Electronic Supplementary Information

A strategy for dissolution and separation of rare earth oxides by novel Brønsted acidic deep eutectic solvents

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Table of the contents:

Characterization Methods

FTIR and NMR spectra

Fourier transform infrared (FT-IR) spectra were recorded on an FT-IR spectrometer (Tensor 27, Bruker) in the range of 400 to 4000 cm^{-1}. Solution ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer with deuterium oxide (D_2O) as the standard, and the chemical shift data were later processed by the MestReNova Program. All NMR spectra were recorded from neat samples with deuterated external reference (D_2O) sealed in a 1.0 mm capillary tube to avoid the effect of interaction between D_2O and DESs on the characteristic peaks.

DSC and TGA analysis

Differential scanning calorimetry (DSC) was performed in a DSC Q2000 (TA Instruments Inc.) with a heating rate of 10 $^{o}C \cdot min^{-1}$. All the eutectic solvents were run in aluminum hermetic crucibles, which were cooled to −120 ^{o}C before heated up to 30 ^{o}C. Thermal gravimetric analysis (TGA) was conducted by the instrument (Q50, TA Instrument Company, America) from room temperature to 350 ^{o}C at a heating rate of 10 $^{o}C \cdot min^{-1}$ in nitrogen atmosphere.

Density and viscosity

The density was measured at 25, 30 and 60 ^{o}C using an Anton Paar DMA 5000 M density meter, and the accuracy of density measurements was $\pm 5 \times 10^{-6}$ $g \cdot cm^{-3}$. The viscosity was determined using an Anton Paar AMVn viscometer with a repeatability of <0.1%. The density and viscosity of each sample were measured three times and the average was reported.

pH and pK_a measurement

For the determination of pH value, an aqueous solution of each DES with Milli-Q water in a concentration of 2 $mol \cdot L^{-1}$ was prepared, and the pH values were measured by the pH-meter (PHS-3C, Shanghai INESA Scientific Instrument Co., Ltd, China) at 25 ^{o}C. The pH values reported are average of three independent measurements. The dissociation constants (pK_a) of synthesized DESs were obtained by acid-base titration, and the standard method of

determining pK_a values was described in the literature.[1, 2] 0.1 mol·L^{-1} aqueous solution of KCl was used to maintain the ionic strength during the titration. The temperature was kept at 25 ± 0.1 °C by circulating water from a thermostat. Stirring the N_2 protected (reduce the negative effect of carbon dioxide) DESs solution by magneton in glassware. After calibration of the pH electrode, the DES solutions (0.01 mol·L^{-1}) were titrated with 0.01 mol·L^{-1} NaOH. The volume of NaOH solution and the corresponding pH value were recorded (acid-base titration curve). The maximum value of the first derivative was used to confirm the titration end point. pK_a of DES is approximately equal to the pH value of midpoint (in volume), at which the concentration of pristine acid is equal to the concentration of dissociated one. pK_a values of DESs were determined in triplicate, and the average values are reported.

Kamlet-Taft solvatochromic parameters (α, β, π^*)

The α parameter was determined by ^{13}C nuclear magnetic resonance spectra using the probe pyridine-N-oxide (PyO), deuterium oxide (D_2O) as solvent. The ^{13}C NMR chemical shifts (δ, in ppm) of the carbons atoms in positions 2 and 4 of pyridine-N-oxide were determined, and α parameter was calculated by equation: α=2.32-0.15×d_{24}, where $d_{24}=\delta_2-\delta_4$. For the measurement of solvatochromic parameters β and π^*, stock solution of two probes (4-nitroaniline (NH_2), N,N-diethyl-4-nitroaniline (NEt_2), 1×10^{-3} mol·L^{-1}) were prepared in methanol. Then 50 μL stock solution was added to a quartz cuvette containing 0.5 mL of DES. Methanol was removed by heated at 40 °C in a vacuum. A UV-visible spectrophotometer (Cary 5.0, Varian) was used to obtain λ_{max} (nm), and triplicates of each DES were measured. β and π^* can be calculated using the following equations: π^*=0.314×(27.52-ν(NEt_2)), β=(1.035×ν(NEt_2)+2.64-ν(NH_2))/2.8, in which ν(probe)=10^4/λ_{max}.

ICP-OES and XRD analysis

The concentration of rare earth was analyzed by inductively coupled plasma optical atomic emission spectrometry (ICP-OES) using an Agilent 715-ES (USA). The stripping efficiency can be expressed as: E%=($[RE]_0$-$[RE]_t$)/$[RE]_0$×100, in which $[RE]_0$ means the original concentration of rare earth in DES, while $[RE]_t$ means the residual concentration of rare earth in DES after stripped by oxalic acid. The XRD patterns of the samples were recorded by a Shimadzu XRD-

7000 X-ray diffractometer (Shimadzu, Japan) using Cu K radiation at a scanning rate of $2^{o} \cdot min^{-1}$.

Supplementary Figures

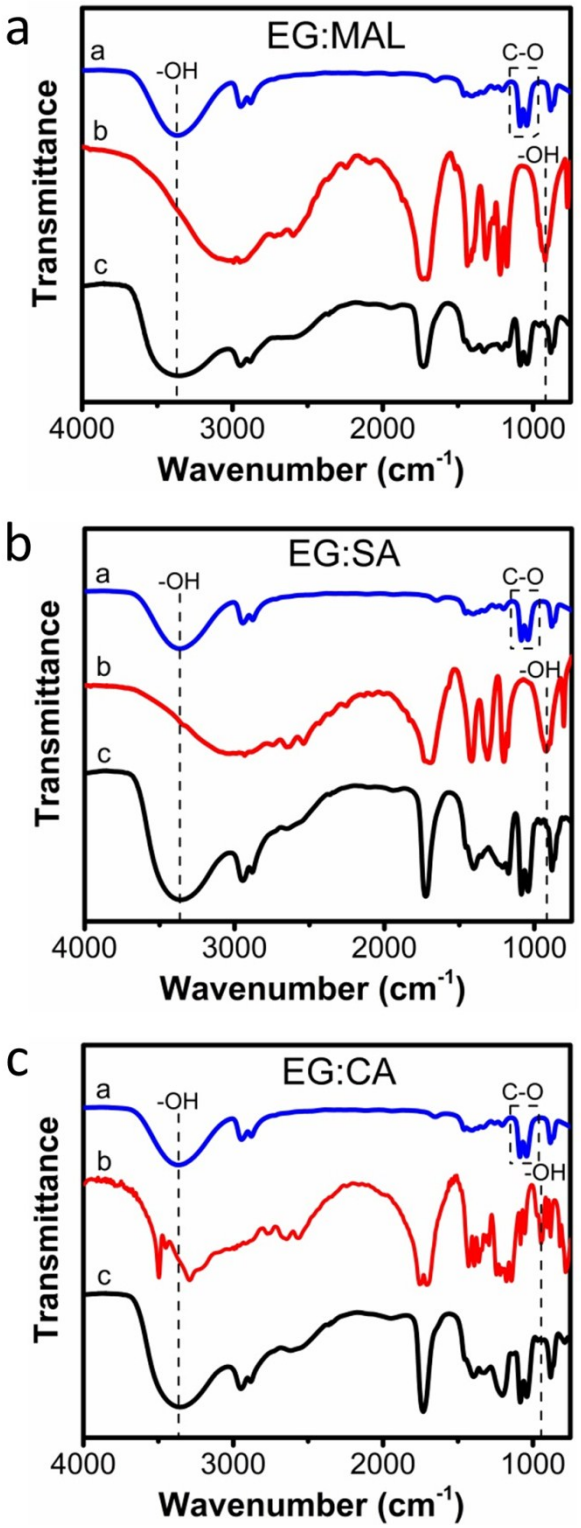

Fig. S1. FTIR spectra of pure components and Brønsted acidic DESs (in which (a) is pure polyols, (b) is pure carboxylic acids and (c) is corresponding DESs): a) EG:MAL, b) EG:SA and c) EG:CA.

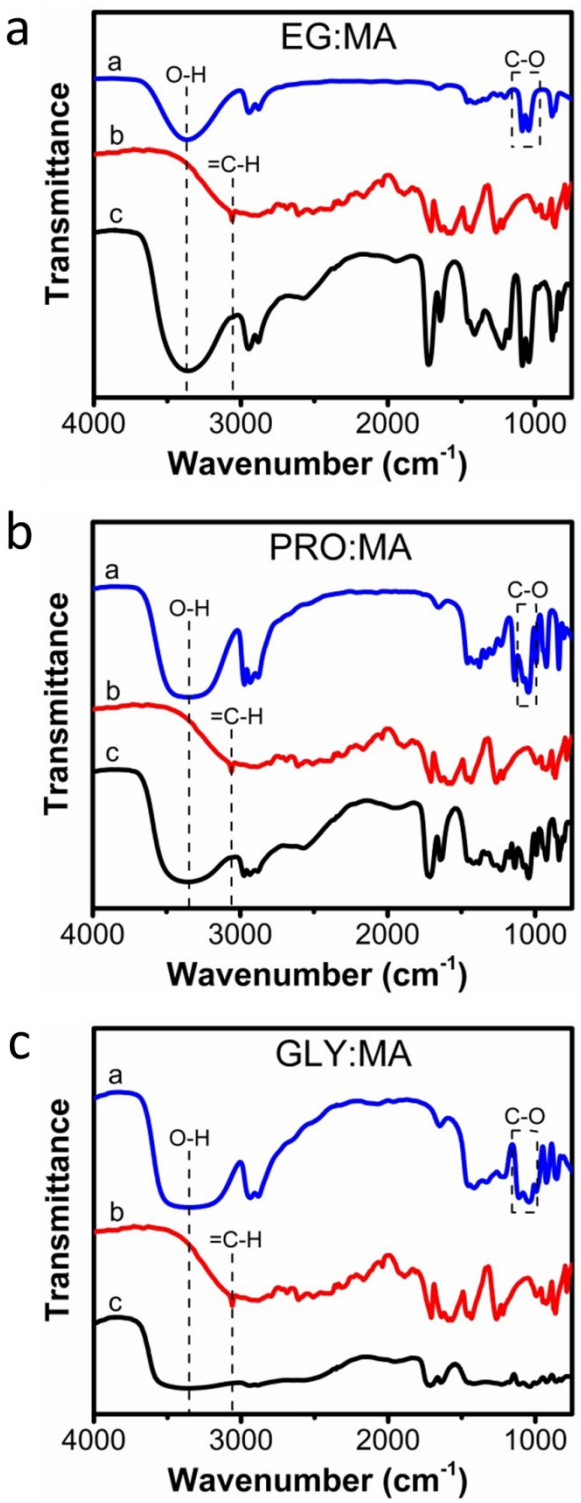

Fig. S2. FTIR spectra of pure components and Brønsted acidic DESs (in which (a) is pure polyols, (b) is pure carboxylic acids and (c) is corresponding DESs): a) EG:MA, b) PRO:MA and c) GLY:MA.

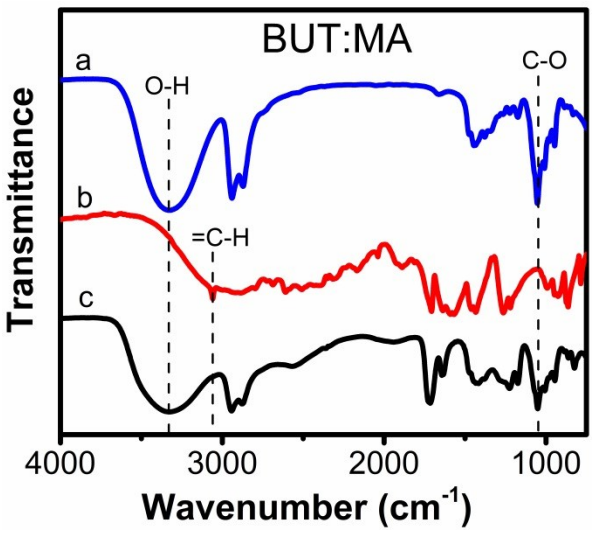

Fig. S3. FTIR spectra of pure components and Brønsted acidic DESs (in which (a) is pure polyols, (b) is pure carboxylic acids and (c) is corresponding DESs): BUT:MA.

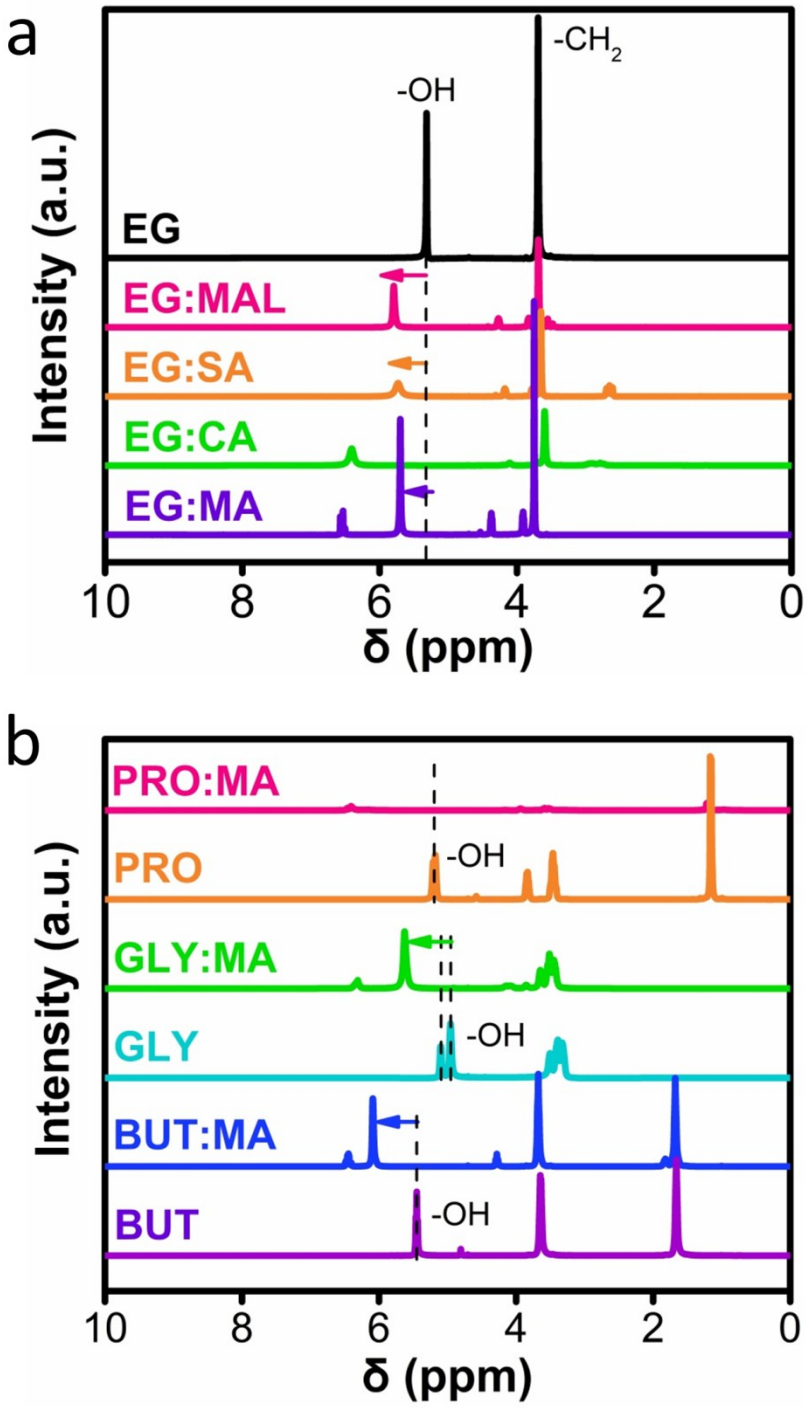

Fig. S4. ^{1}H NMR spectra of pure alcohols and corresponding Brønsted acidic DESs.

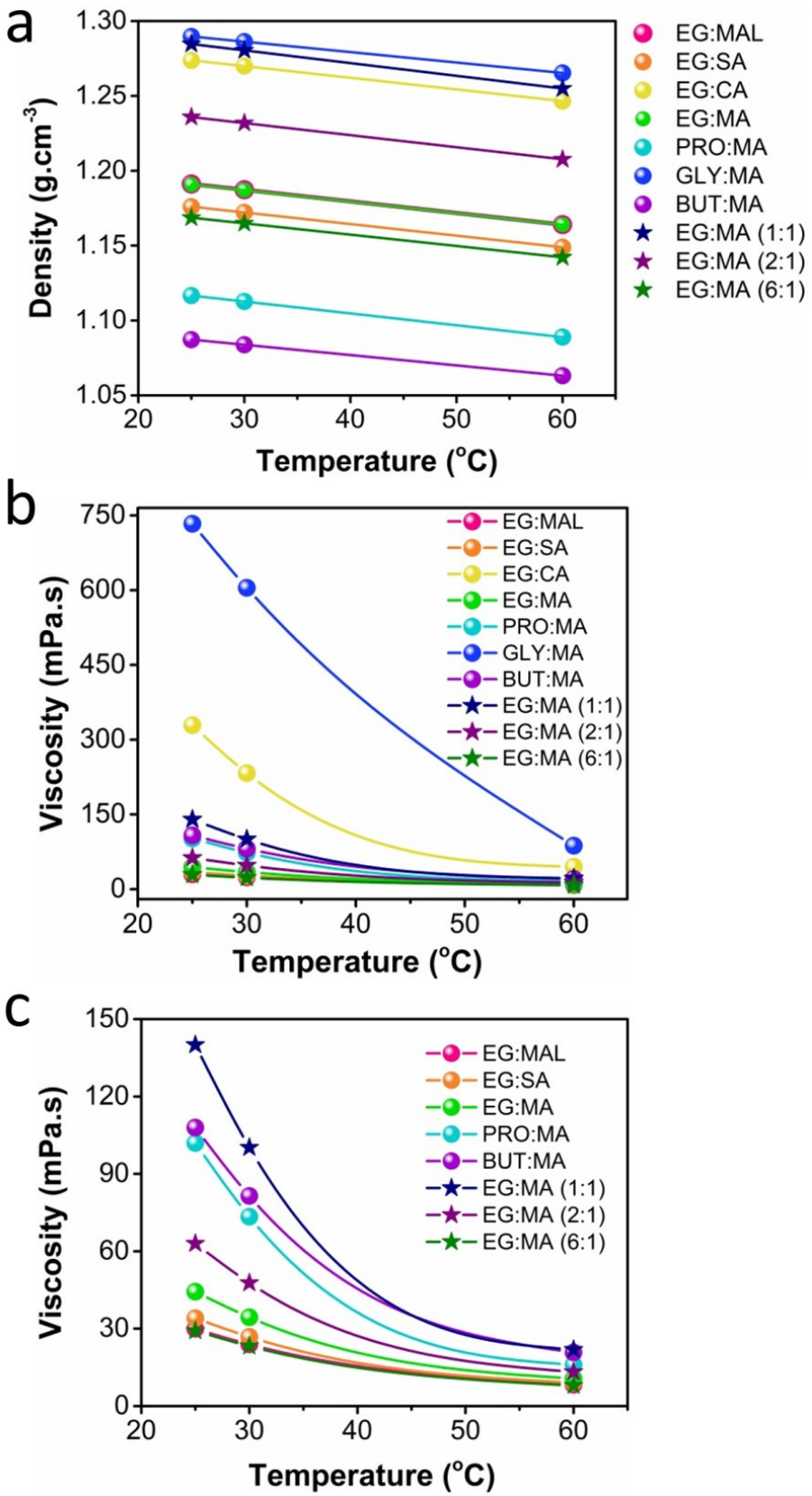

Fig. S5. a) Density and b-c) viscosity of novel Brønsted acidic DESs at 25, 30 and 60 °C.

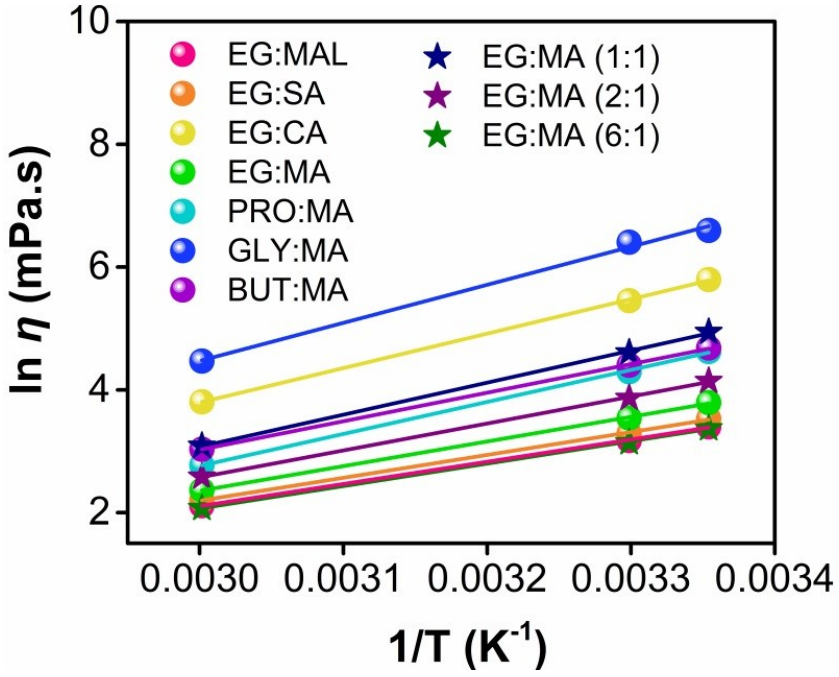

Fig. S6. Plot of ln η vs. reciprocal of temperature for novel Brønsted acidic DESs.

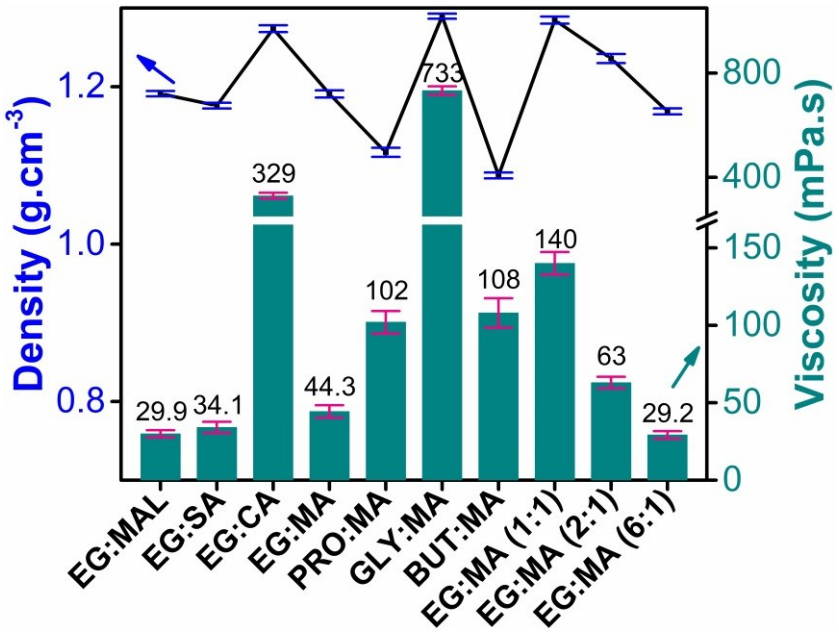

Fig. S7. Density and viscosity of novel Brønsted acidic DESs at 25 ^{o}C (The values represent an average of three independent measurements).

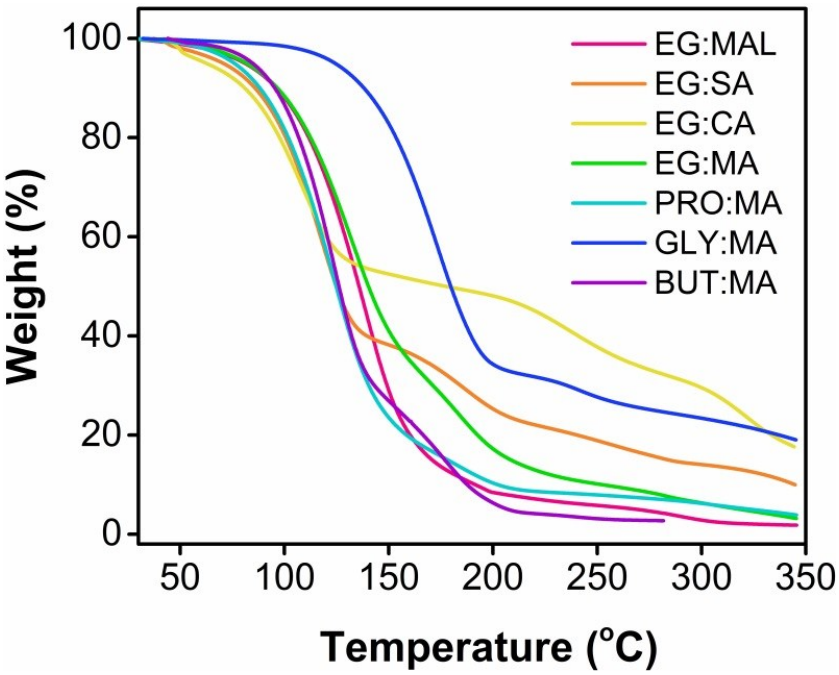

Fig. S8. Thermal stability of Brønsted acidic DESs.

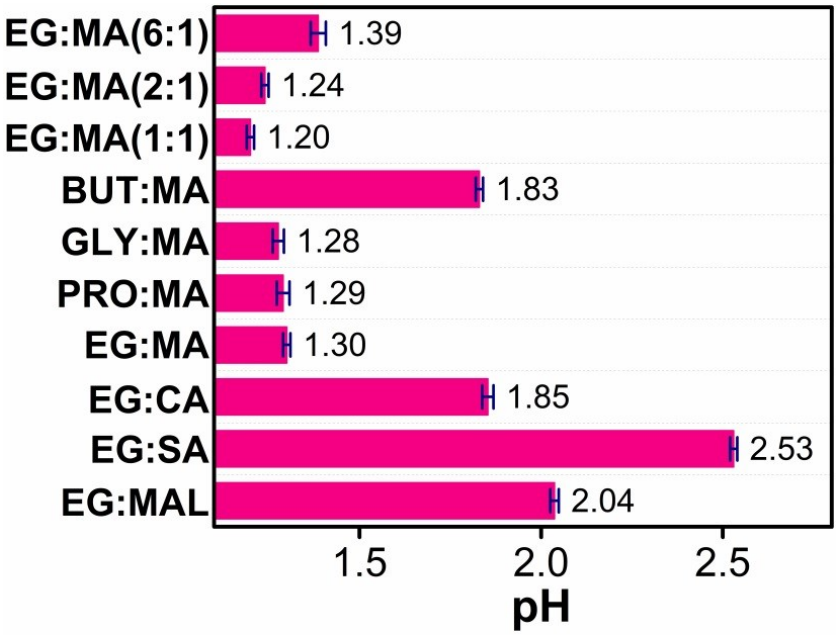

Fig. S9. pH values of Brønsted acidic DESs (determined for 2 mol·L^{-1} solutions with water).

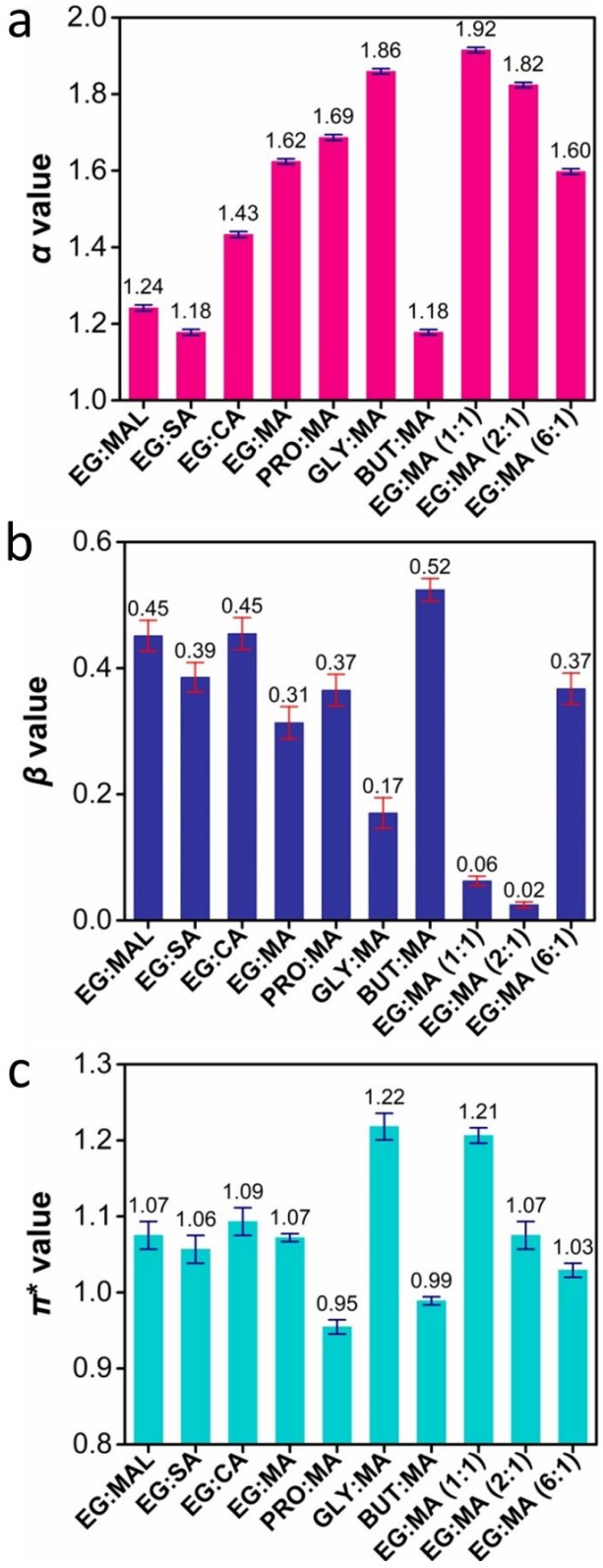

Fig. S10. Kamlet-Taft parameters of Brønsted acidic DESs: a) α values, b) β values and c) π^* values measured at room temperature (The values represent an average of three independent measurements).

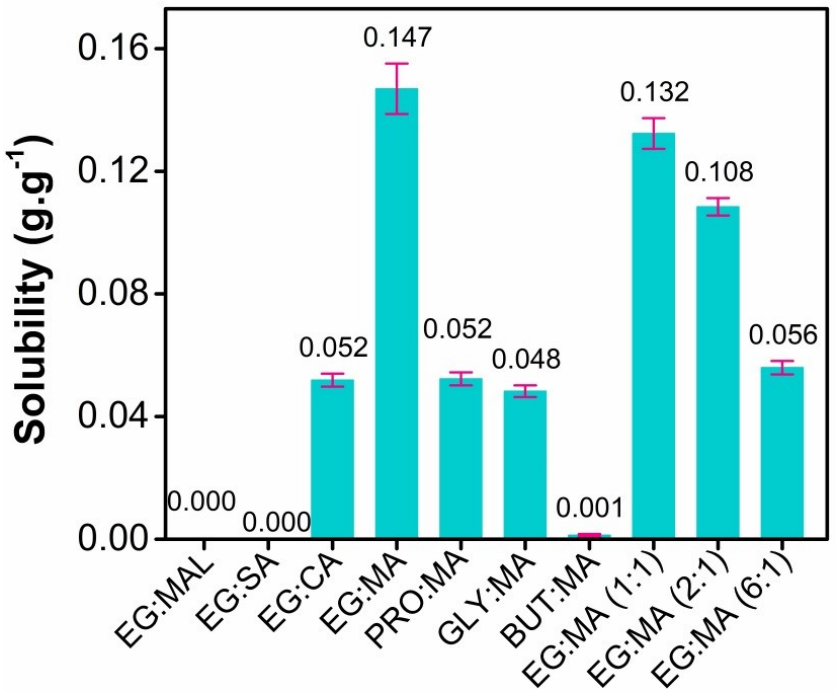

Fig. S11. Solubility of La_2O_3 in different Brønsted acidic DESs at 60 °C (The values represent an average of three independent measurements).

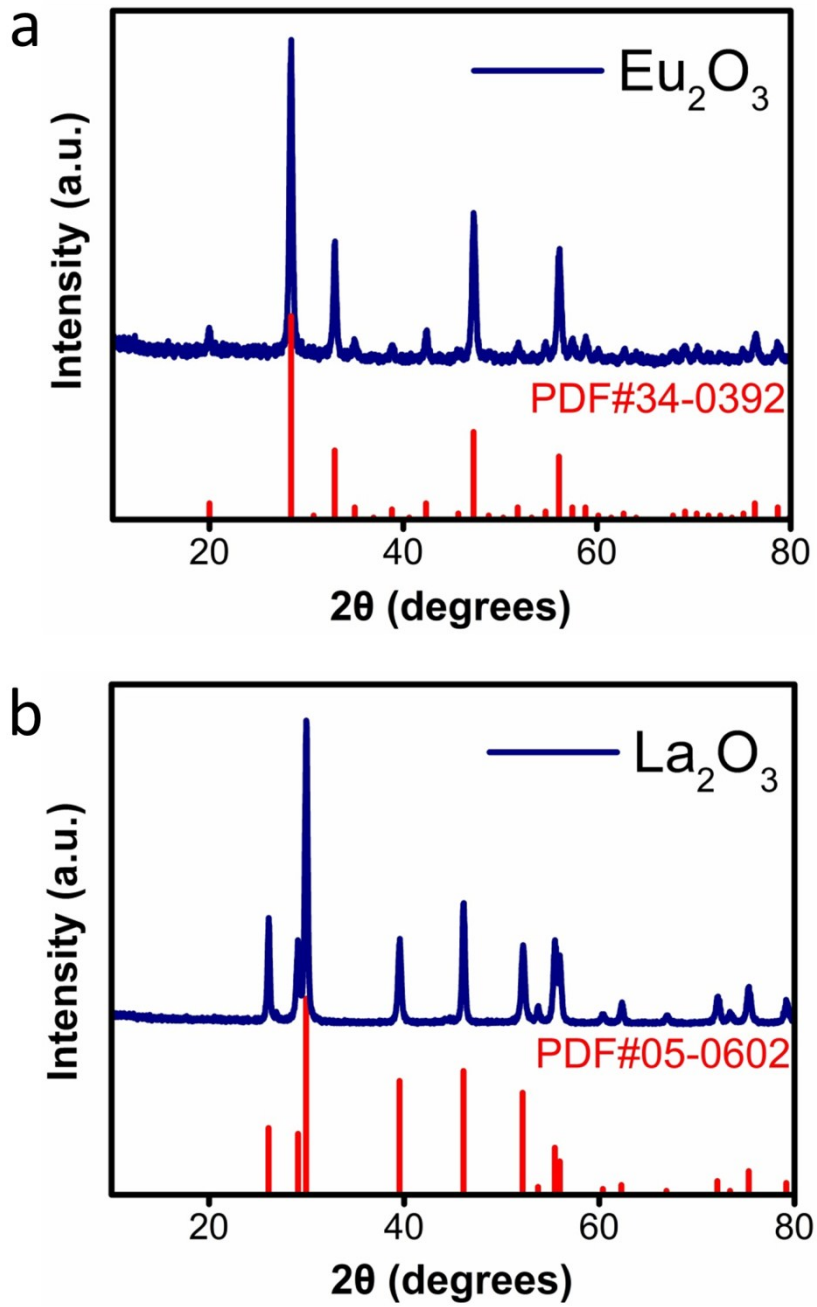

Fig. S12. XRD patterns of as-obtained a) Eu_2O_3 and b) La_2O_3 powder (full scale).

Supplementary References

1. Y. Chen, H. Wang and J. Wang, Effects of alkyl chain length and solvents on thermodynamic dissociation constants of the ionic liquids with one carboxyl group in the alkyl chain of imidazolium cations, *J. Phys. Chem. B*, 2014, **118**, 4630-4635.
2. G. Cai, S. Yang, Q. Zhou, L. Liu, X. Lu, J. Xu and S. Zhang, Physicochemical Properties of Various 2-Hydroxyethylammonium Sulfonate-Based Protic Ionic Liquids and Their Potential Application in Hydrodeoxygenation, *Front. Chem.*, 2019, **7**, 196.