. Xu and J. Wang, *Phys. Chem. Chem. Phys.*, 2018, **20**, 12808-12816.
2. J. Wang, H. Wang, S. Zhang, H. Zhang and Y. Zhao, *J. Phys. Chem. B*, 2007, **111**, 6181-6188.
3. J. D. Holbrey and K. R. Seddon, *J. Chem. Soc., Dalton Trans.*, 1999, 2133.
4. N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771-778.
5. L. Yang, K. Zhuo, X. Xu, Z. Zhang, Q. Du, G. Bai and J. Wang, *Electrochim. Acta*, 2021, **393** 139057.
6. A. Stoppa, J. Hunger and R. Buchner, *J. Chem. Eng. Data*, 2009, **54**, 472-479.
7. S. K. Bharti and R. Roy, *TrAC, Trends Anal. Chem.*, 2012, **35**, 5-26.