Supporting Information

Slow magnetic relaxation in cobalt(II) complexes with one-dimensional hydrogen-bonded networks

Ryoji Mitsuhashi,[1,*] Hiroshi Sakiyama,[2] Yoshihito Hayashi[3]

[1] Institute of Liberal Arts and Science, Kanazawa University; Kakuma, Kanazawa, Ishikawa 920-1192, Japan
[2] Department of Science, Faculty of Science, Yamagata University; 1-4-12 Kojirakawa, Yamagata 990-8560, Japan
[3] Department of Chemistry, Kanazawa University; Kakuma, Kanazawa, Ishikawa 920-1192, Japan
E-mail mitsuhashi@staff.kanazawa-u.ac.jp

Contents:

1. X-Ray crystallography

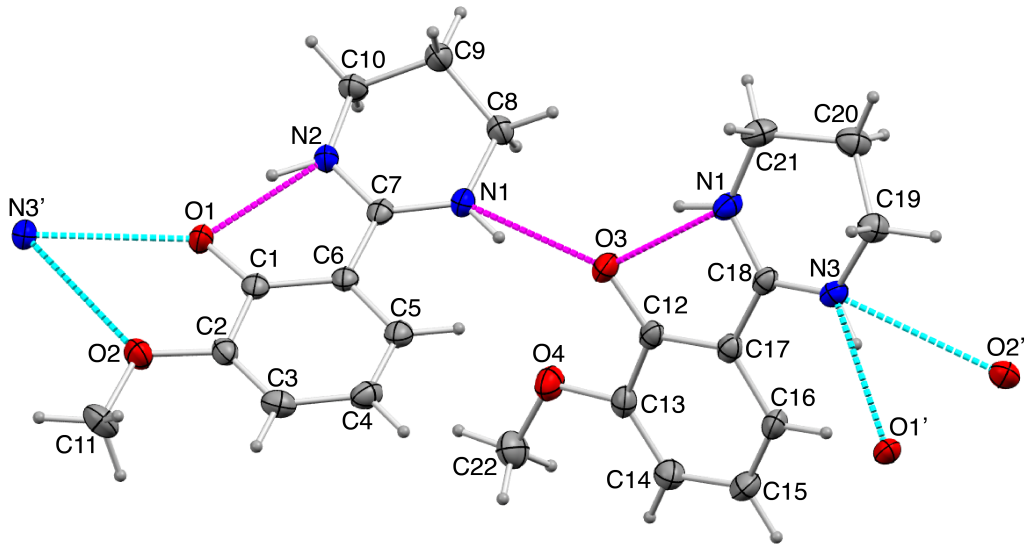

Figure S1. Molecular structure of H_2mthp (50% probability levels). Magenta and cyan dashed lines are hydrogen bonds.

Table S1. Hydrogen-bond distances and angles.

	D–H···A			D–H / Å	H···A / Å	D···A /Å	D–H···A / °
H_2mthp	N1	H1	O3	0.861(18)	1.93(2)	2.729(2)	154(2)
	N2	H2	O1	0.912(19)	1.68(2)	2.527(2)	152(2)
	N3	H3A	O1^{i}	0.869(19)	1.96(2)	2.791(2)	160(2)
	N4	H4A	O3	0.887(19)	1.78(2)	2.565(2)	146(2)
1·C_2H_5OH	N1	H1	O3^{ii}	0.78(4)	2.10(4)	2.826(4)	154(4)
	N1	H1	O4^{ii}	0.78(4)	2.47(4)	3.065(4)	134(4)
	N3	H3A	O1^{iii}	0.80(4)	2.14(4)	2.869(4)	152(4)
2BF_4·1.5C_2H_5OH	N4	H4N	O3	0.865(19)	1.84(3)	2.560(5)	140(4)
	N6	H6N	O5	0.87(2)	1.74(3)	2.577(5)	162(6)
	N5	H5N	O1^{iv}	0.85(2)	2.00(4)	2.781(5)	153(8)

Symmetry code: (*i* = '–x+1/2, –y+1, z+1/2', *ii* = '–x+1, –y+1, –z+2', *iii* = '–x+1, –y+1, – z+1', *iv* = –x+2, –y+1, –z+1).

2. Ac susceptibility measurements

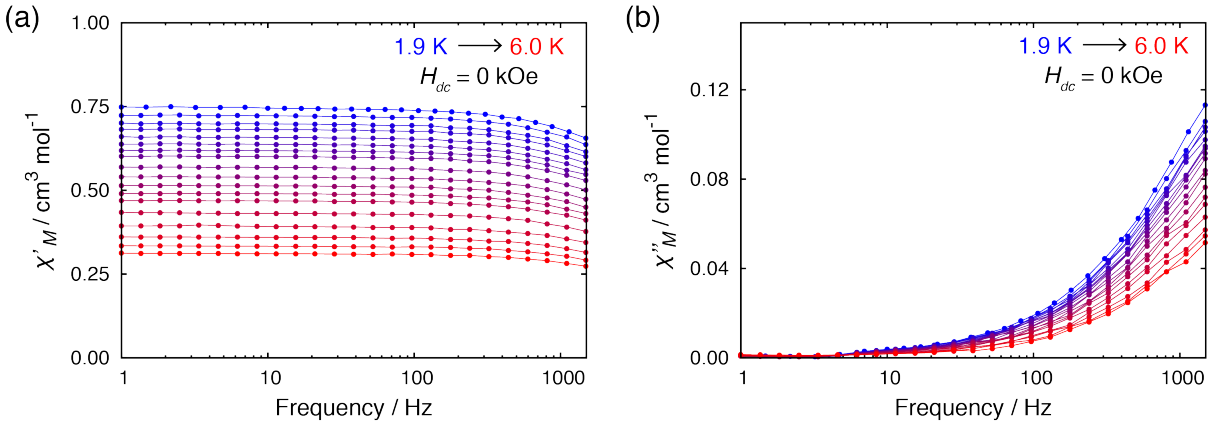

Figure S2. Temperature dependence of (a) the in-phase χ_M' vs. frequency plots and (b) out-of-phase χ_M'' vs. frequency plots for **1**·C_2H_5OH in the absence of a dc field with ac frequency of 1–1488 Hz. The lines are guide for the eye.

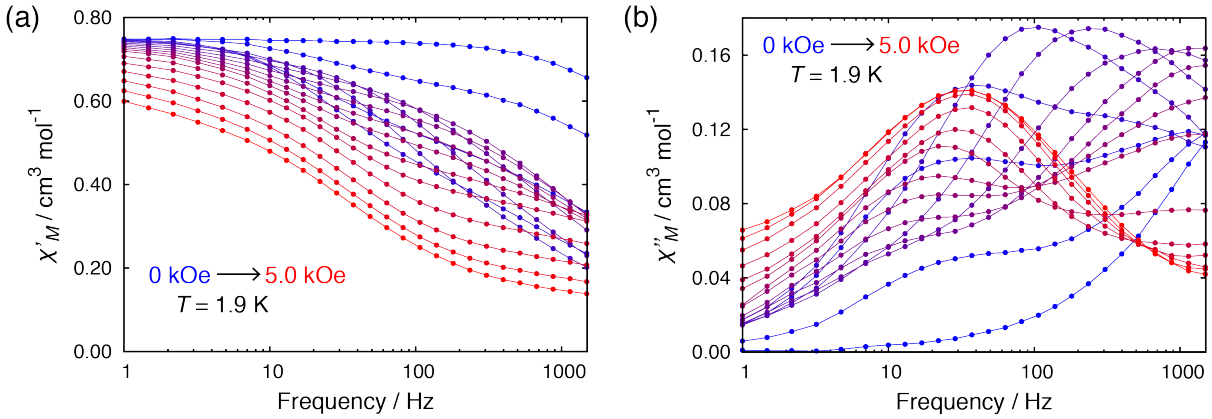

Figure S3. Dc field dependence of (a) the in-phase χ_M' vs. frequency plots and (b) out-of-phase χ_M'' vs. frequency plots for **1**·C_2H_5OH at 1.9 K with ac frequency of 1–1488 Hz. The lines are guide for the eye.

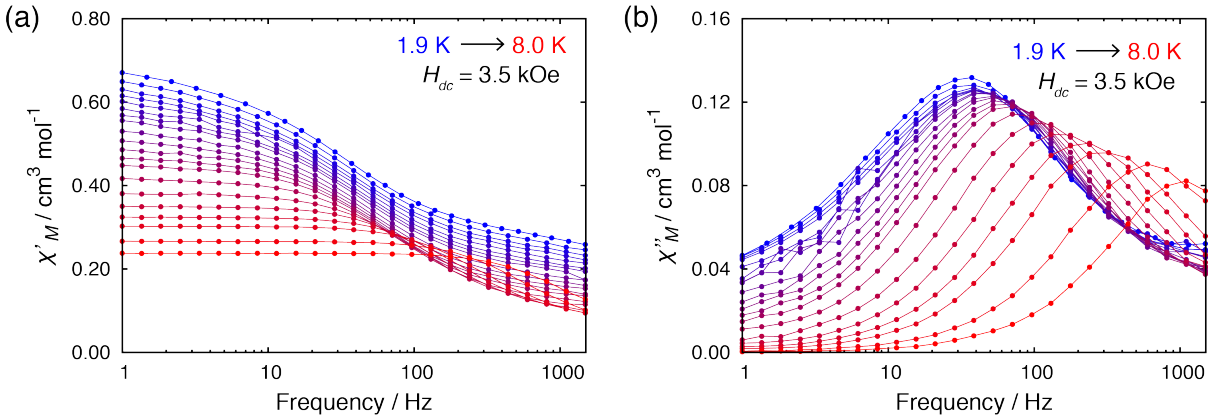

Figure S4. Temperature dependence of (a) the in-phase χ_M' vs. frequency plots and (b) out-of-phase χ_M'' vs. frequency plots for **1**·C_2H_5OH in the presence of 3.5 kOe with ac frequency of 1–1488 Hz. The lines are guide for the eye.

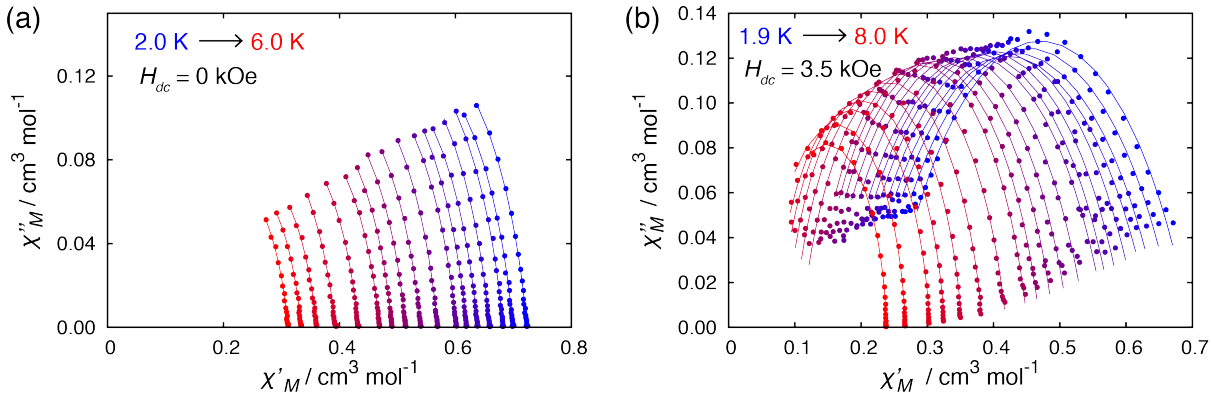

Figure S5. Cole–Cole plot for **1**·C_2H_5OH (a) in the absence and (b) in the presence of 3.5 kOe dc field. The solid lines represent the fit to a generalized Debye model.

Table S2. Cole-Cole fit values for **1**·C_2H_5OH in 3.5 kOe dc field from 1.9 to 8.0 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	τ / s	α
1.9	0.2440	0.6970	5.13×10^{-3}	0.347
2.0	0.2266	0.6760	4.93×10^{-3}	0.356
2.1	0.2117	0.6549	4.73×10^{-3}	0.358
2.2	0.2009	0.6398	4.51×10^{-3}	0.358
2.3	0.1946	0.6197	4.29×10^{-3}	0.333
2.4	0.1852	0.5994	4.04×10^{-3}	0.320
2.5	0.1768	0.5825	3.85×10^{-3}	0.313
2.6	0.1671	0.5702	3.70×10^{-3}	0.313
2.8	0.1573	0.5395	3.38×10^{-3}	0.284
3.0	0.1485	0.5139	3.10×10^{-3}	0.260
3.2	0.1399	0.4915	2.84×10^{-3}	0.242
3.4	0.1327	0.4705	2.58×10^{-3}	0.223
3.6	0.1267	0.4515	2.36×10^{-3}	0.204
4.0	0.1096	0.4193	1.86×10^{-3}	0.196
4.5	0.0980	0.3837	1.38×10^{-3}	0.168
5.0	0.0870	0.3524	9.89×10^{-4}	0.145
5.5	0.0776	0.3264	7.02×10^{-4}	0.130
6.0	0.0699	0.3041	4.99×10^{-4}	0.118
7.0	0.0592	0.2672	2.62×10^{-4}	0.088
8.0	0.0594	0.2382	1.49×10^{-4}	0.058

Table S3. Cole-Cole fit values for **1**·C_2H_5OH in 0 kOe dc field from 1.9 to 6.0 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	τ / s	α
2.0	0.3615	0.7237	4.15×10^{-5}	0.200
2.1	0.3536	0.6995	4.22×10^{-5}	0.202
2.2	0.3216	0.6825	3.88×10^{-5}	0.203
2.3	0.3035	0.6592	3.72×10^{-5}	0.207
2.4	0.3079	0.6385	3.99×10^{-5}	0.206
2.5	0.2746	0.6195	3.57×10^{-5}	0.213

2.6	0.2711	0.6019	3.68×10^{-5}	0.212
2.8	0.2448	0.5693	3.58×10^{-5}	0.205
3.0	0.2363	0.5403	3.65×10^{-5}	0.210
3.2	0.2276	0.5141	3.80×10^{-5}	0.204
3.4	0.2164	0.4907	3.67×10^{-5}	0.208
3.6	0.2108	0.4694	3.71×10^{-5}	0.216
4.0	0.1892	0.4322	3.78×10^{-5}	0.206
4.5	0.1179	0.3935	2.56×10^{-5}	0.246
5.0	0.1560	0.3604	3.69×10^{-5}	0.208
5.5	0.1448	0.3337	3.82×10^{-5}	0.192
6.0	0.1192	0.3114	3.36×10^{-5}	0.203

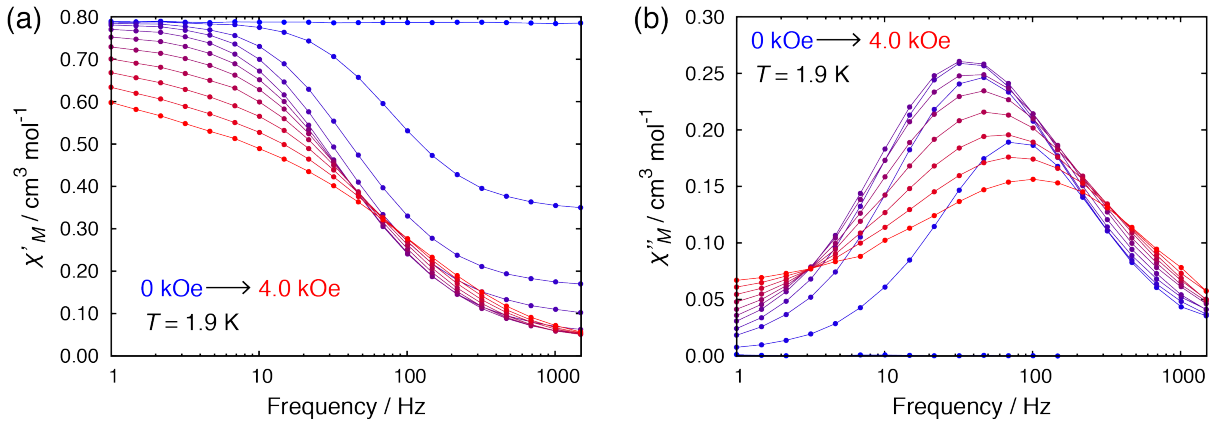

Figure S6. Dc field dependence of (a) the in-phase χ_M' vs. frequency plots and (b) out-of-phase χ_M'' vs. frequency plots for **2**·1.5C_2H_5OH at 1.9 K with ac frequency of 1–1488 Hz. The lines are guide for the eye.

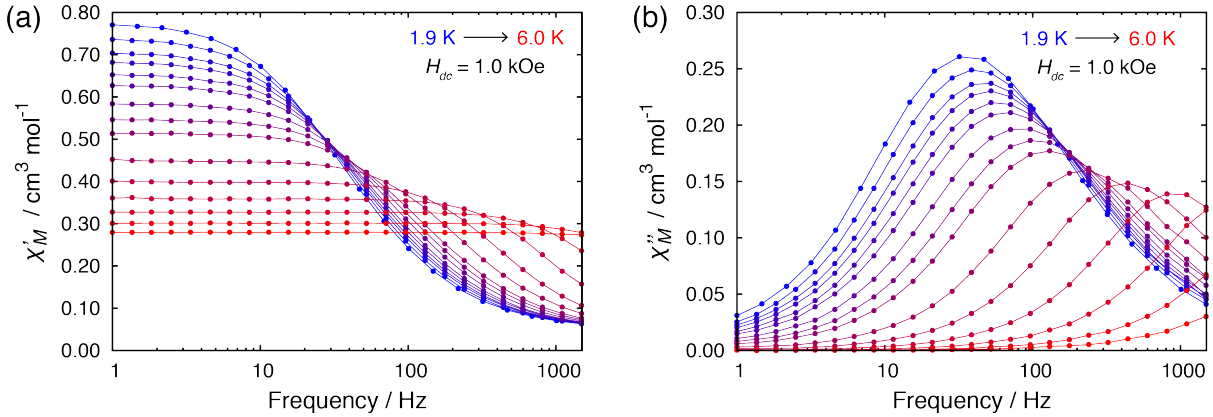

Figure S7. Temperature dependence of (a) the in-phase χ_M' vs. frequency plots and (b) out-of-phase χ_M'' vs. frequency plots for **2**·1.5C_2H_5OH in the presence of 1.0 kOe with ac frequency of 1–1488 Hz. The lines are guide for the eye.

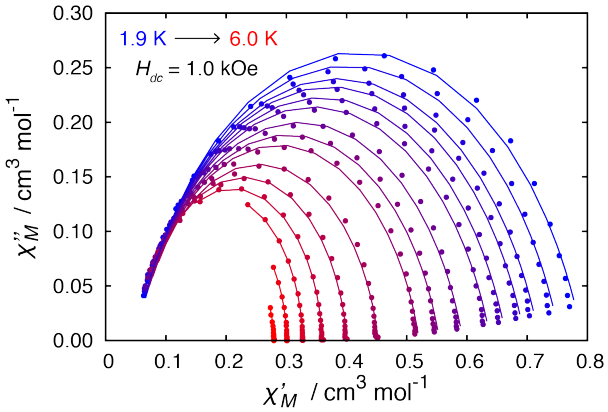

Figure S8. Cole–Cole plot for **2**·1.5C_2H_5OH in the presence of 1.0 kOe dc field. The solid lines represent the fit to a generalized Debye model.

Table S4. Cole-Cole fit values for **2**BF_4·1.5C_2H_5OH in 1.0 kOe dc field from 1.9 to 6.0 K.

T / K	χ_S / cm^3 mol^{-1}	χ_T / cm^3 mol^{-1}	τ / s	α
1.9	0.0505	0.7924	4.00×10^{-3}	0.212
2.0	0.0500	0.7553	3.49×10^{-3}	0.211
2.1	0.0494	0.7209	3.06×10^{-3}	0.210
2.2	0.0504	0.6969	2.79×10^{-3}	0.206
2.3	0.0508	0.6661	2.44×10^{-3}	0.203
2.4	0.0509	0.6394	2.16×10^{-3}	0.199
2.6	0.0519	0.5934	1.72×10^{-3}	0.190
2.8	0.0522	0.5544	1.37×10^{-3}	0.180
3.0	0.0542	0.5207	1.11×10^{-3}	0.166
3.5	0.0577	0.4526	6.47×10^{-4}	0.128
4.0	0.0597	0.4005	3.56×10^{-4}	0.082
4.5	0.0618	0.3597	1.74×10^{-4}	0.043
5.0	0.0503	0.3273	7.43×10^{-5}	0.025
5.5	0.0410	0.3011	2.97×10^{-5}	0.030
6.0	0.0527	0.2795	1.35×10^{-5}	0.046

3. ^{1}H NMR spectrum

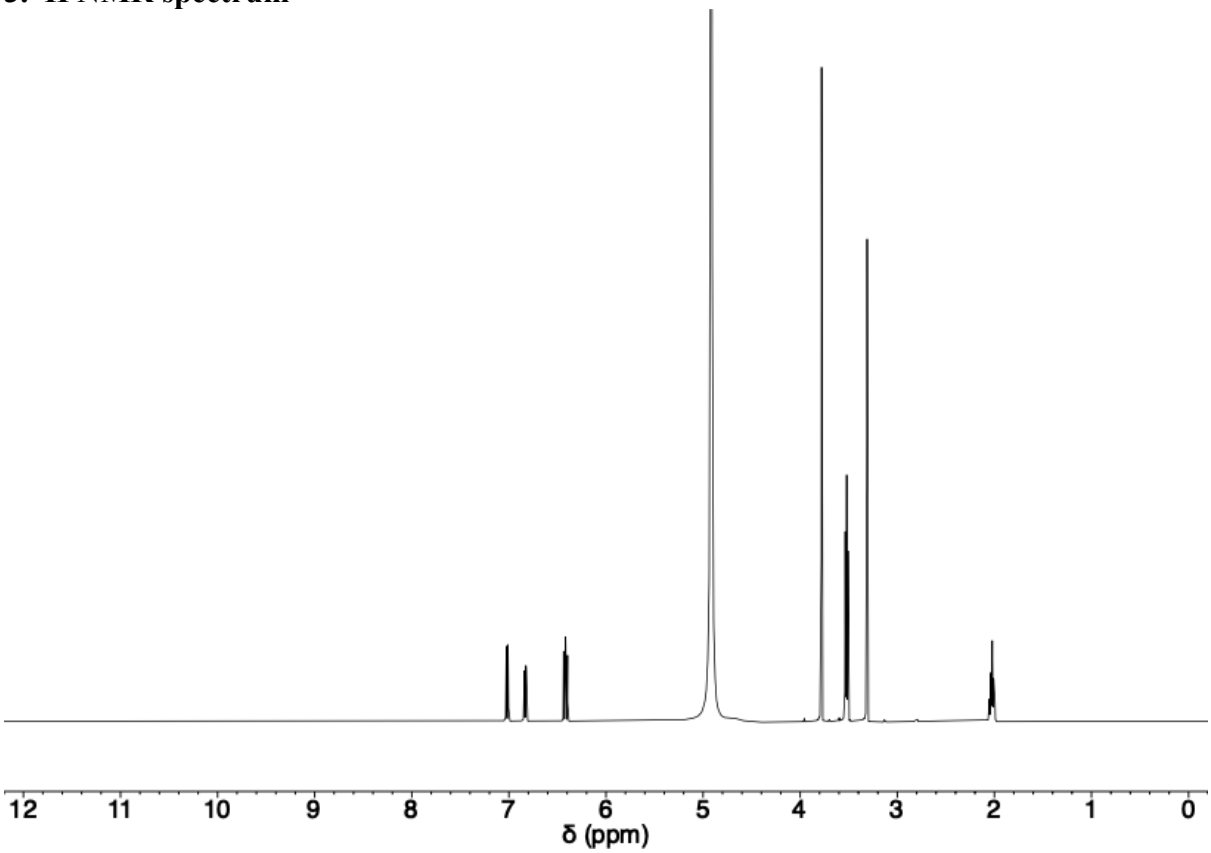

Figure S9. ^{1}H NMR spectrum of H_2mthp in CD_3OD.

4. Infrared spectra

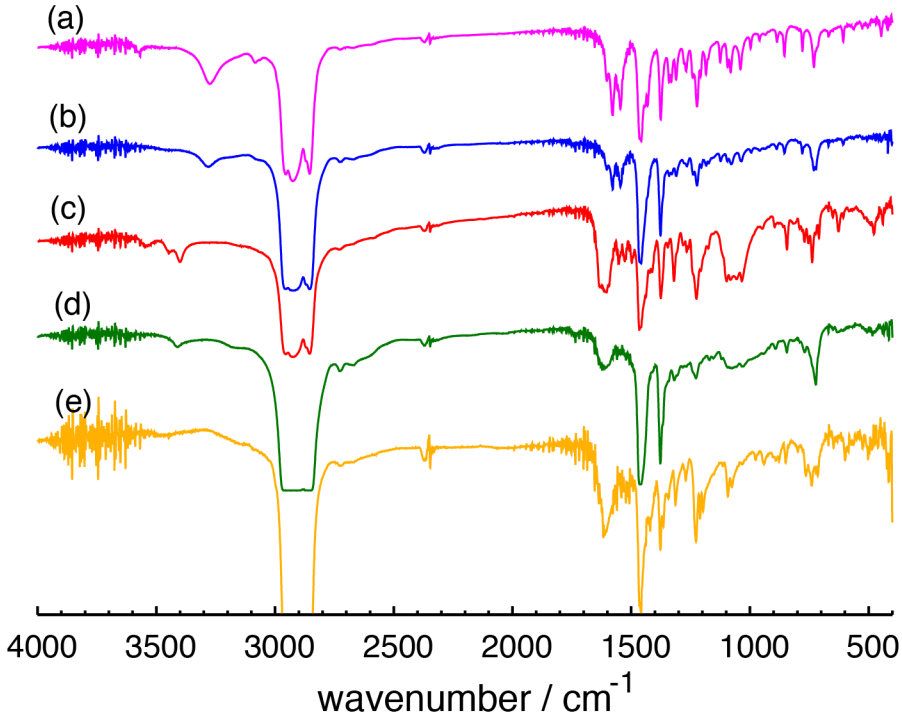

Figure S10. Infrared spectra of (a) pristine **1**·C_2H_5OH, (b) hydrated **1**·C_2H_5OH, (c) pristine **2**BF_4·1.5C_2H_5OH, (d) hydrated **2**BF_4·1.5C_2H_5OH, and H_2mthp (nujol mull).