Supporting Information

Efficient and Reversible Absorption of Ammonia by Cobalt Ionic Liquids through Lewis Acid-Base and Cooperative Hydrogen Bond Interactions

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1. Stability constants of coordination ions

Table S1. Stability constants of several coordination ions[1]

Coordination ions	Stability constants	Coordination ions	Stability constants
$[Co(NCS)_4]^{2-}$	1.0×10^3	$[Ni(NH_3)_6]^{2+}$	5.5×10^8
$[Co(NH_3)_6]^{2+}$	1.3×10^5	$[Zn(NH_3)_4]^{2+}$	2.9×10^9
$[Cd(NH_3)_6]^{2+}$	1.4×10^5	$[Cu(NH_3)_4]^{2+}$	4.8×10^{12}
$[Ag(NH_3)_2]^{+}$	1.6×10^7	$[Co(NH_3)_6]^{3+}$	2×10^{35}

2. Theoretical considerations and equations

The experimental data in Table 2 showed that the effects of cations on the capacities of CO_2 and NH_3 are negligible. Therefore, we only included anions in the DFT calculations. Due to the complexity of the MILs, we calculated the vibrational spectra individually for all the important species. This simplified treatment allows us to clearly assign every band in the experimental IR spectra and to understand the absorption mechanism. The absorption mechanism is essentially the same and is independent on the type of cations. Therefore, only Bmim cation is considered in the simulated IR spectra.

The final Gibbs energies in solution were calculated from the gas-phase single point electronic energies plus the gas-phase thermostatistical contributions, and the COSMO-RS solvation Gibbs free energies (Equation S1).

$$\Delta G = \Delta E + \Delta G_{\mathrm{RROH}} + \Delta\delta G_{\mathrm{sol}} \quad \text{(S1)}$$

where ΔE is the reaction electronic energy, ΔG_{RROH} is the thermostatistical contributions (Equation S2) and $\Delta\delta G_{\mathrm{sol}}$ is the solvation Gibbs free energy.

The thermostatistical contributions are computed as follows:

$$\Delta G_{RROH} = ZPE + E_{therm} + PV - T \times S \quad \text{(S2)}$$

where ZPE is the zero point vibrational energy, E_{therm} is the thermal energy, and P, V, T, and S denote pressure, volume, temperature and entropy, respectively.

The selectivity of NH_3 over CO_2 by conversional ILs is estimated via Equation S3.

$$k = \frac{k_b T}{h} e^{\frac{-\Delta G^{\neq}}{RT}} \quad \text{(S3)}$$

where R= 1.987×10^{-3} kcal·mol^{-1}·K^{-1}. T is the temperature. $\Delta G^{\neq}$ is the Gibbs activation energy. k_b and h are the Boltzmann and Planck constants, respectively.

The reaction Gibbs free energies (ΔG) are calculated for following reactions:

$$NH_3 + SCN^- \rightarrow NH_3\cdots SCN^- \quad \text{(S4)}$$

$$CO_2 + SCN^- \rightarrow CO_2\cdots SCN^- \quad \text{(S5)}$$

$$Co(NCS)_4^{2-} + 6NH_3 \rightarrow [Co(NH_3)_6(NCS)_4]^{2-} \quad \text{(S6)}$$

$$Co(NCS)_2 + 4NH_3 \rightarrow [Co(NH_3)_4(NCS)_2] \quad \text{(S7)}$$

3. Optimized structures

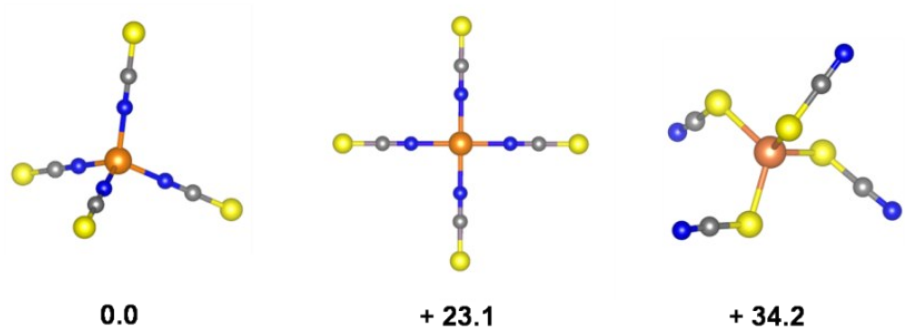

Figure S1. Optimized structures of $Co(SCN)_4^{2-}$ and their relative energies. The calculations are carried at PBE0/def2-TZVPP//TPSS-D3/def2-TZVP level of theory. The energies are given in kcal·mol^{-1}. Color legend: Co orange, S yellow, N blue, C black.

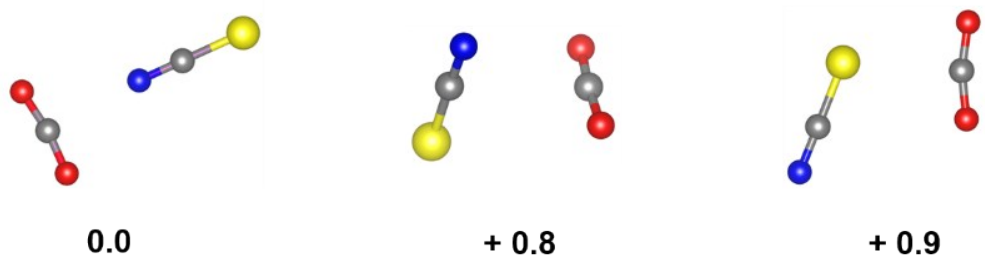

Figure S2. Optimized structures of $CO_2\cdots SCN$ and their relative energies. The calculations are carried at PBE0/def2-TZVPP//TPSS-D3/def2-TZVP level of theory. The energies are given in kcal·mol^{-1}. Color legend: S yellow, N blue, C black and O red.

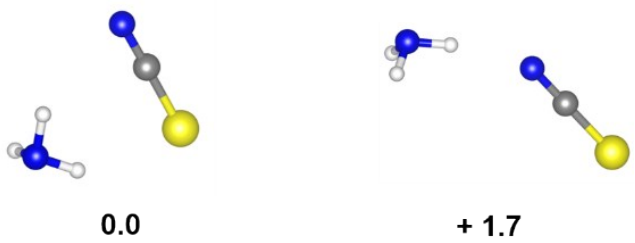

Figure S3. Optimized structures of $NH_3\cdots SCN$ and their relative energies. The calculations are carried at PBE0/def2-TZVPP//TPSS-D3/def2-TZVP level of theory. The energies are given in kcal·mol^{-1}. Color legend: S yellow, N blue, C black and H white.

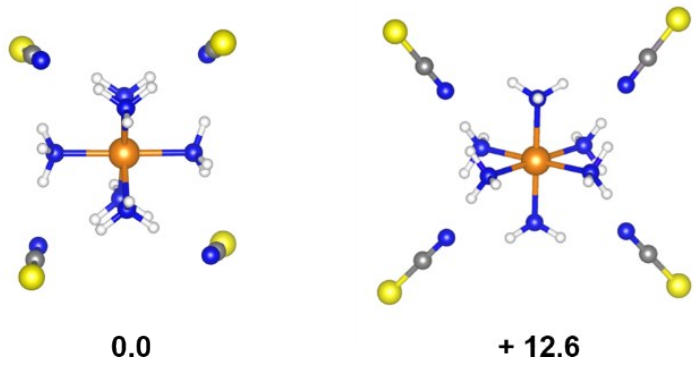

Figure S4. Optimized structures of $[Co(NH_3)_6(SCN)_4]^{2-}$ and their relative energies. The calculations are carried at PBE0/def2-TZVPP//TPSS-D3/def2-TZVP level of theory. The energies are given in kcal·mol^{-1}. Color legend: S yellow, N blue, C black, H white and Co orange.

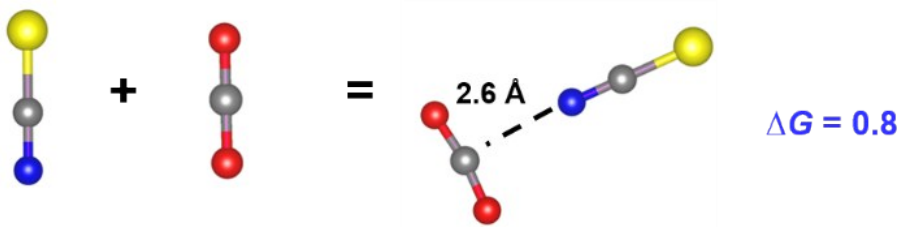

Figure S5. Optimized structures and computed Gibbs free energy for the reaction Equation S4. The selected distances and the energies are given in Å and kcal· mol^{-1}, respectively. Color legend: S yellow, N blue, C black and O red.

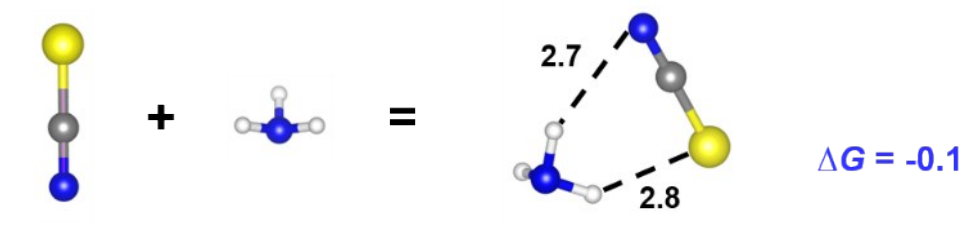

Figure S6. Optimized structures and computed Gibbs free energy for the reaction Equation S5. The selected distances and the energies are given in Å and kcal·mol^{-1}, respectively. Color legend: S yellow, N blue, C black and H white.

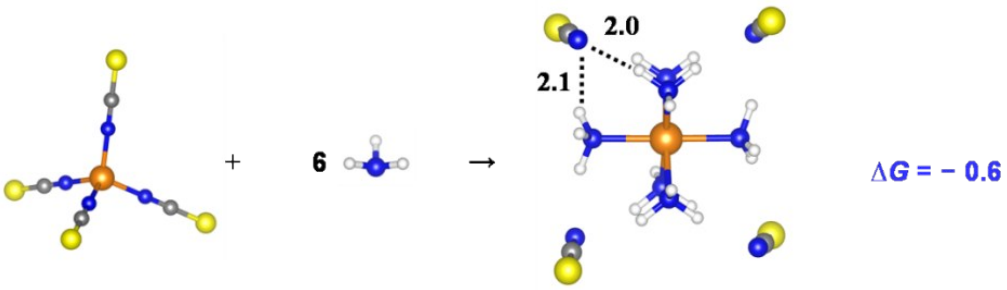

Figure S7. Optimized structures and computed Gibbs free energy for the reaction Equation S6. The selected distances and the energies are given in Å and kcal·mol^{-1}, respectively. Color legend: S yellow, N blue, C black, H white and Co orange.

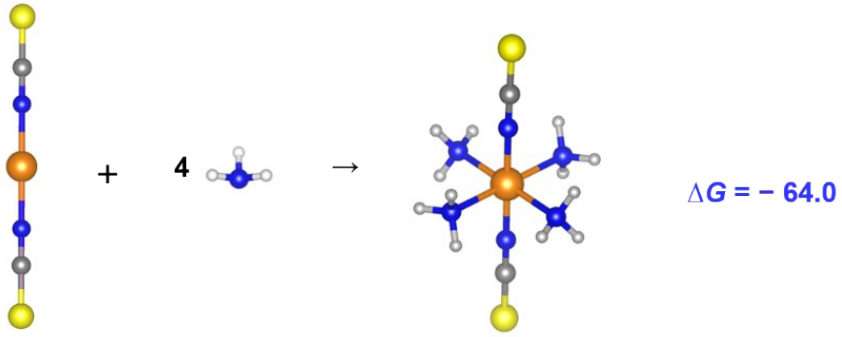

Figure S8. Optimized structures and computed Gibbs free energy for the reaction Equation S7. The selected distances and the energies are given in Å and kcal·mol^{-1}, respectively. Color legend: S yellow, N blue, C black, H white and Co orange.

4. The recycle of cobalt ILs with saturated water

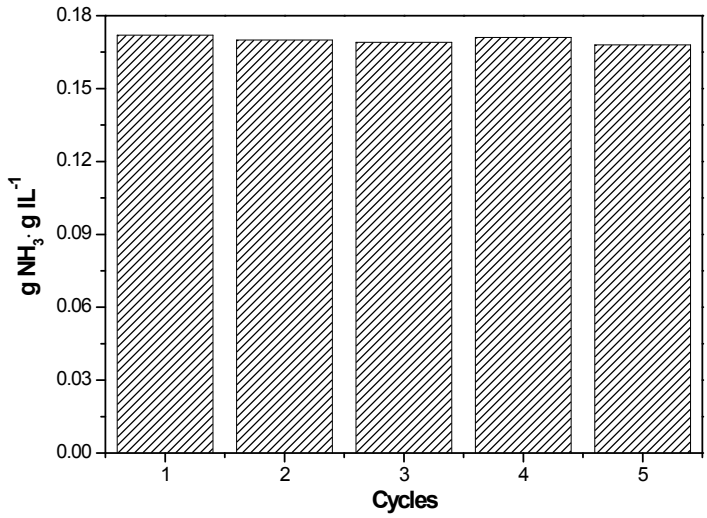

Figure S9. NH_3 absorption and desorption in $[Bmim]_2[Co(NCS)_4]$ with saturated water (1.22 wt%).

NH_3 absorption: 30℃ and 0.10 MPa, and NH_3 desorption: 80℃ under N_2.

5. Experimental IR and NMR spectra

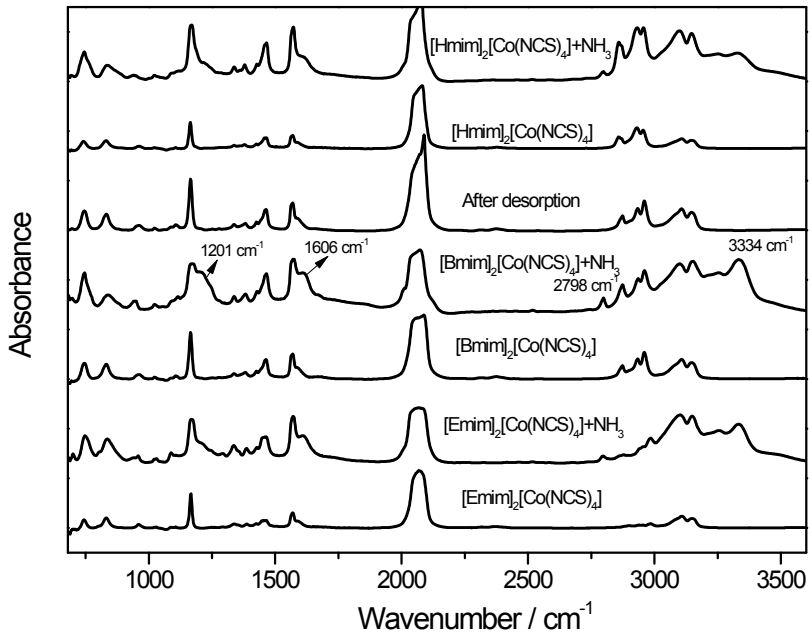

Figure S10. Experimental IR spectra of $[C_nmim]_2[Co(NCS)_4]$ before/after NH_3 absorption and after NH_3 desorption.

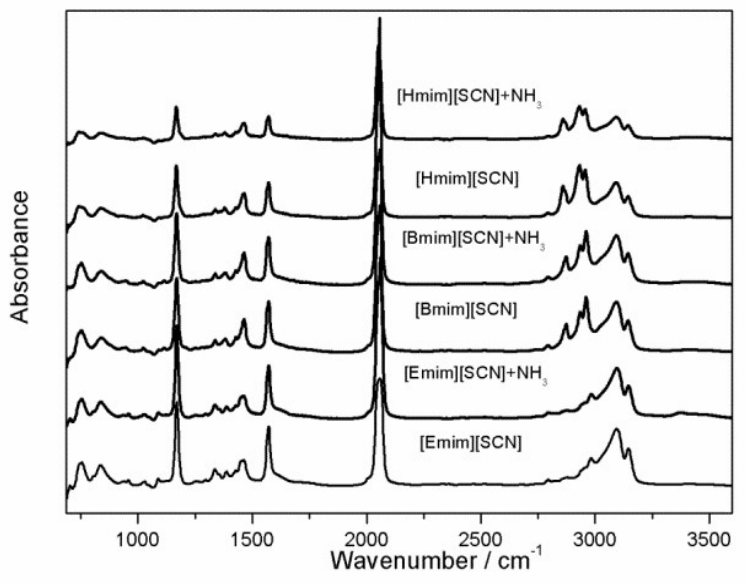

Figure S11. Experimental IR spectra of $[C_nmim][SCN]$ before and after NH_3 absorption

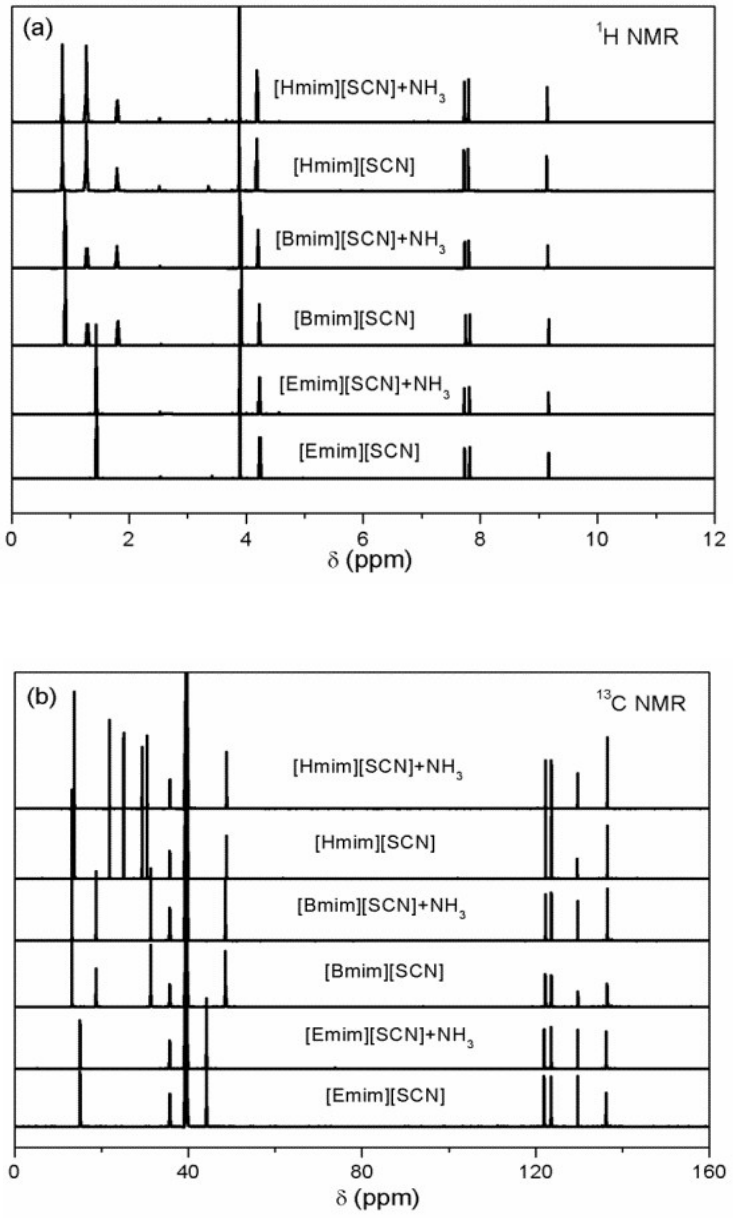

Figure S12. Experimental ^{1}H NMR and ^{13}C NMR spectra of [$C_n$mim][SCN] before and after NH_3 absorption.

6. Simulated IR spectra

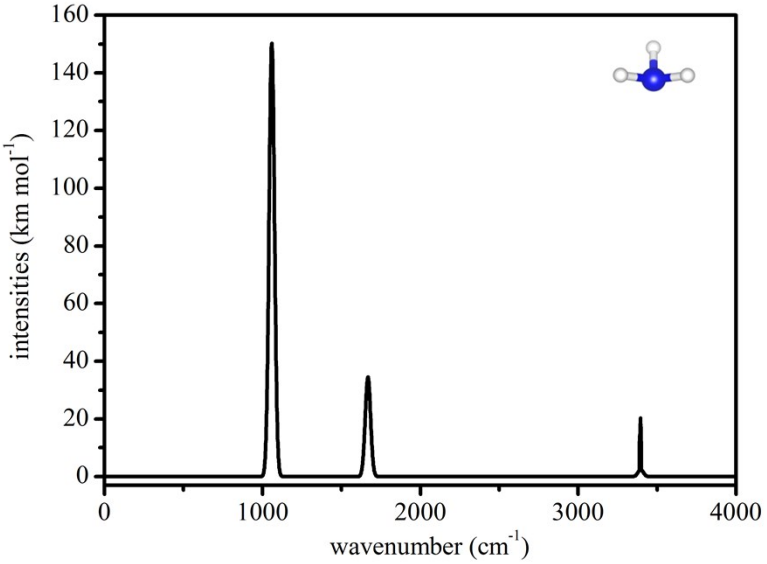

Figure S13. Simulated IR spectra of free NH_3. The calculations are carried at TPSS-D3/def2-TZVP level of theory and simulated IR spectra of free NH_3 is unscaled.

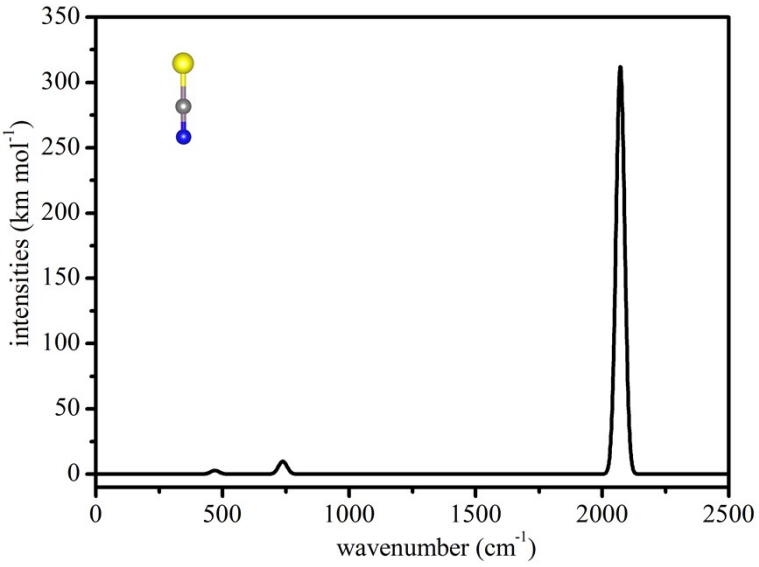

Figure S14. Simulated IR spectra of SCN anion. The calculations are carried at TPSS-D3/def2-TZVP level of theory and simulated IR spectra of SCN anion is unscaled.

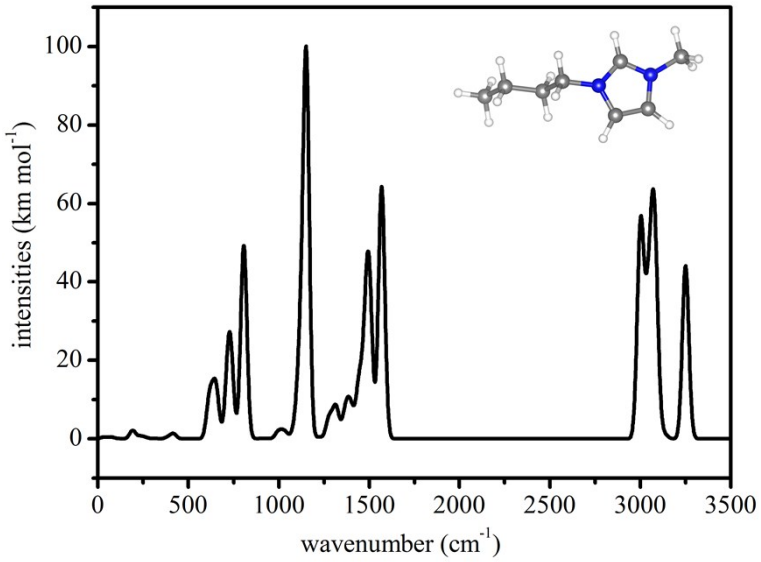

Figure S15. Simulated IR spectra of Bmim cation. The calculations are carried at TPSS-D3/def2-TZVP level of theory and simulated IR spectra of Bmim cation is unscaled.

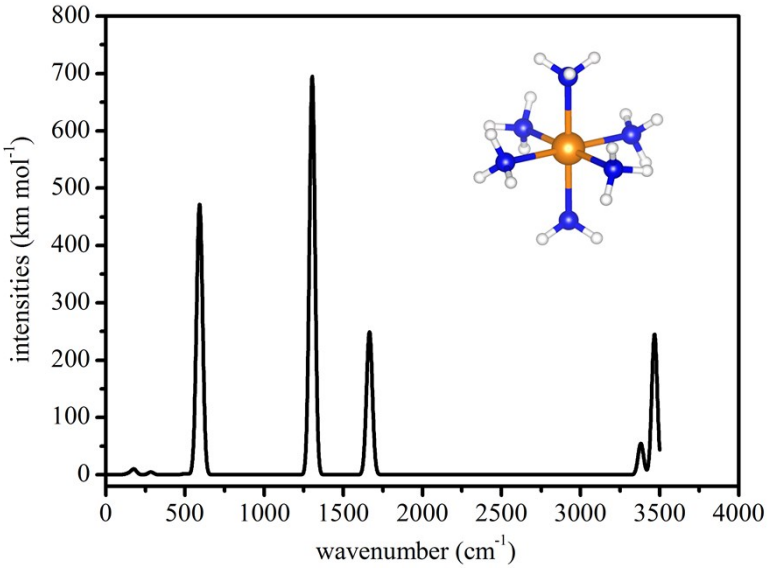

Figure S16. Simulated IR spectra of $[Co(NH_3)_6]^{2+}$. The calculations are carried at TPSS-D3/def2-TZVP level of theory and simulated IR spectra of $[Co(NH_3)_6]^{2+}$ is unscaled.

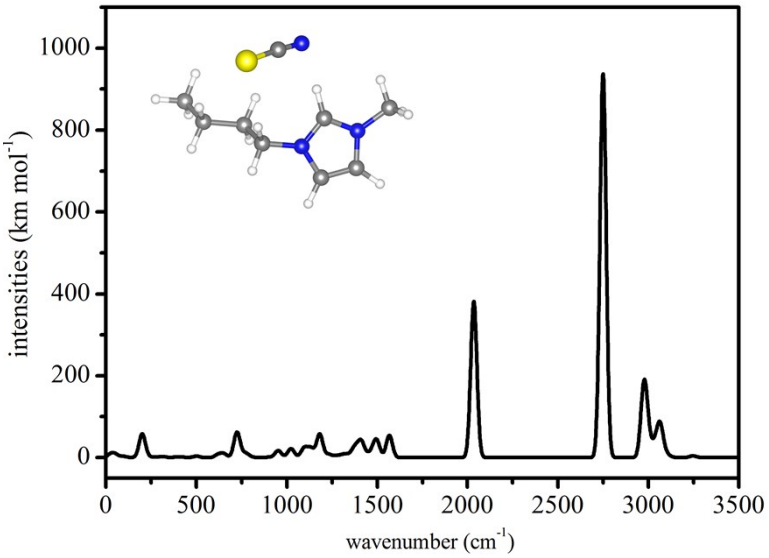

Figure S17. Simulated IR spectra of [Bmim][SCN]. The calculations are carried at TPSS-D3/def2-TZVP level of theory and simulated IR spectra of [Bmim][SCN] is unscaled.

7. Cartesian coordinates

CO_2

C	0.0000000	0.0000000	0.0000000
O	0.0000000	0.0000000	-1.1690447
O	0.0000000	0.0000000	1.1690447

NH_3

N	0.0000000	0.0000000	0.2911879
H	0.4715119	0.8166825	-0.0970626
H	0.4715119	-0.8166825	-0.0970626
H	-0.9430237	0.0000000	-0.0970626

SCN^-

C	0.0000000	0.0000000	0.1582564
S	0.0000000	0.0000000	-1.5004608
N	0.0000000	0.0000000	1.3422044

CO_2··· SCN

C	-1.8156042	0.6971372	0.0000000
O	-1.5136787	1.8289765	0.0000000
O	-2.2900202	-0.3739151	0.0000000
C	1.7301854	-0.6547615	0.0000000
S	3.2402251	-1.3237479	0.0000000
N	0.6488927	-0.1736892	0.0000000

NH_3··· SCN

C	1.4442767	-0.9814600	0.0198347
S	0.7624793	-1.8571376	-1.2110079
N	1.9088697	-0.3420297	0.9011754
N	-1.3211683	0.8425195	0.2161233
H	-0.5162204	0.7857731	0.8481511
H	-1.2199277	-0.0232257	-0.3271617
H	-1.0583093	1.5755604	-0.4471148

$Co(SCN)_4^{2-}$

Co	0.0000000	0.0000000	0.0000000
N	1.1231469	-1.1231469	-1.1231469
N	1.1231469	1.1231469	1.1231469
N	-1.1231469	1.1231469	-1.1231469
N	-1.1231469	-1.1231469	1.1231469
C	1.8030079	1.8030079	1.8030079
S	2.7440098	2.7440098	2.7440098
C	-1.8030079	-1.8030079	1.8030079
S	-2.7440098	-2.7440098	2.7440098
C	-1.8030079	1.8030079	-1.8030079
S	-2.7440098	2.7440098	-2.7440098
C	1.8030079	-1.8030079	-1.8030079
S	2.7440098	-2.7440098	-2.7440098

$Co(NH_3)_6(SCN)_4^{2-}$

N	1.7702071	-0.4354658	-1.2685600
N	-1.7246413	0.4470159	1.2672641
N	0.2038411	-1.9837471	0.8475297
Co	0.0227551	0.0010043	0.0010787
N	-0.1550165	1.9879747	-0.8396955

N	0.9924149	0.7884478	1.8174193
N	-0.9438547	-0.7984240	-1.8098632
H	1.6358478	0.1084132	-2.1368366
H	1.6992670	-1.4322381	-1.5164339
H	2.7147633	-0.2585198	-0.9305611
H	-1.6484123	1.4420734	1.5183803
H	-1.5962630	-0.0997792	2.1352161
H	-2.6699312	0.2769665	0.9276897
H	1.1753739	-2.1298305	1.1212506
H	0.0047596	-2.7175198	0.1592721
H	-0.3447507	-2.0811732	1.7104407
H	0.0349225	2.7161093	-0.1418342
H	-1.1215590	2.1361113	-1.1294733
H	0.4058681	2.0919841	-1.6931664
H	2.0077167	0.8442675	1.8781454
H	0.6557533	0.2054871	2.5955528
H	0.6119991	1.7394236	1.9567065
H	-0.6179018	-0.2111359	-2.5896910
H	-1.9583479	-0.8694260	-1.8682679
H	-0.5494422	-1.7431547	-1.9506604
C	0.7491395	1.6990265	-4.6597088
S	0.7427380	2.3964233	-6.1388110
N	0.7507862	1.1949943	-3.5836092
C	-0.8890918	4.4458181	2.1360358
S	-1.3285336	5.9543635	2.5893267
N	-0.5711855	3.3504424	1.8027215
C	1.0041235	-4.4355793	-2.1032303
S	1.4628274	-5.9483409	-2.5228821
N	0.6726816	-3.3371011	-1.7943267
C	-1.0311254	-1.7153434	4.6093583
S	-1.4290691	-2.4325197	6.0236753
N	-0.7386598	-1.1970483	3.5805480

$Co(SCN)_4(CO_2)_4^{2-}$

Co	-0.5460499	-0.4605262	-0.3309460
N	-0.1981667	0.4583408	-2.0025373
N	-1.9070033	0.5181237	0.6429288
N	-1.1198168	-2.2812802	-0.6527497
N	1.0871142	-0.4931202	0.7200241
C	-2.7135128	1.1526924	1.2324159
S	-3.8097292	2.0392815	2.0412818
C	2.0843225	-0.5174084	1.3573307
S	3.4533372	-0.5502041	2.2313445
C	-1.4391078	-3.4065960	-0.8302810
S	-1.8644059	-4.9587090	-1.0658437
C	0.0240677	1.0628264	-2.9953600
S	0.3340622	1.9074040	-4.3490699
O	3.3175979	0.2093637	-1.9248123
C	2.9770645	1.1947996	-1.3957504
O	2.6792655	2.1995708	-0.8790247
O	-3.0457466	2.5665707	-2.0114709
C	-2.1615584	3.0825411	-1.4462258
O	-1.2963989	3.6406782	-0.8943116
O	2.0178375	-3.7995868	-0.0563109
C	1.3905643	-3.7741594	0.9295316
O	0.7880816	-3.7881864	1.9309796
O	0.3397298	2.3013985	2.7026933

C	-0.0196435	1.3254195	3.2351680
O	-0.3719052	0.3707656	3.8109962

$Co(SCN)_2$

C	-2.9892265	0.0000000	0.0012474
N	-1.7884909	0.0000000	-0.0006142
Co	0.0000000	0.0000000	-0.0008319
N	1.7884909	-0.0000000	-0.0006142
C	2.9892265	-0.0000000	0.0012474
S	4.5707285	0.0000000	0.0039209
S	-4.5707285	-0.0000000	0.0039209

$Co(SCN)_2(NH_3)_4$

N	1.9841891	0.0568306	-0.0506750
Co	-0.0002841	0.0005154	0.0007889
N	0.0921854	-2.0098020	0.9762001
N	-1.9846467	-0.0571863	0.0490543
N	0.0383250	0.8933284	2.0494648
N	-0.0378534	-0.8927678	-2.0481682
N	-0.0929632	2.0098240	-0.9759737
H	0.9631170	0.7478179	2.4547953
H	-0.6597575	0.4577469	2.6517041
H	-0.1469361	1.8956321	2.0736392
H	0.6612012	-0.4577263	-2.6497082
H	-0.9619870	-0.7476498	-2.4551796
H	0.1474676	-1.8950841	-2.0715001
H	0.6724650	2.5981413	-0.6470643
H	-0.9781986	2.4566362	-0.7364117
H	-0.0331636	1.9973754	-1.9936552
H	0.9771554	-2.4564417	0.7353421
H	-0.6735977	-2.5970097	0.6461276
H	0.0326523	-1.9995496	1.9939215
C	3.1738322	0.0744440	-0.1101596
S	4.7847573	0.0973104	-0.1896146
C	-3.1755975	-0.0801554	0.0616062
S	-4.7882850	-0.1106710	0.0781281

[Bmim][SCN]

N	1.9360515	0.7389627	-1.9102795
C	1.1833074	1.7414585	-2.5009245
C	-0.0912199	1.5951995	-2.0361864
N	-0.0928945	0.5092012	-1.1780546
C	1.1455880	0.0003691	-1.1140797
C	-1.2477275	-0.0124016	-0.4067602
C	-1.0795838	0.2255451	1.0931387
C	-2.2759636	-0.3363858	1.8695114
C	-2.0915683	-0.1982982	3.3830296
C	3.3668011	0.4759634	-2.1024897
N	1.9375105	-2.1875818	0.6432847
H	-0.9865020	2.1598404	-2.2399067
H	1.4794417	-0.8483834	-0.4808676
H	1.6111273	2.4533801	-3.1881203
H	3.5561437	0.2253249	-3.1485069
H	3.9409345	1.3608561	-1.8200643
H	3.6388788	-0.3643829	-1.4632562
H	-2.3858287	-1.3955430	1.6084800
H	-3.1947998	0.1788107	1.5554919

H	-0.9601783	1.2995970	1.2917958
H	-0.1659815	-0.2828088	1.4225894
H	-1.3104620	-1.0911509	-0.5999010
H	-2.1335332	0.4895544	-0.8052934
H	-1.2042041	-0.7488504	3.7124603
H	-2.9560138	-0.6001497	3.9211929
H	-1.9692713	0.8514705	3.6761489
C	0.9030063	-2.7615257	0.5216198
S	-0.5530585	-3.4780713	0.2959478

References

1. X. Cao, T. Song and X. Wang, eds., *Inorganic Chemistry*, Higher Education Press, Beijing, 1994.