Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Acidity Scales of Deep Eutectic Solvents based on IR and NMR

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Table S1 Components and molar ratios of the prepared DESs

Type	HBA : HBD	Molar ratio	Heating Temperature/℃
I	ChCl : $ZnCl_2$	1 : 2	80
	ChCl : $FeCl_3$	1 : 2	80
	ChCl : $SnCl_2$	1 : 2	80
	ChCl : $CuCl_2$	1 : 2	80
II	ChCl : $MgCl_2·6H_2O$	1 : 1	80
	ChCl : $CoCl_2·6H_2O$	1 : 1	80
	ChCl : $CuCl_2·2H_2O$	1 : 1	80
	ChCl : $CaCl_2·6H_2O$	1 : 2	80
	ChCl : $CrCl_3·6H_2O$	1 : 1	80
III	ChCl : Ethylene glycol	1 : 2	60
	ChCl : Formic acid	1 : 2	45
	ChCl : Acetic acid	1 : 2	45
	ChCl : Propionic acid	1 : 2	45
	ChCl : Lactic acid	1 : 2	45
	ChCl : Oxalic acid	1 : 2	60
	ChCl : Malonic acid	1 : 2	60
IV	$ZnCl_2$: 1,2-Propylene glycol	1 : 4	60
	$ZnCl_2$: 1,3-Propylene glycol	1 : 4	60
	$ZnCl_2$: Ethylene glycol	1 : 4	60
	$ZnCl_2$: 1,2-Butanediol	1 : 4	60
	$ZnCl_2$: 1,3-Butanediol	1 : 4	60
	$ZnCl_2$: 1,4-Butanediol	1 : 4	60
	$ZnCl_2$: 1,6-hexanediol	1 : 3	60
	$ZnCl_2$: Glycerol	1 : 4	60
	$CuCl_2$: Ethylene glycol	1 : 4	60
	$CuCl_2$: Ethylene glycol	1 : 3	60
	$CuCl_2$: Ethylene glycol	1 : 2	60
	$CuCl_2$: Ethylene glycol	1 : 1	60
	$CuCl_2$: Glycerol	1 : 4	60
	$CuCl_2$: 1,2-Propylene glycol	1 : 4	60
	$CuCl_2$: 1,4-Butanediol	1 : 4	60
	$FeCl_3$: Ethylene glycol	1 : 4	60

The effect of different molar ratios

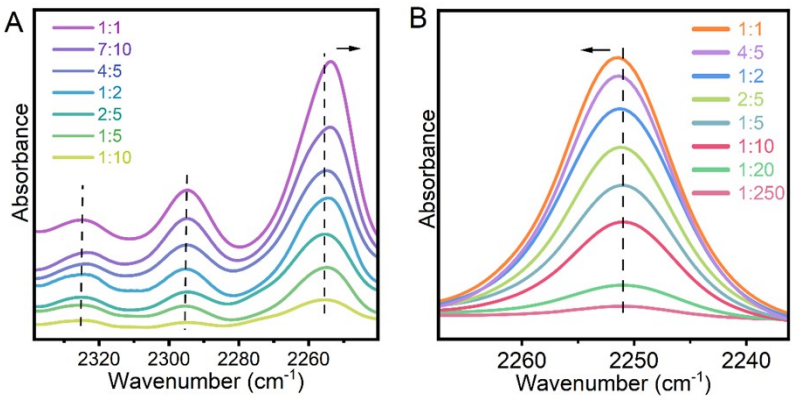

Fig. S1 FT-IR spectra in the *ν*(C≡N) region of (A) CH_3CN-$CuCl_2$:4EG and (B) CH_3CN- ChCl:2EG systems with increasing molar ratio from bottom to top.

For ADESs, it is crucial to find out the appropriate quantity of the probe to prevent breaking the weak interactions in DES as possible. As shown in Fig.S1, the proper molar ratio is 1:10, A closer look will find that the peak at 2255 cm^{-1} shifts to 2253 cm^{-1} with the increasing molar ratio (Fig. S1A), and Fig. S1B shows the blue shift to 2253 cm^{-1}. It suggests the free acetonitrile gradually appears because the pure acetonitrile has the peak of *ν*(C≡N) at 2253 cm^{-1}.

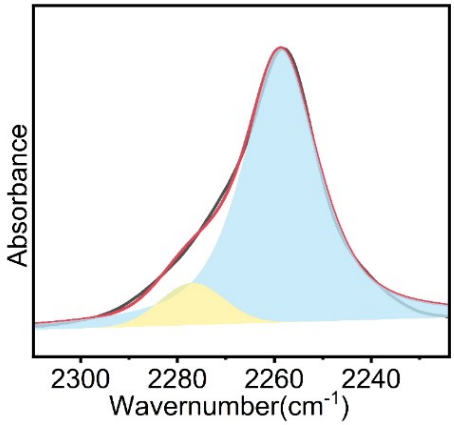

Fig. S2 The IR spectra and the fitted bands in the *ν*(C≡N) region for ChCl:2$SnCl_2$ containing CD_3CN, the global fit is in red. The absorption bands at 2278 and 2260 cm^{-1} are attributed to the C≡N stretches of CD_3CN coordinated to Sn^{2+} and the other ion species, respectively.

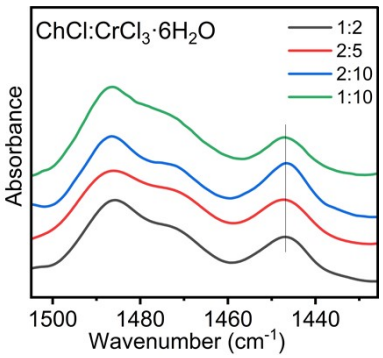

Fig. S3 FT-IR spectra of pyridine-ChCl:5HCOOH systems with increasing molar ratio from bottom to top.

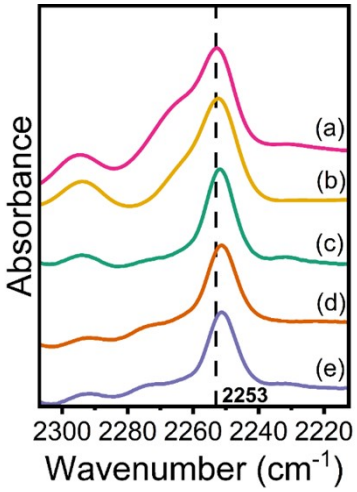

Fig. S4 C≡N stretching vibration of acetonitrile in type III DESs. (a)ChCl:2$(COOH)_2$ (b) ChCl:2$CH_3(COOH)_2$ (c) ChCl:2HCOOH (d) ChCl:2CH_3COOH (e) ChCl:2C_2H_5COOH.

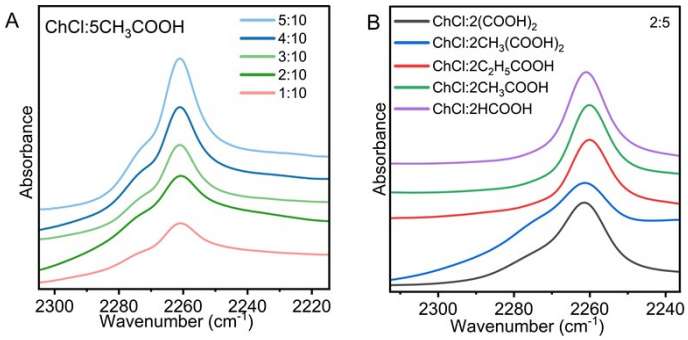

Fig. S5 (A) FT-IR spectra in the *ν*(C≡N) region of CD_3CN-ChCl:5CH_3COOH systems with increasing molar ratio from bottom to top. (B) FT-IR spectra in the *ν*(C≡N) region of different CD_3CN-BADES systems with a molar ratio of 2:5.

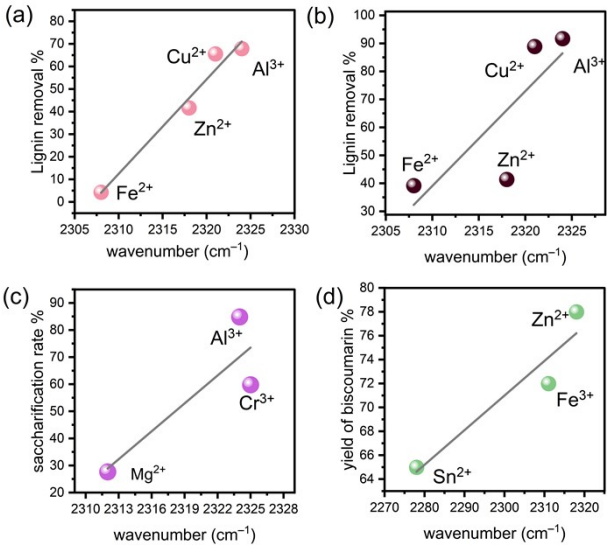

Fig. S6 The correlation between Lewis acidity of metal ions and performance in different applications. (a) The data of lignin removal were taken from Ref. [1]. (b) The data of lignin removal were taken from Ref. [2]. (c)The data of rates were taken from Ref. [3]. (d)The data of yields were taken from Ref. [4].

To prove the IR acetonitrile approach could be used as guidance for practical applications. We made a correlation between Lewis acidity of metal ions and performance in different applications. By neglecting the difference between these DESs, we presumed that Lewis acidity metal ions do not change with the HBAs. Although the reactions are influenced by many factors, it still could be found that the performance of different applications corresponds to the trend of Lewis acidity.

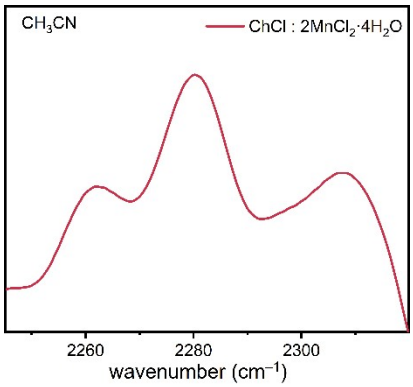

Fig. S7 C≡N stretching vibration of acetonitrile in ChCl: 2$MnCl_2$·4H_2O.

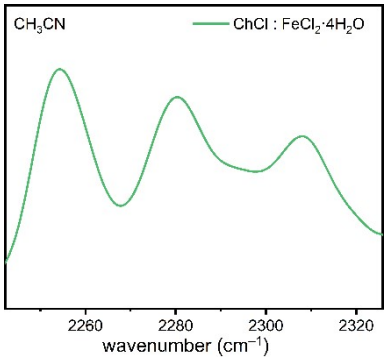

Fig. S8 C≡N stretching vibration of acetonitrile in ChCl: $FeCl_2 \cdot 4H_2O$.

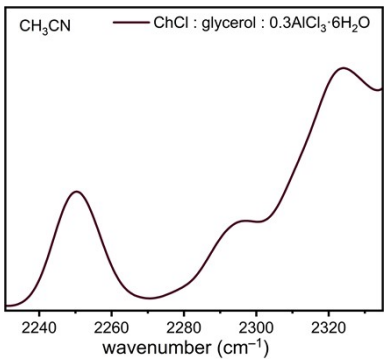

Fig. S9 C≡N stretching vibration of acetonitrile in ChCl: glycerol:0.3$AlCl_3 \cdot 6H_2O$.

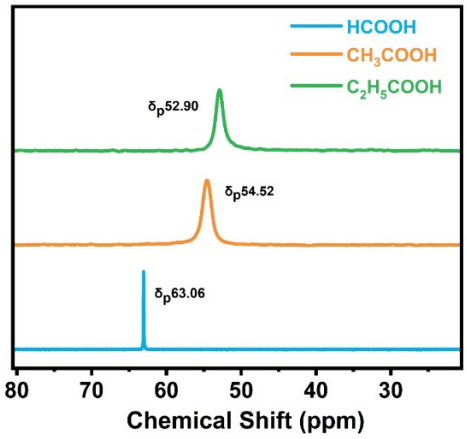

Fig. S10 ^{31}P NMR spectra of TMPO as probe in Brønsted acid.

Calculations of radius (Å)/ charge (e) ratio (r/z) of metal cations：

Cr^{3+} r=0.615 vi z=3

Cu^{2+} r=0.57 iv z=2

Co^{2+} r=0.65 vi z=2

Mg^{2+}r=0.72 vi z=2

Ca^{2+} r=1 vi z=2

All data of radius were taken from reference[5].

Table S2 Comparison of the solvatochromic parameter α with ^{31}P chemical shift in different BADES.

BADES	α	^{31}P chemical shift (ppm)
ChCl ：2oxalic acid	2.173 [6, a]	75.21
ChCl ：2malonic acid	1.39 [7,a]	59.31
ChCl ：2formic acid	1.293 [8]	54.43
ChCl ：2acetic acid	1.232 [8]	51.87
ChCl ：2propionic acid	1.193 [8]	51.29
ChCl ：2ethyle glycol	0.891 [9]	47.59

Note: [a] The molar ratio of BADES in reference is 1:1.

1. Z.-K. Wang, H. Li, X.-C. Lin, L. Tang, J.-J. Chen, J.-W. Mo, R.-S. Yu and X.-J. Shen, *Bioresour. Technol.*, 2020, **307**, 123237.
2. Z.-K. Wang, S. Hong, J.-l. Wen, C.-Y. Ma, L. Tang, H. Jiang, J.-J. Chen, S. Li, X.-J. Shen and T.-Q. Yuan, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 1050-1057.
3. Q. Ji, X. Yu, A. E. A. Yagoub, L. Chen, A. T. Mustapha and C. Zhou, *Renewable Energy*, 2021, **172**, 304-316.
4. F. Abbasi, N. Azizi and M. Abdoli-Senejani, *Journal of the Iranian Chemical Society*, 2017, **14**, 2097-2103.
5. R. D. Shannon, *Acta Crystallographica Section A*, 1976, **32**, 751-767.
6. C. Cai, W. Yu, C. Wang, L. Liu, F. Li and Z. Tan, *J. Mol. Liq.*, 2019, **287**, 110957.
7. C. Florindo, A. J. S. McIntosh, T. Welton, L. C. Branco and I. M. Marrucho, *Phys. Chem. Chem. Phys.*, 2018, **20**, 206-213.
8. Y. Oh, S. Park, D. Jung, K. K. Oh and S. H. Lee, *Int. J. Biol. Macromol.*, 2020, **165**, 187-197.
9. S. H. Kim, S. Park, H. Yu, J. H. Kim, H. J. Kim, Y.-H. Yang, Y. H. Kim, K. J. Kim, E. Kan and S. H. Lee, *J. Mol. Catal. B: Enzym.*, 2016, **128**, 65-72.