Supporting Information

Double-line Hammett Relationship Revealed Through Precise Acidity Measurement of Benzenethiols in Neat Ionic Media: A Typical "Ionic Liquid Effect"?

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Contents:

1. Experimental Section

Materials. Ionic liquids were synthesized and purified based on the literature procedures,[1] the water content in all the ILs used in this work was less than 15 ppm, which was measured by Karl-Fisher method. The indicator used were synthesized and characterized by known methods.[2] The aryl thiols were commercially available with analytical grade and used as received unless otherwise noted. Solid substrates and other commercial reagents for the synthetic purpose were carefully recrystallized and dried until no further weight loss. The solutions of indicators, acids and the base were prepared by the procedure described in the previous work.[3]

Equipment. The indicator and acid reservoirs, pK cell, and syringes for pK_a measurement in ionic liquids were the same as those for C-H acids.[3] All weights were recorded to ±0.0001 g, and the absorbance was measured with a UV-Vis spectrophotometer.

Preparation of Solutions for Indicators and Acids. The solutions of indicators and acids were prepared in a glove box. The indicator (or acid) was weighed (ca. 10 mg) into the reservoir, and then the reservoir was weighed. A desired amount of ionic liquid (usually 1 to 1.5 ml) was added by a syringe. The exact amount of ionic liquid was determined gravimetrically.

pK_a Measurement in ILs. All manipulations were carried out under dry argon using standard Schlenk techniques. The measurement procedure used for benzenethiols was similar to that for C-H acids.[3] In a typical run, the pK cell was degassed and fulfilled with dry argon gas at least 3 times. The cell was then weighted and 1.5 ml IL and 40 mg base were added. An indicator with known pK_a was added dropwise after the cell was weighted again and a baseline was recorded on a UV-Vis instrument. After the base was fully consumed by 6-8 additions of the indicator, which was monitored by the UV-Vis instrument, an excess amount of indicator solution was added, total amount indicator added was about 1 to 1.5 mg. Both of the spectrum and weight for each addition was recorded. Then the target acid of interest was added in several aliquots (typically 6-8 consecutive titrations, total amount of acid added was about 0.5 to 1 mg). The weight of the cell and the corresponding spectrum were recorded upon each addition, with the data derived from the change of absorbance, the corresponding pK_a was obtained. Each acidity data reported in Table 1 was the average value of two to three independent runs (SD ≤ 0.05 pK units).

2. Titration of benzenethiol with 9-CNFH in BmimNTf$_2$

Table S1. The pK_as of benzenethiol in BmimNTf$_2$ measured with 9-CNFH (9-cyanofluorene) by using the indicator overlapping method upon adding respective droplet of acid.

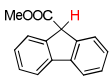
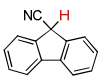
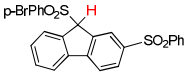
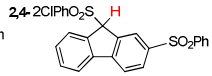
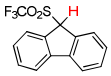
Acid droplet	1	2	3	4	5	6
Measured pK_a	17.16	17.15	17.15	17.15	17.14	17.14

Table S2**.** The individual pK_a value of benzenethiol measured with 9-CNFH (9-cyanofluorene) as the indicator from different run in $BmimNTf_2$.

Run	1	2	3	4	5	6
pK_a	17.15	17.18	17.16	17.14	17.15	17.13

3. Indicators used in this work

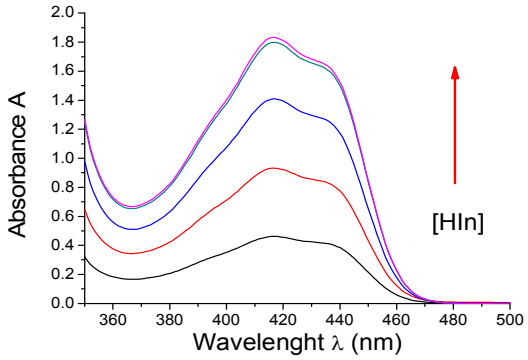
Table S3. Indicators were used in this work and the corresponding pK_as in ILs [3,4]

	 MOF	 CNF	 BPPF	 DCPF	 TFMF
$BmimNTf_2$	18.3	16.7	16.1	15.0	12.7
$BmpyNTf_2$	18.4	16.6	16.0	15.0_5	12.6
Bm_2imNTf_2	19.2	17.4	16.5	–	13.2
BmimOTf	15.3	13.8	13.3	12.4	10.0

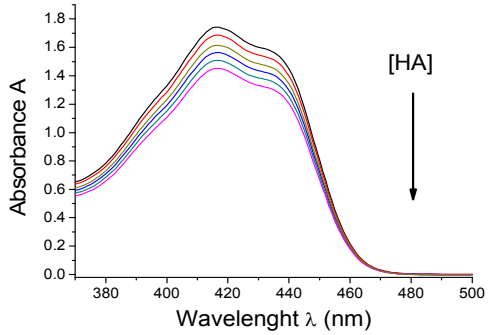
4. UV-Vis spectra of the representitive titration of bnezenethiols with base and indicator in $BmimNTf_2$

Note

Because all the pK_a measurements in the ionic liquids involved in this work were strictly performed under the standard conditions and the quality of the recorded spectra is similar, therefore not all the spectra recorded during the pK_a measurement are shown in this section. Hence, the UV-Vis spectra of 3 representative benzenethiols in $BmimNTf_2$ are presented here as shown in Figures S1-S3.

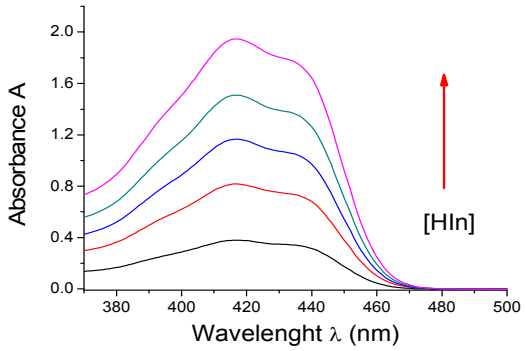


(a)



(b)

Figure S1. (a) The increasing absorbance during the deprotonation of the acid indicator (9-CNFH) by the base. (b) The decreasing absorbance during the titration of the acid indicator anion by 4-methyl benzenethiol during the titration in $BmimNTf_2$.



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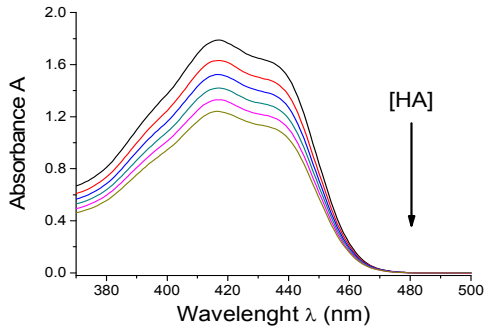
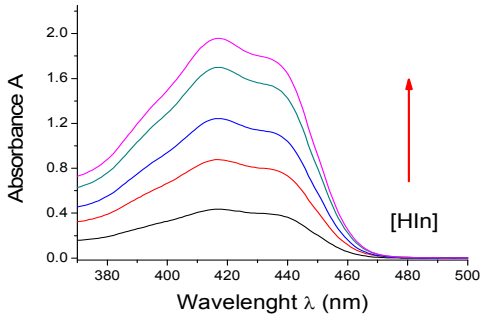


(b)

Figure S2. (a) The increasing absorbance during the deprotonation of the acid indicator (9-CNFH) by the base. (b) The decreasing absorbance during the titration of the acid indicator anion by benzenethiol during the titration in $BmimNTf_2$.



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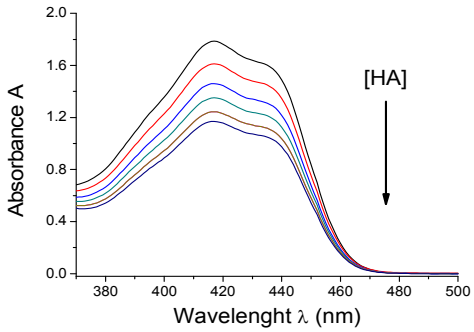

(b)

Figure S3. (a) The increasing absorbance during the deprotonation of the acid indicator (9-CNFH) by the base. (b) The decreasing absorbance during the titration of the acid indicator anion by 4-fluorobenzenethiol during the titration in $BmimNTf_2$.

5. References

1. Burrell, A. K.; Sesto, R. E. D.; Baker, S. N.; McCleskey, T. M.; Baker, G. A. *Green Chem.* **2007**, *9*, 449-454.

2. Brown, H. C.; McDaniel, D. H.; Häfliger, O.; Nachod, F. C. *Determination of Organic Structures by Physical Methods*, (Eds.: Braude, E. A.; Nachod, F. C.), Academic Press, New York, 1955.

3. Deng, H.; Li, X.; Yuan, C.; He, J.; Cheng, J. -P. *J. Org. Chem.* **2012**, *77*, 7291-7298.

4. Wang, Z.; Deng, H.; Li, X.; Ji, P.; Cheng, J. -P. *J. Org. Chem*. **2013**, *78*, 12487-12493.