

Effects of weak intramolecular interactions and distortions from trigonal prismatic coordination on the magnetic properties of zero-field Co(II) single-ion magnets

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Electronic Supplementary Information

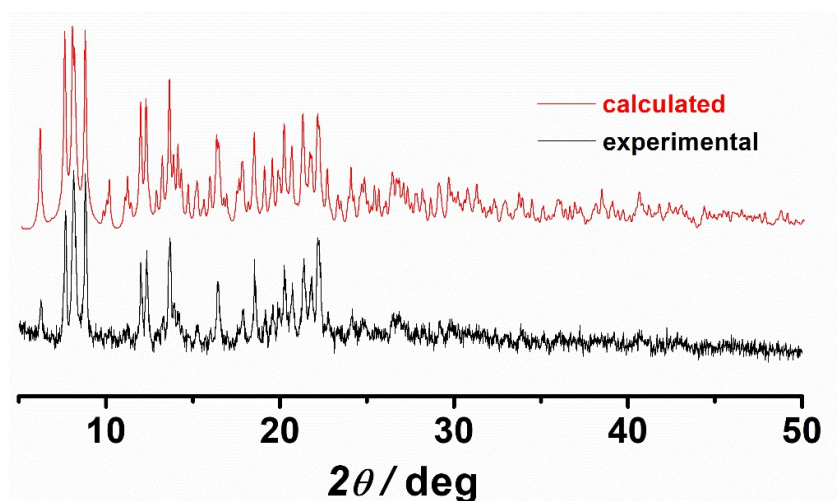


Figure S1. PXRD pattern for 1-BPh₄.

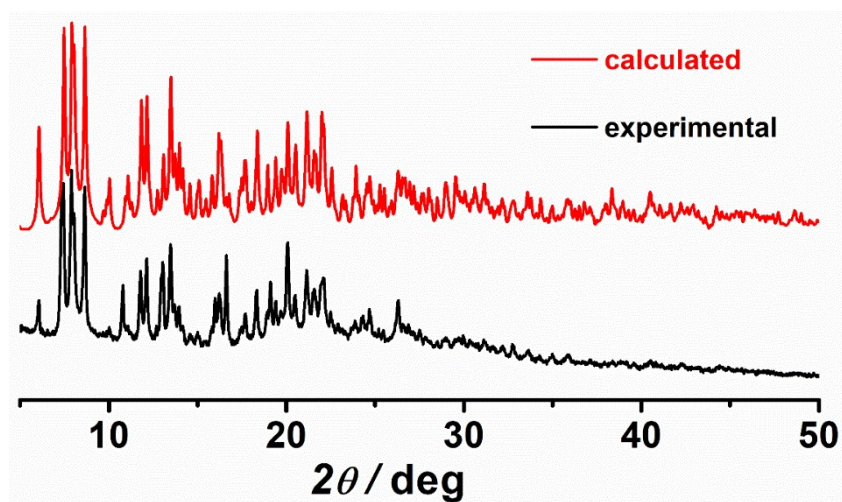


Figure S2. PXRD pattern for 1-BPh₄@Zn.

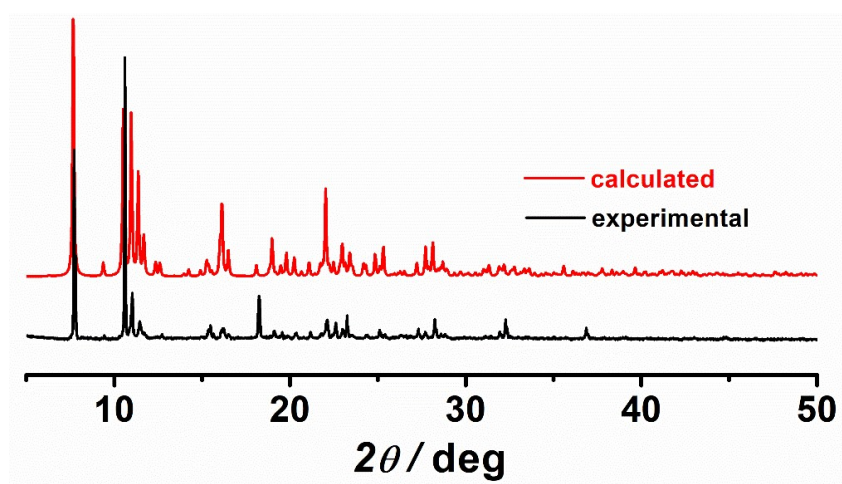


Figure S3. PXRD pattern for 2-NO₃.

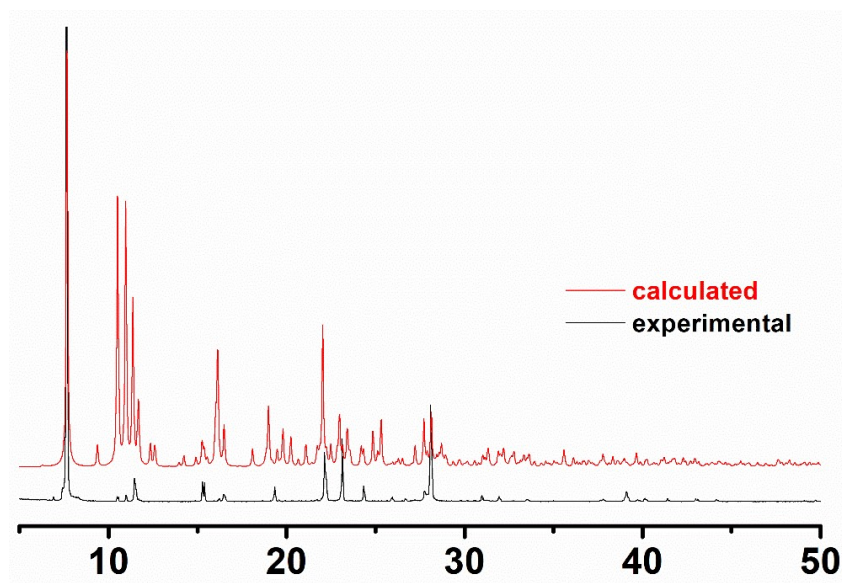


Figure S4. PXRD pattern for 2-NO₃@Zn.

Table S1. Crystal data and structure refinement for complexes **1-BPh₄**, **Zn-BPh₄** and **2-NO₃**.

	1-BPh₄	Zn-BPh₄	2-NO₃
Molecular formula	C ₈₄ H ₉₀ B ₂ CoN ₈ O	C ₈₄ H ₉₀ B ₂ ZnN ₈ O	C ₃₄ H ₄₃ CoN ₁₁ O ₆
CCDC no	2302669	2325454	2302668
Formula weight	1308.18	1314.62	760.72
Temperature / K	296(2)	293(2) K	296(2)
Wavelength / Å	0.71073	1.54178	0.71073
crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	13.4362(10)	13.4678(4)	9.4565(13)
<i>b</i> / Å	14.8855(9)	14.9264(4)	13.8712(19)
<i>c</i> / Å	18.3909(10)	18.4215(7)	14.7616(19)
α / deg	84.615(4)	84.4150(10)	72.077(9)
β / deg	83.752(3)	83.5480(10)	85.635(9)
γ / deg	78.677(4)	78.6270(10)	87.040(9)
<i>V</i> / Å ³	3575.3(4)	3596.7(2)	1836.2(4)
<i>Z</i>	2	2	2
<i>D</i> _{calc} , g/cm ³	1.215	1.214	1.376
μ / mm ⁻¹	0.293	0.871	0.527
<i>F</i> (000)	1390	1396	798
Goodness-of-fit on <i>F</i> ²	1.029	1.134	1.025
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.0569, <i>wR</i> ₂ = 0.1389	<i>R</i> ₁ = 0.0581, <i>wR</i> ₂ = 0.1582	<i>R</i> ₁ = 0.0382, <i>wR</i> ₂ = 0.0862
<i>R</i> indices (all data) ^a	<i>R</i> ₁ = 0.1107, <i>wR</i> ₂ = 0.1586	<i>R</i> ₁ = 0.0709, <i>wR</i> ₂ = 0.1715	<i>R</i> ₁ = 0.0559, <i>wR</i> ₂ = 0.0931

$$^a wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}, R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|.$$

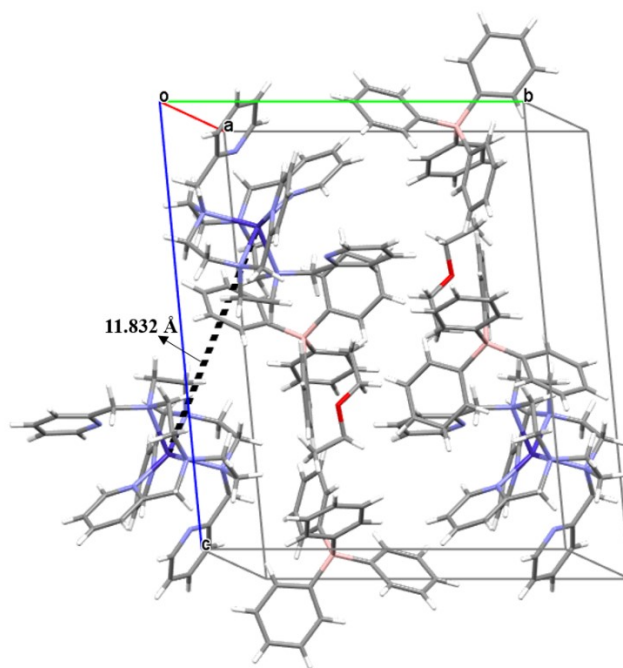


Figure S6. Stacking between adjacent complexes in **1-BPh₄**.

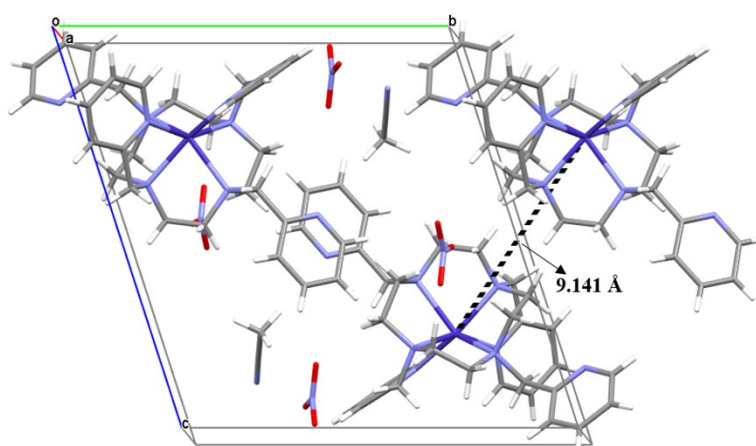


Figure S7. Stacking between adjacent complexes in **2-NO₃**.

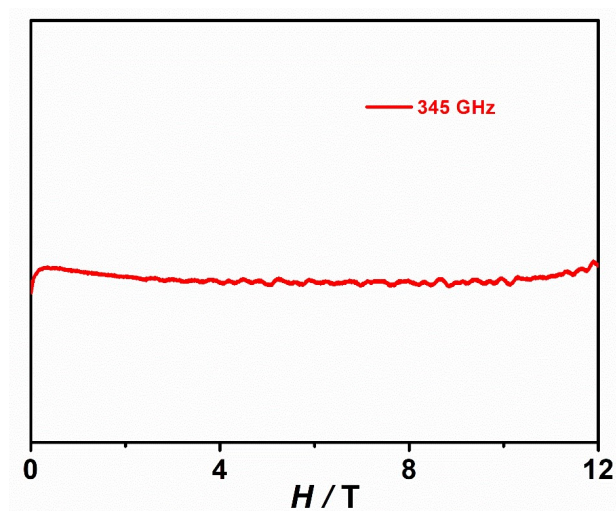


Figure S8. HFEPR spectra for **1-BPh₄** at 2 K.

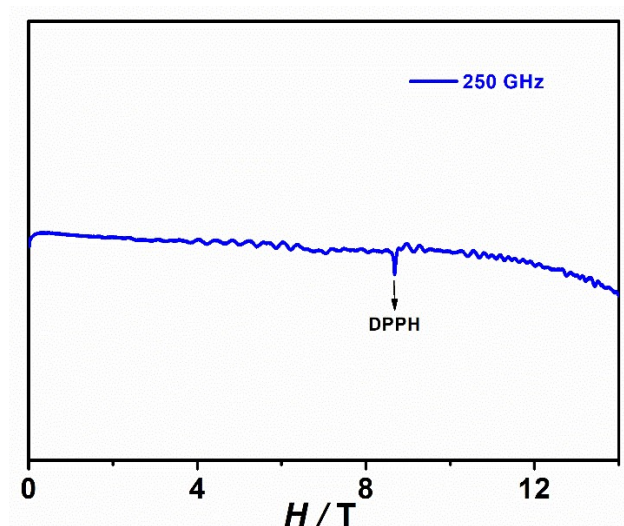


Figure S9. The HFEPR spectra for 2-NO₃ at 2 K.

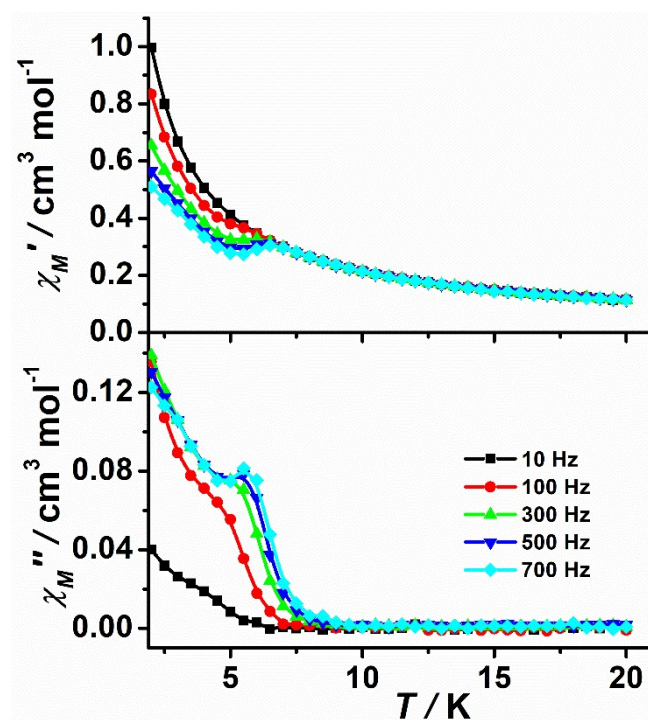


Figure S10. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for 1-BPh₄ in zero dc field; solid lines are guides for the eye.

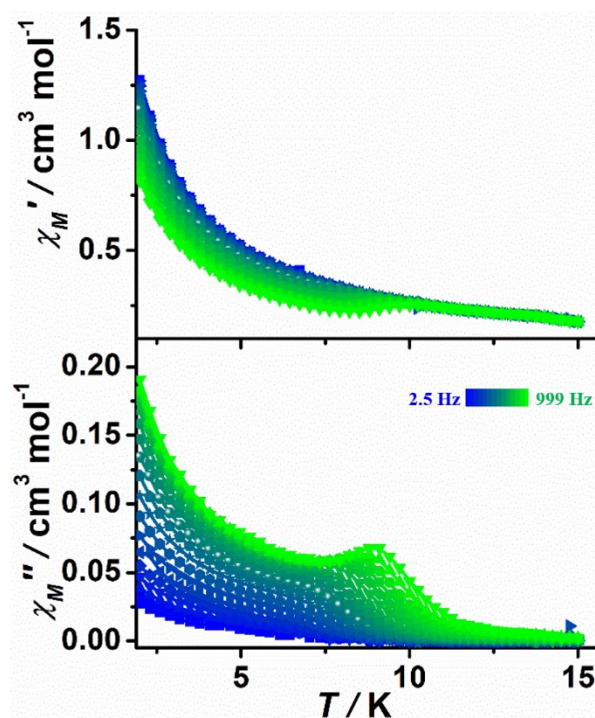


Figure S11. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **2-NO₃** in zero dc field; solid lines are guides for the eye.

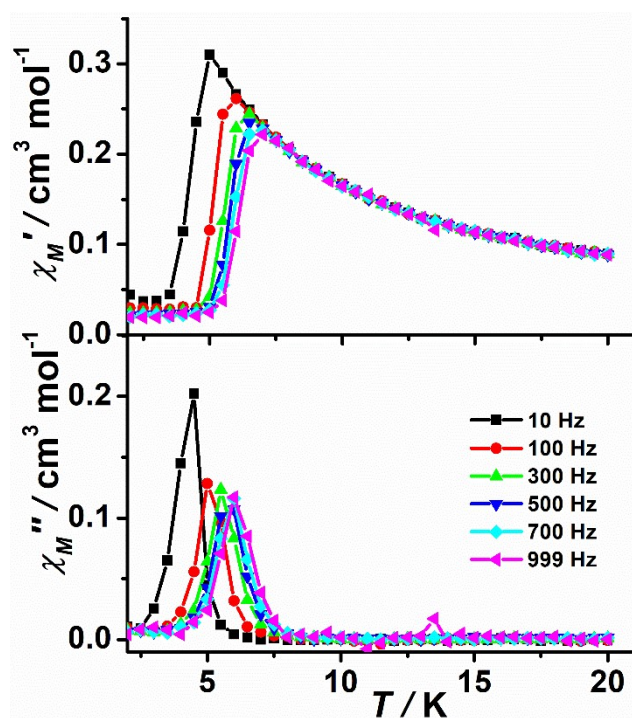


Figure S12. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **1-BPh₄** in the dc field of 200 Oe; solid lines are guides for the eye.

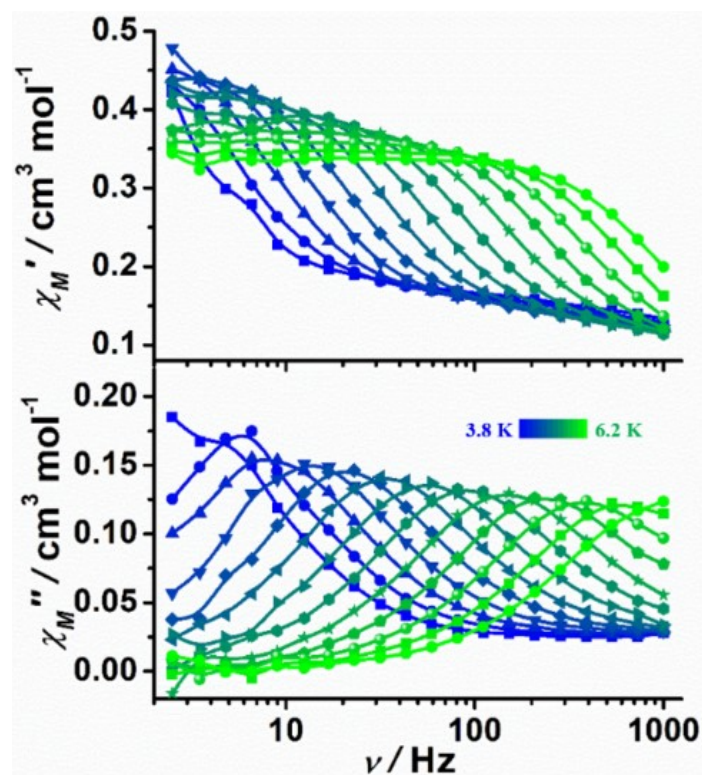


Figure S13. Frequency dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **1-BPh₄** in the dc field of 200 Oe; solid lines are guides for the eye.

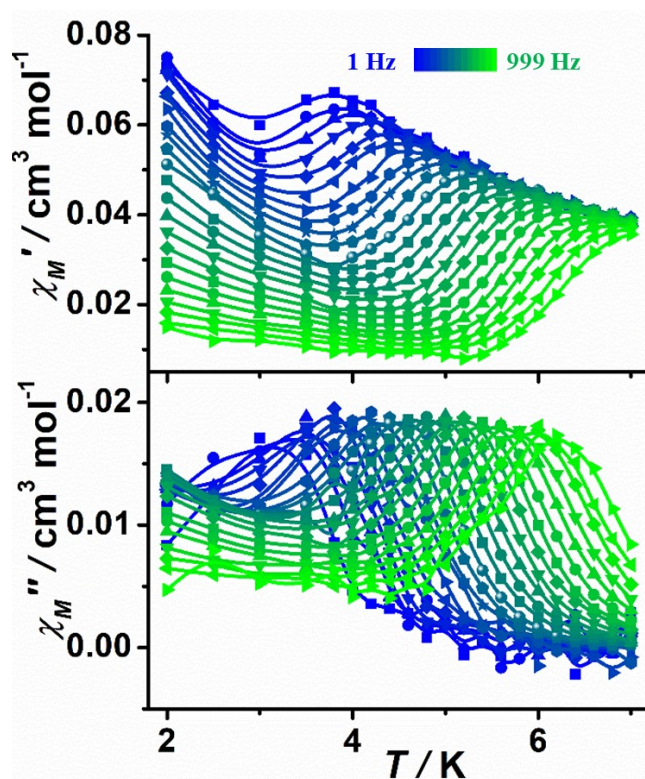


Figure S14. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **1-BPh₄@Zn** in zero dc field; solid lines are guides for the eye.

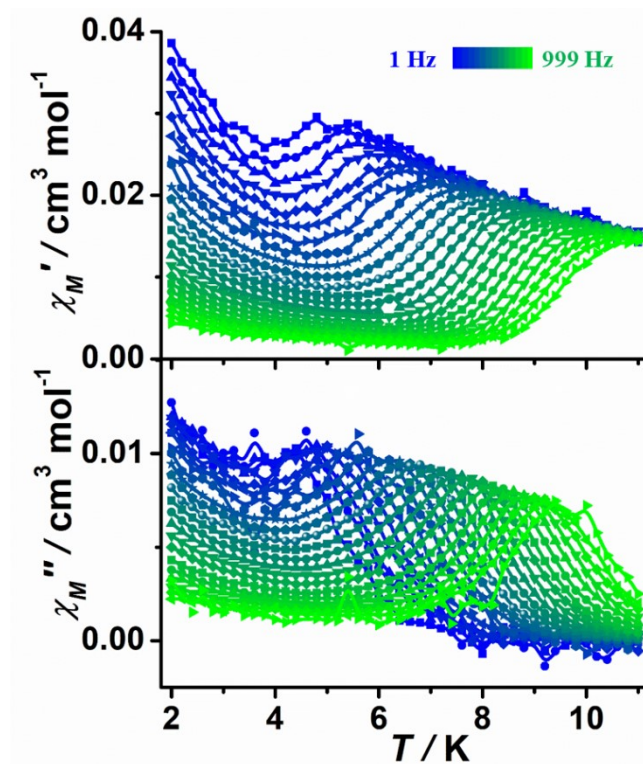


Figure S15. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **2-NO₃@Zn** in zero dc field; solid lines are guides for the eye.

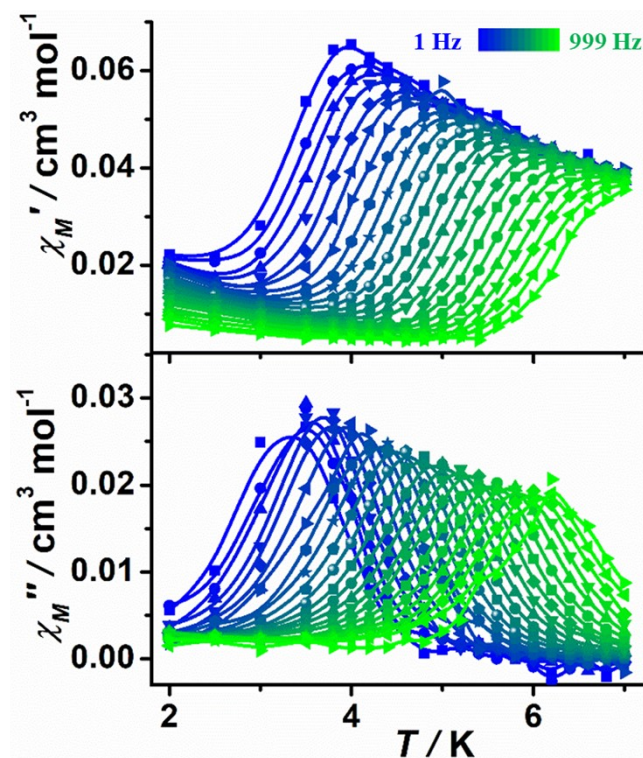


Figure S16. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **1-BPh₄@Zn** in 200 Oe dc field; solid lines are guides for the eye.

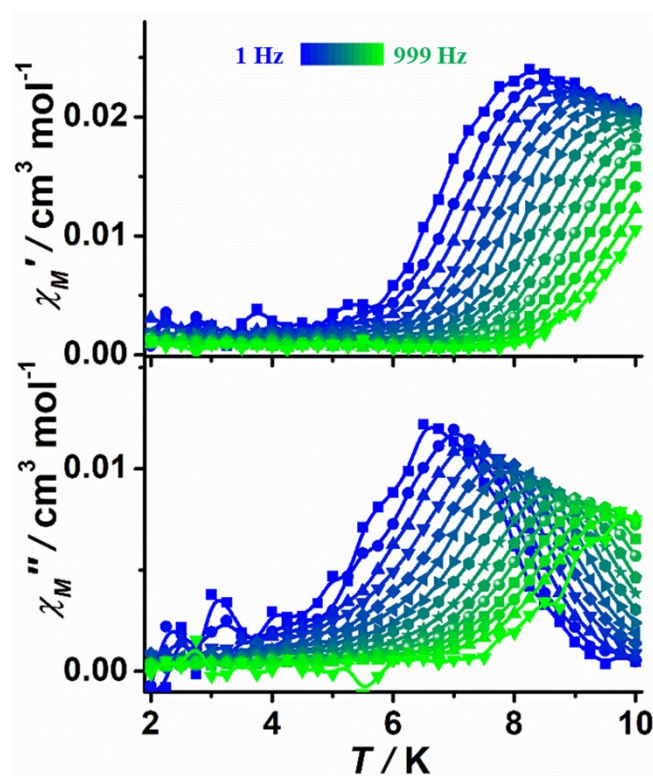


Figure S17. Temperature dependence of in-phase (top) and out-of-phase (bottom) ac susceptibility for **2-NO₃@Zn** in the dc field of 1000 Oe; solid lines are guides for the eye.

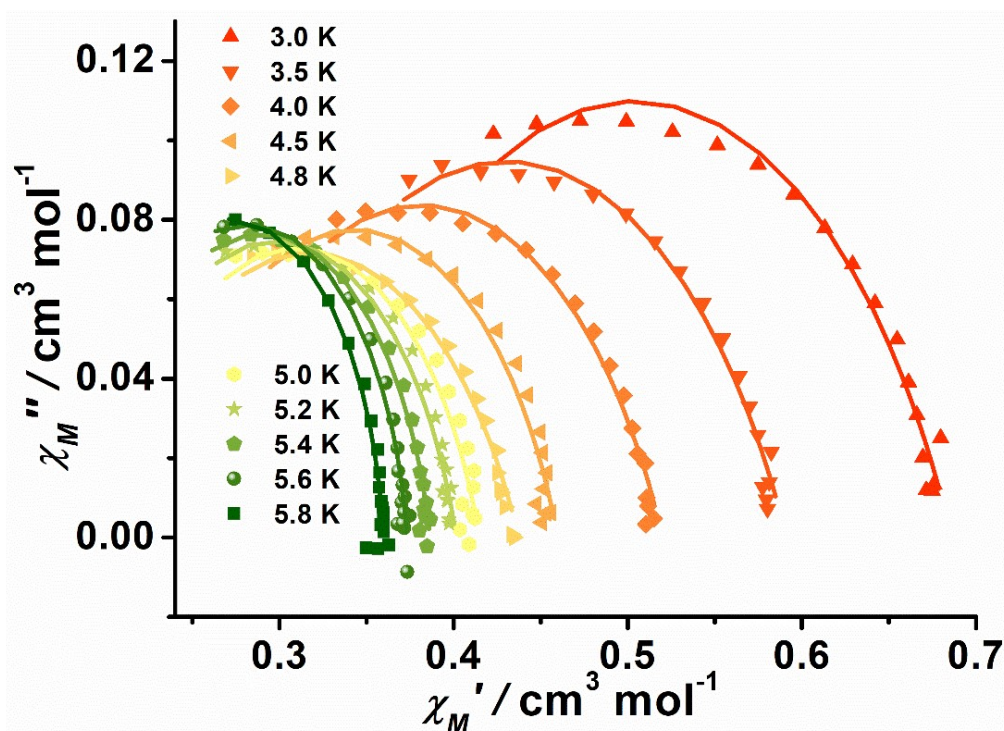


Figure S18. Cole-Cole plots for the ac susceptibilities under zero dc field for **1-BPh₄**. Solid lines represent the best fit for the generalized Debye model.

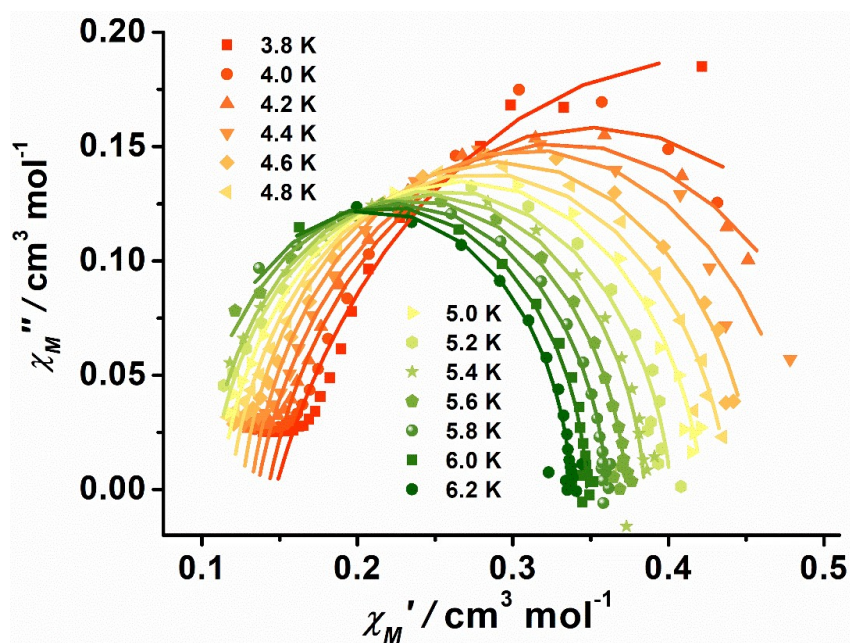


Figure S19. Cole-Cole plots for the ac susceptibilities under 200 Oe dc field for **1-BPh₄**. Solid lines represent the best fit for the generalized Debye model.

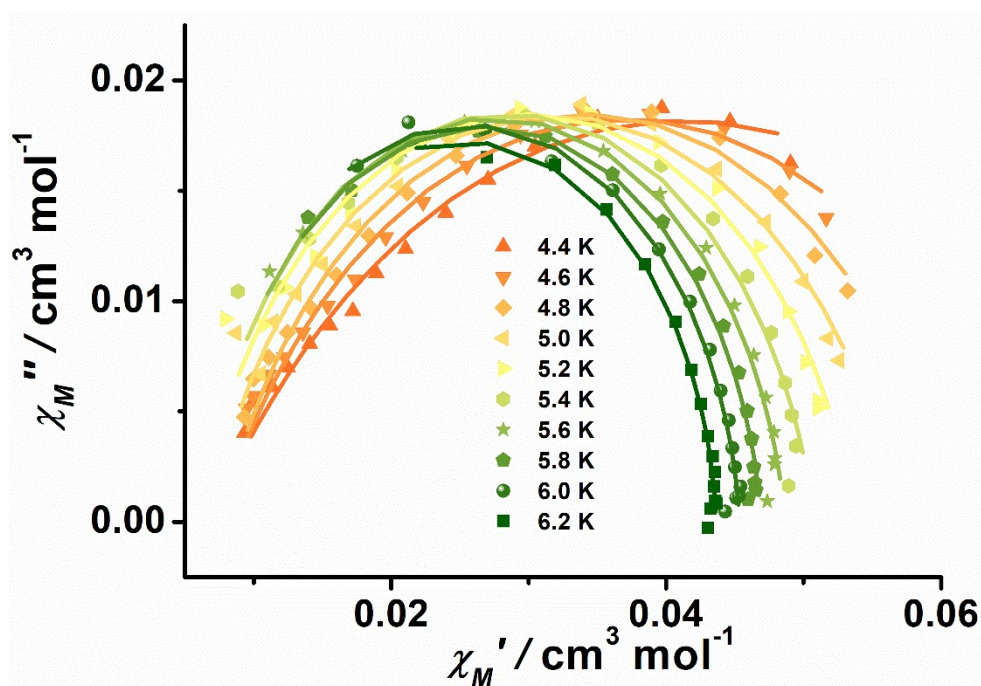


Figure S20. Cole-Cole plots for the ac susceptibilities under zero dc field for **1-BPh₄@Zn**. Solid lines represent the best fit for the generalized Debye model.

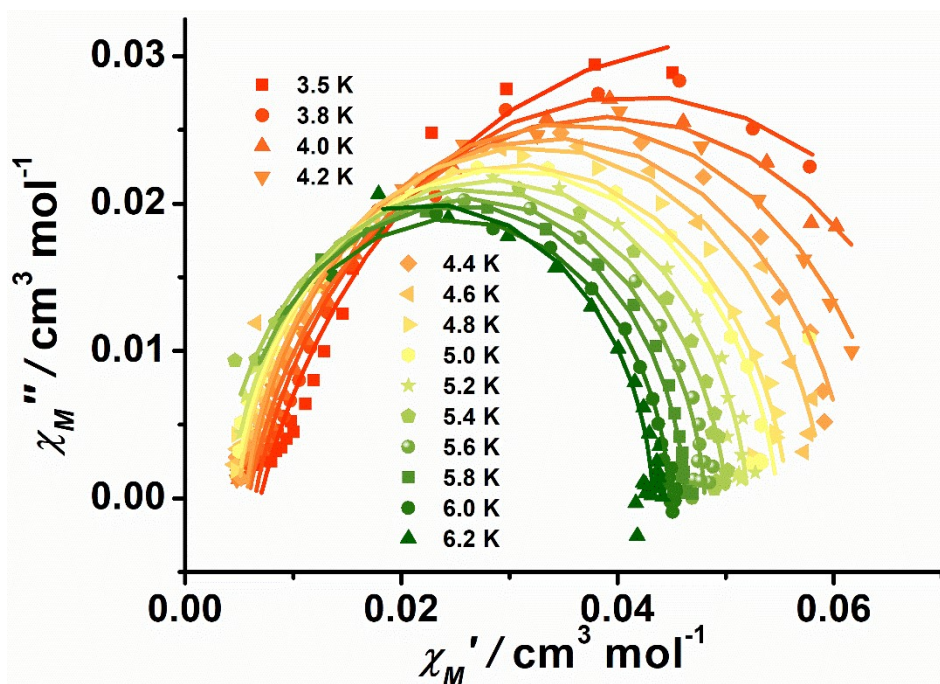


Figure S21. Cole-Cole plots for the ac susceptibilities under 200 Oe dc field for **1-BPh₄@Zn**. Solid lines represent the best fit for the generalized Debye model.

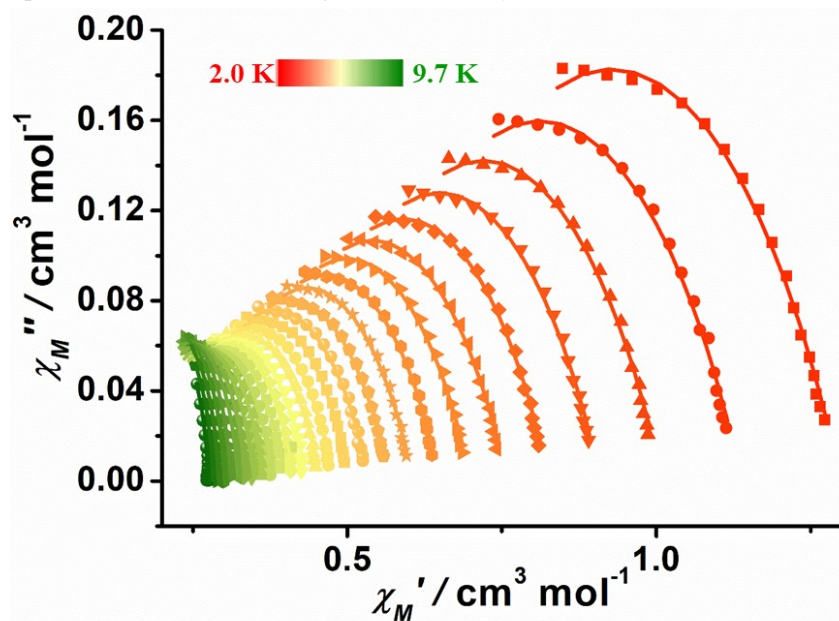


Figure S22. Cole-Cole plots for the ac susceptibilities under zero dc field for **2-NO₃**. Solid lines represent the best fit for the generalized Debye model.

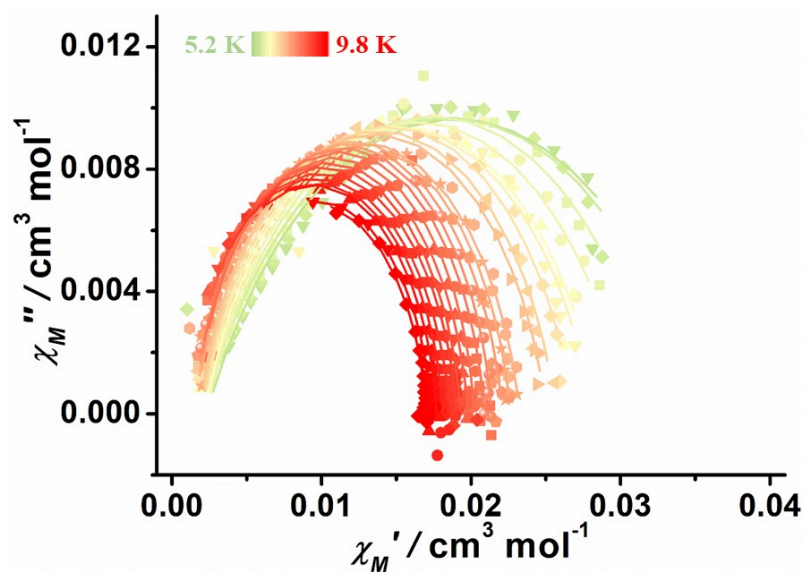


Figure S23. Cole-Cole plots for the ac susceptibilities under zero dc field for **2-NO₃@Zn**. Solid lines represent the best fit for the generalized Debye model.

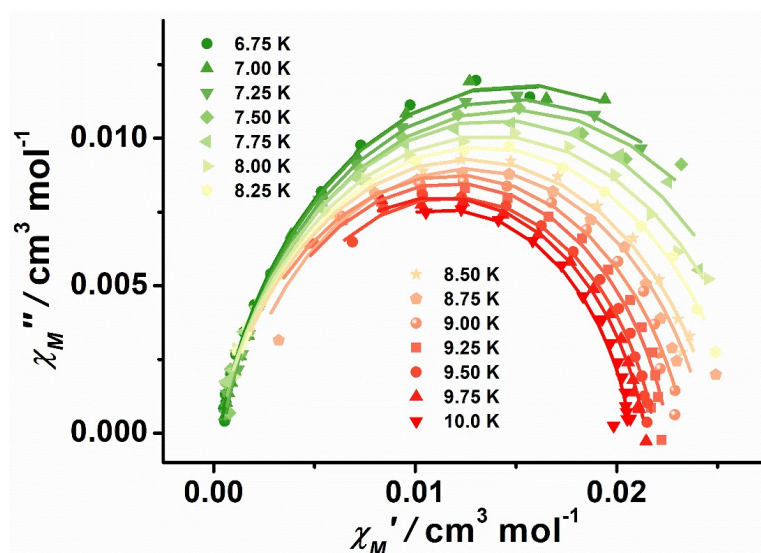


Figure S24. Cole-Cole plots for the ac susceptibilities under 1000 Oe dc field for **2-NO₃@Zn**. Solid lines represent the best fit for the generalized Debye model.

Table S5. Parameters obtained by fitting the Cole-Cole plot under zero dc field for **1-BPh₄**.

T / K	χ_s	χ_T	τ	a
3	0.32	0.69	0.02289	0.31
3.5	0.27	0.59	0.02003	0.32
4	0.24	0.52	0.02015	0.31
4.5	0.23	0.46	0.01959	0.25
4.8	0.20	0.44	0.01757	0.31
5	0.20	0.41	0.01767	0.23
5.2	0.19	0.40	0.01521	0.20
5.4	0.19	0.39	0.01338	0.15
5.6	0.19	0.37	0.01114	0.09
5.8	0.18	0.36	0.00865	0.06

Table S6. Parameters obtained by fitting the Cole-Cole plot under 200 Oe dc field for **1-BPh₄**.

T / K	χ_s	χ_T	τ	a
3.8	0.15	0.71	3.11175	0.25
4	0.14	0.56	1.29383	0.17
4.2	0.14	0.52	0.76138	0.15
4.4	0.13	0.49	0.45309	0.11
4.6	0.13	0.46	0.27496	0.09
4.8	0.12	0.44	0.17117	0.09
5.0	0.11	0.42	0.10622	0.09
5.2	0.11	0.40	0.0644	0.08
5.4	0.10	0.38	0.0399	0.05
5.6	0.094	0.37	0.02492	0.06
5.8	0.089	0.36	0.01588	0.05
6.0	0.087	0.35	0.01041	0.03
6.2	0.080	0.34	0.00686	0.03

Table S7. Parameters obtained by fitting the Cole-Cole plot under zero dc field for **1-BPh₄@Zn**.

T / K	χ_s	χ_T	τ	a
4.4	0.0068	0.076	0.41774	0.38
4.6	0.0073	0.067	0.23153	0.30
4.8	0.0076	0.061	0.14165	0.23
5.0	0.0068	0.057	0.08875	0.19
5.2	0.0061	0.054	0.056	0.16
5.4	0.0061	0.051	0.03645	0.12
5.6	0.0065	0.049	0.02467	0.09
5.8	0.0068	0.047	0.01651	0.07
6.0	0.0058	0.045	0.01088	0.06
6.2	0.0067	0.044	0.00772	0.04

Table S8. Parameters obtained by fitting the Cole-Cole plot under 200 Oe dc field for **1-BPh₄@Zn**.

T / K	χ_s	χ_T	τ	a
3.5	0.0069	0.093	5.66722	0.21
3.8	0.0064	0.077	2.14289	0.16
4.0	0.0058	0.072	1.29762	0.15
4.2	0.0057	0.066	0.77692	0.11
4.4	0.0055	0.062	0.47585	0.09
4.6	0.0049	0.059	0.29971	0.08
4.8	0.0048	0.056	0.1847	0.07
5.0	0.0046	0.055	0.11856	0.07
5.2	0.0042	0.052	0.0745	0.06
5.4	0.0032	0.050	0.04484	0.07
5.6	0.0041	0.048	0.02982	0.05
5.8	0.0042	0.046	0.01888	0.03
6.0	0.0047	0.045	0.01284	0.04
6.2	0.0010	0.043	0.00769	0.04

Table S9. Parameters obtained by fitting the Cole-Cole plot under zero dc field for **2-NO₃**.

T / K	χ_s	χ_T	τ	a
2.0	0.56	1.30	0.01673	0.42
2.3	0.48	1.14	0.01644	0.42
2.6	0.43	1.01	0.01609	0.42
2.9	0.39	0.91	0.016	0.42
3.2	0.35	0.83	0.01595	0.42
3.5	0.32	0.76	0.01557	0.42
3.8	0.30	0.70	0.01556	0.42
4.1	0.28	0.65	0.01564	0.42
4.4	0.26	0.61	0.0159	0.41
4.7	0.25	0.57	0.01572	0.41
5.0	0.23	0.54	0.01535	0.41
5.3	0.23	0.51	0.01634	0.40
5.6	0.22	0.48	0.01662	0.39
5.9	0.21	0.46	0.01726	0.38
6.1	0.20	0.43	0.01749	0.36
6.4	0.20	0.41	0.01795	0.34
6.7	0.19	0.40	0.01718	0.35
7.0	0.19	0.38	0.01814	0.29
7.3	0.19	0.36	0.01751	0.25
7.6	0.18	0.35	0.01615	0.21
7.9	0.18	0.34	0.01422	0.16
8.2	0.17	0.32	0.01146	0.13
8.5	0.16	0.31	0.0091	0.10
8.8	0.16	0.30	0.00699	0.08
9.1	0.16	0.29	0.0052	0.06
9.4	0.14	0.28	0.0038	0.05
9.7	0.13	0.27	0.00303	0.04

Table S10. Parameters obtained by fitting the Cole-Cole plot under zero dc field for **2-NO₃@Zn**.

T / K	χ_s	χ_T	τ_1	a_1
5.2	0.0023	0.035	1.43305	0.33
5.4	0.0021	0.035	1.2276	0.32
5.6	0.0023	0.033	0.96422	0.27
5.8	0.0022	0.031	0.72923	0.24
6	0.0022	0.029	0.57377	0.21
6.2	0.0020	0.028	0.47297	0.21
6.4	0.0021	0.027	0.39316	0.17
6.6	0.0020	0.026	0.31153	0.16
6.8	0.0018	0.025	0.25176	0.15
7.2	0.0015	0.023	0.15504	0.13
7.4	0.0017	0.023	0.12252	0.11
7.6	0.0015	0.022	0.0963	0.10

7.8	0.0016	0.021	0.07366	0.08
8	0.0016	0.021	0.05682	0.08
8.2	0.0018	0.020	0.04347	0.06
8.4	0.0012	0.020	0.03176	0.08
8.6	0.0012	0.019	0.02392	0.07
8.8	0.0011	0.019	0.01825	0.08
9.0	0.00087	0.019	0.01358	0.09
9.2	0.0012	0.018	0.01067	0.07
9.4	0.0012	0.018	0.00818	0.06
9.6	0.0020	0.017	0.00673	0.06
9.8	0.0018	0.017	0.00514	0.07

Table S11. Parameters obtained by fitting the Cole-Cole plot under 1000 Oe dc field for 2-**NO₃@Zn**.

T / K	χ_s	χ_T	τ	a
6.75	~0	0.030	0.6334	0.14
7	~0	0.030	0.46498	0.14
7.25	~0	0.029	0.34678	0.15
7.5	~0	0.029	0.25992	0.18
7.75	~0	0.028	0.17752	0.17
8	~0	0.027	0.12383	0.18
8.25	~0	0.026	0.08405	0.18
8.5	~0	0.025	0.05698	0.18
8.75	~0	0.024	0.04235	0.17
9	~0	0.023	0.0274	0.17
9.25	~0	0.023	0.01965	0.15
9.5	0.0017	0.022	0.01467	0.15
9.75	0.0011	0.021	0.00993	0.15
10	0.0021	0.021	0.00765	0.13

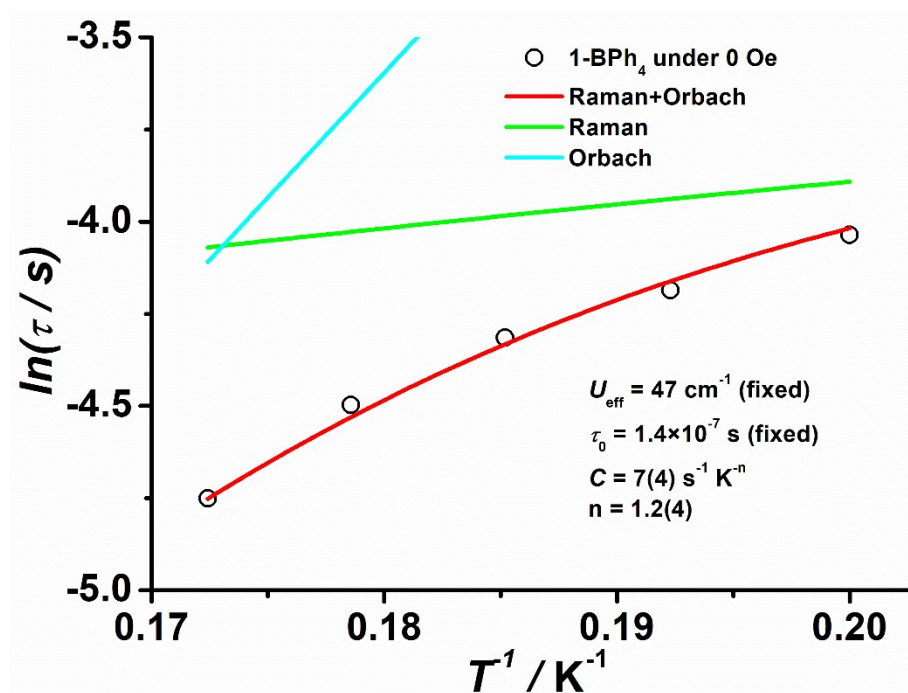


Figure S25. Temperature dependence of the magnetization relaxation rates under 0 Oe dc field for 1-BPh₄. The red line represents the best fit to a combination of Raman and Orbach processes, while the green and cyan lines represent the Raman and Orbach contributions to the magnetic relaxation, respectively.

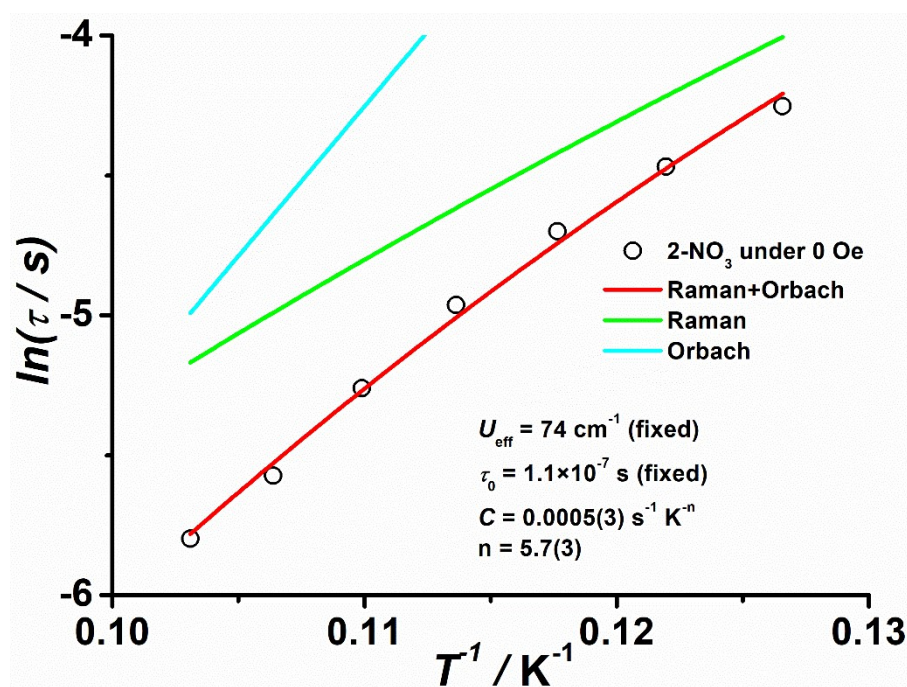


Figure S26. Temperature dependence of the magnetization relaxation rates under 0 Oe dc field for 2-NO₃. The red line represents the best fit to a combination of Raman and Orbach processes, while the green and cyan lines represent the Raman and Orbach contributions to the magnetic relaxation, respectively.

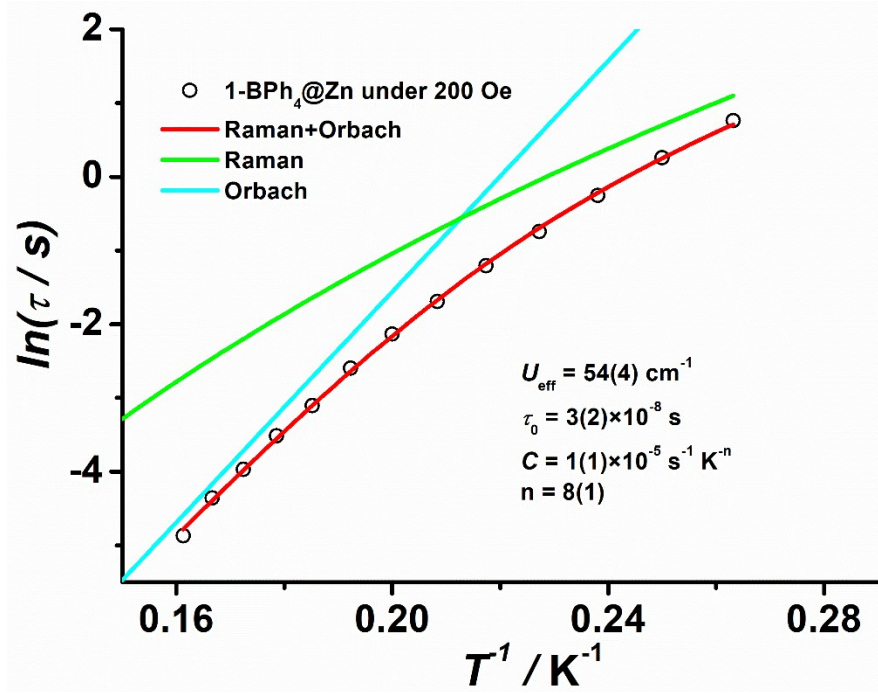


Figure S27. Temperature dependence of the magnetization relaxation rates under 200 Oe dc field for 1-BPh₄@Zn. The red line represents the best fit to a combination of Raman and Orbach processes, while the green and cyan lines represent the Raman and Orbach contributions to the magnetic relaxation, respectively.

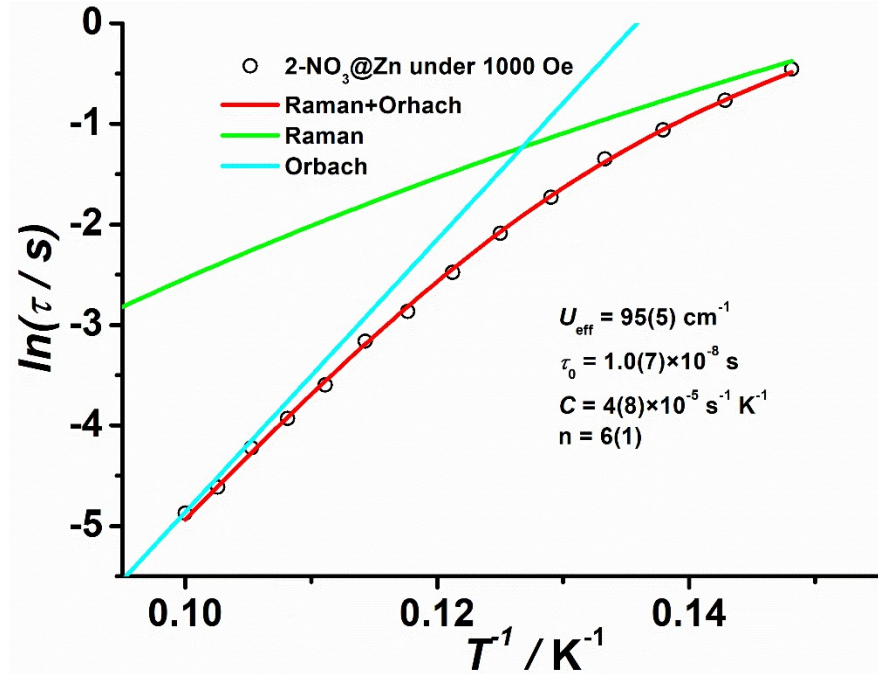


Figure S28. Temperature dependence of the magnetization relaxation rates under 1000 Oe dc field for 2-NO₃@Zn. The red line represents the best fit to a combination of Raman and Orbach processes, while the green and cyan lines represent the Raman and Orbach contributions to the magnetic relaxation, respectively.

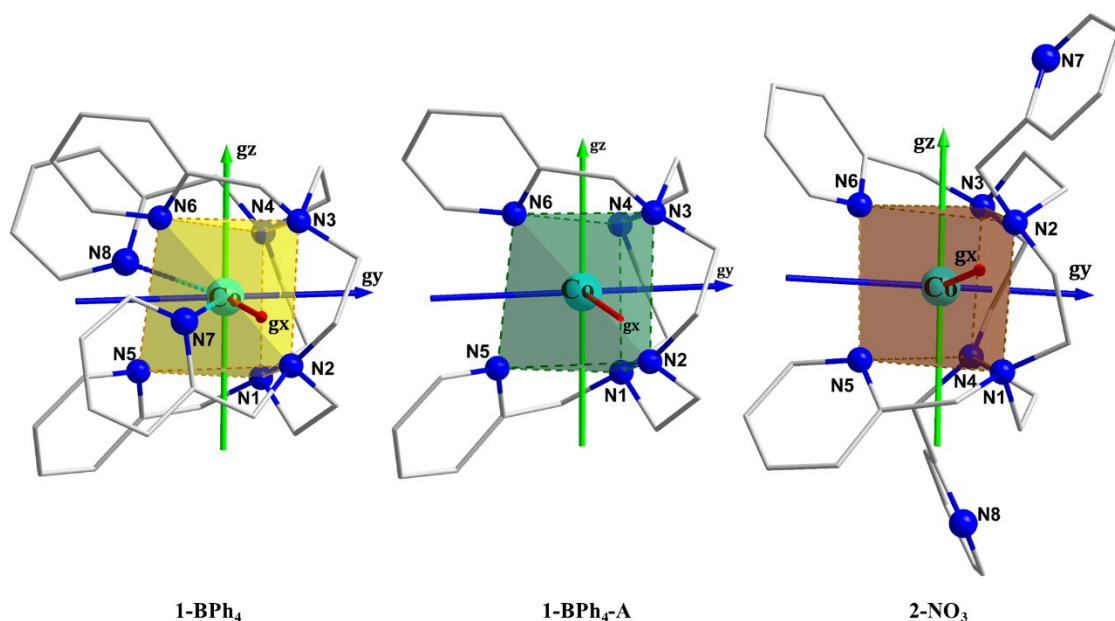


Figure S29. Orientations of the local magnetic axes (red: g_x ; blue: g_y ; green: g_z) on the Co(II) ions in all complexes in their ground spin-orbit states (results from NEVPT2 with the program Orca 5.0.4).

Table S12. Calculated ZFS parameters $D(E)$ (cm⁻¹) and ground $\mathbf{g}$ (g_x , g_y , g_z) tensors of complexes 1-BPh₄, 1-BPh₄-A and 2-NO₃ using NEVPT2 with the program Orca 5.0.4.

Complexes	NEVPT2				
	D_{cal}	E_{cal}	g_x	g_y	g_z
1-BPh ₄	-26.3	-1.0	2.155	2.191	2.492
1-BPh ₄ -A	-32.7	-0.7	2.148	2.178	2.555
2-NO ₃	-50.8	-0.7	2.111	2.138	2.725

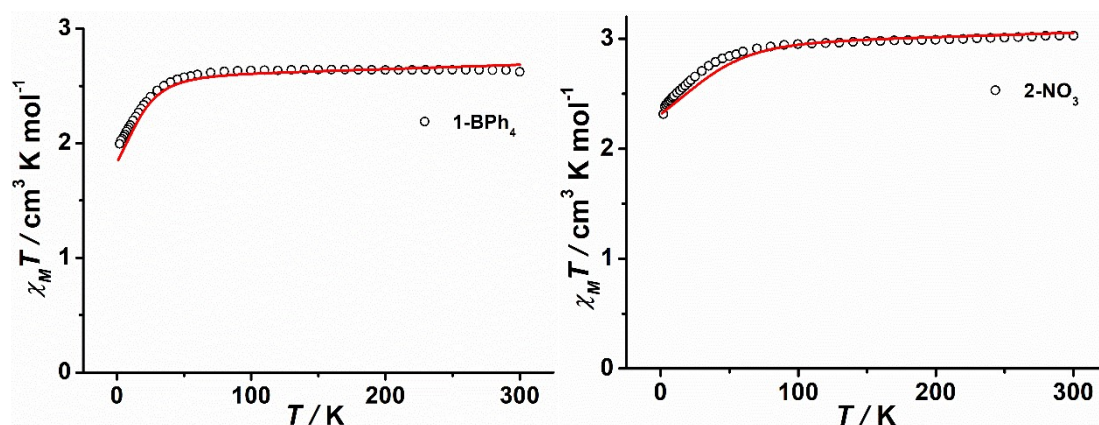


Figure S30. Calculated (red solid line) data of magnetic susceptibilities of 1-BPh₄ and 2-NO₃ using NEVPT2 with the program Orca 5.0.4.

Table S13. Selected important contributions of the spin-free excited states (with relative energy cm^{-1}) to D values (cm^{-1}) for complexes **1-BPh₄** and **2-NO₃** using NEVPT2 with the program Orca 5.0.4.

Complexes	State No.	Mult	Energy	Contribution
1-BPh₄	1	4	1704.8	-44.5
	3	4	4454.1	9.6
	2	4	4164.4	3.4
1-BPh₄-A	1	4	1473.6	-50.6
	3	4	4574.5	9.3
	4	4	6662.2	3.8
2-NO₃	1	4	1022.5	-68.2
	3	4	5078.2	8.4
	4	4	6825.3	4.0

Table S14. Relative energies (cm^{-1}) of ligand field one-electron states (in the basis of d-AOs) of complexes **1-BPh₄** and **2-NO₃** from AILFT analysis using NEVPT2 with the program Orca 5.0.4.

Complexes	No.	LF one-electron state	Energy
1-BPh₄	0	$-0.70 d_{x^2-y^2} + 0.69 d_{z^2}$	0.0
	1	$-0.61 d_{z^2} - 0.59 d_{x^2-y^2} + 0.52 d_{yz}$	566.7
	2	$0.97 d_{xy} - 0.22 d_{xz}$	1566.8
	3	$-0.85 d_{yz} - 0.38 d_{z^2} - 0.34 d_{x^2-y^2}$	5362.3
	4	$-0.95 d_{xz} - 0.22 d_{xy}$	7734.8
1-BPh₄-A	0	$0.91 d_{x^2-y^2} - 0.31 d_{z^2} + 0.23 d_{yz}$	0.0
	1	$0.81 d_{z^2} + 0.54 d_{yz} + 0.16 d_{x^2-y^2}$	465.2
	2	$0.98 d_{xy} + 0.16 d_{xz}$	908.5
	3	$-0.81 d_{yz} + 0.45 d_{z^2} + 0.36 d_{x^2-y^2}$	4908.5
	4	$0.97 d_{xz} - 0.17 d_{xy} + 0.16 d_{z^2}$	7602.5
2-NO₃	0	$0.91 d_{z^2} + 0.42 d_{yz}$	0.0
	1	$0.95 d_{x^2-y^2} + 0.27 d_{yz}$	271.8
	2	$0.98 d_{xy} + 0.17 d_{xz}$	984.6
	3	$-0.86 d_{yz} + 0.40 d_{z^2} + 0.31 d_{x^2-y^2}$	5676.9
	4	$-0.99 d_{xz} + 0.17 d_{xy}$	8240.0

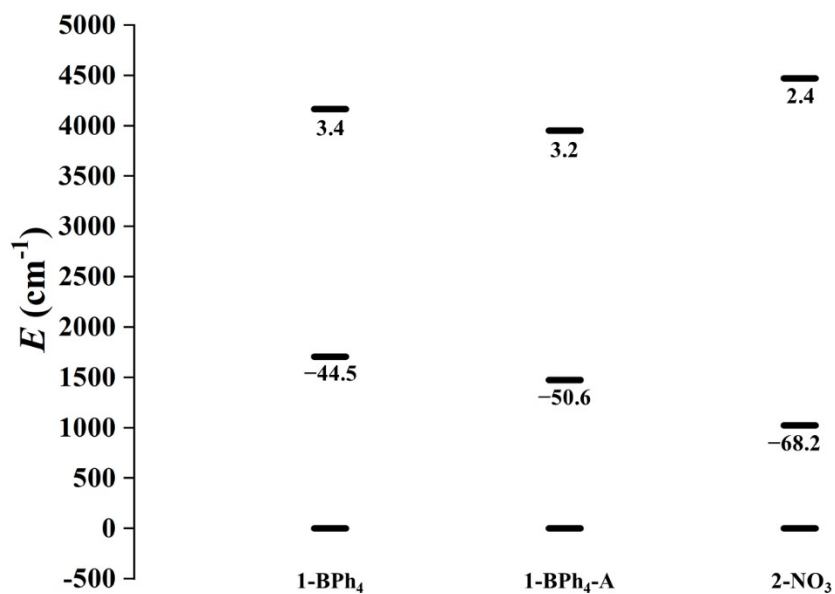


Figure S31. Energy gap between the ground, first and second excited quartet states computed for **1-BPh₄**, **1-BPh₄-A** and **2-NO₃**. The numerical value below each state gives its contribution to the *D* value (in cm⁻¹).

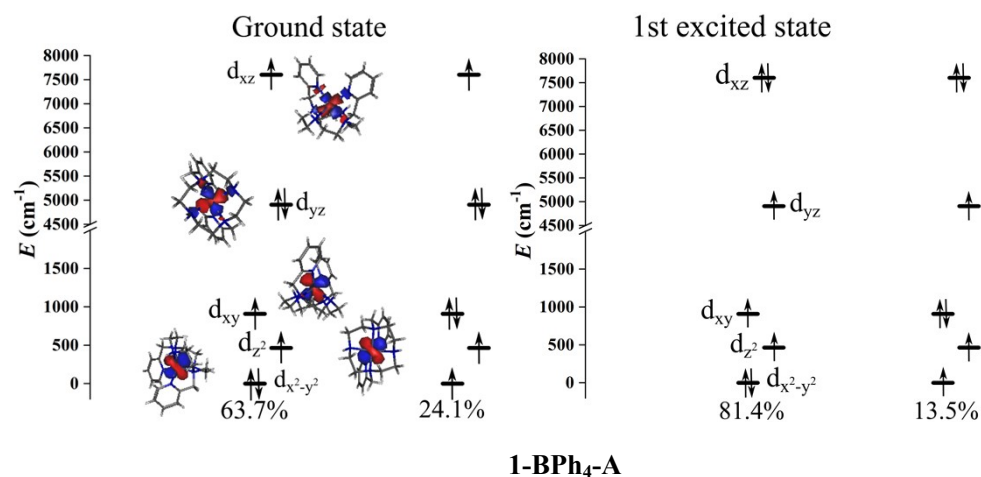


Figure S32. Orbital energies computed for the ground and first excited state of model complex **1-BPh₄-A** using NEVPT2 with the program Orca 5.0.4. Values in percent indicate the contribution to configuration mixing.