Supporting Information

Correlation between slow magnetic relaxation and molecular structures of Dy(III) complexes in N_5O_4 nona-coordination

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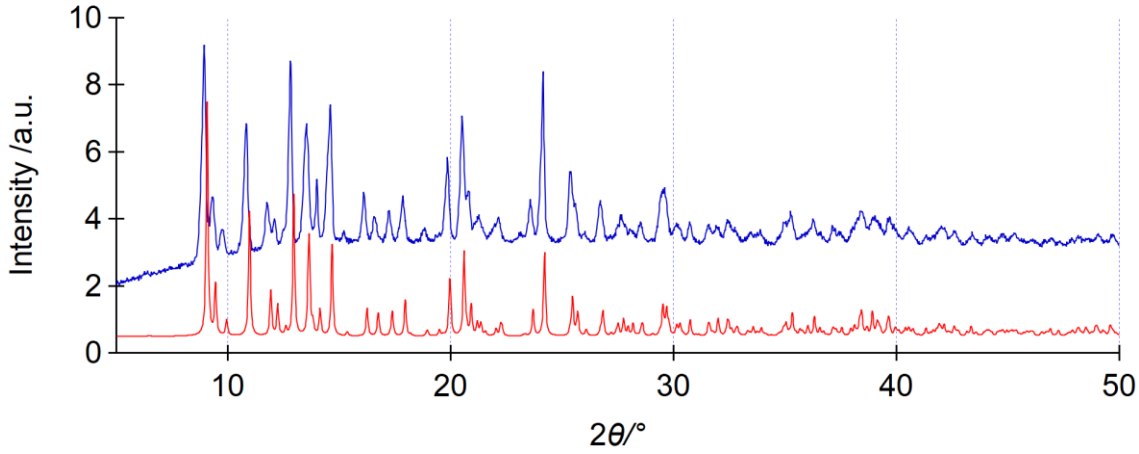
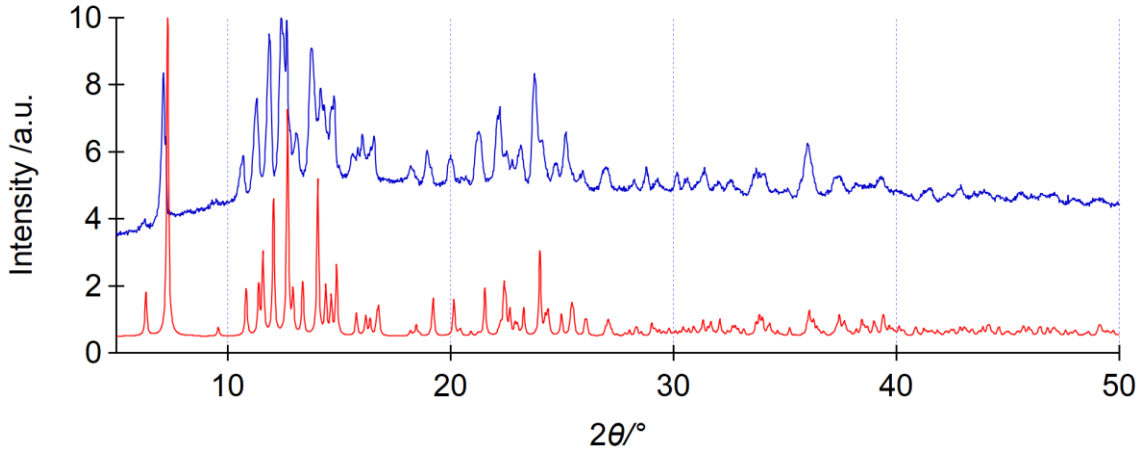
Complex **1**



Complex **2**



Complex **3**

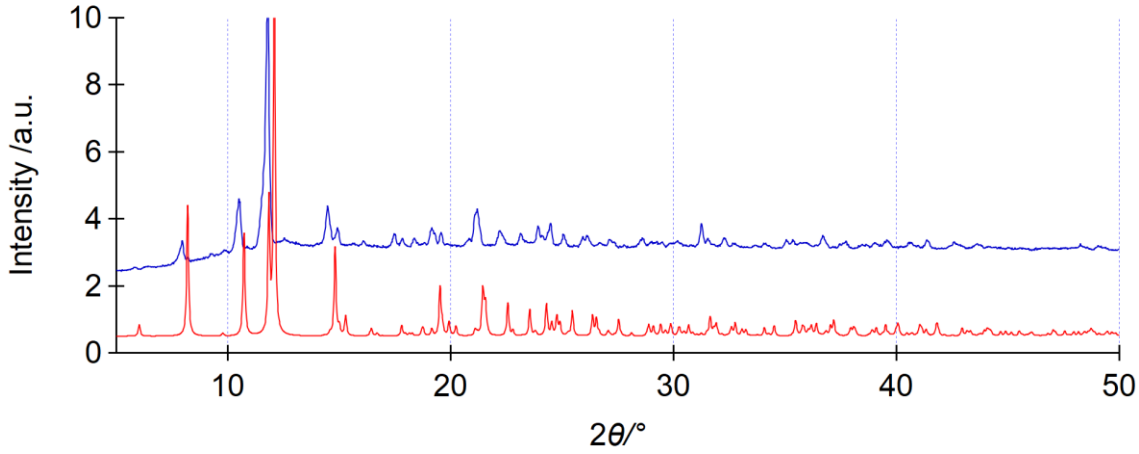


Figure S1. Powder X-ray diffractions measured at room temperature. Blue curves denote observations and red curves denote simulations on the basis of the single-crystal X-ray diffraction data.

Table S1. Crystallographic data for complexes **1–3**.

Complex	**1**	**2**	**3**
Empirical formula	$C_{19}H_{19}DyN_{10}O_9$	$C_{27}H_{30}DyF_3N_7O_8S$	$C_{30}H_{33}DyF_3N_7O_7S$
Formula weight	693.94	832.14	855.19
Temperature / K	153(2)	153(2)	153(2)
Wavelength / Å	0.71075	0.71075	0.71075
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/n$
Unit cell dimensions			
a / Å	9.2700(18)	9.1844(16)	15.639(2)
b/ Å	9.880(2)	12.5291(19)	9.9244(12)
c/ Å	13.827(3)	14.272(2)	22.596(3)
α/°	102.983(4)	75.292(5)	90
β/°	93.513(3)	86.951(4)	108.3924(17)
γ/°	93.610(3)	83.860(4)	90
Volume / Å^3	1227.9(4)	1578.8(4)	3327.9(7)
Z	2	2	4
Density (calcd.) / g m^{-3}	1.877	1.750	1.707
Absorption coefficient / mm^{-1}	3.114	2.510	2.382
F(000)	682	828	1708
θ range for data collection	2.31 to 32.50°.	1.94 to 32.50°.	2.26 to 32.50°.
Index ranges	-14<=h<=14	-13<=h<=13	-23<=h<=23
	-14<=k<=14	-18<=k<=18	-14<=k<=15
	-20<=l<=20	-21<=l<=21	-31<=l<=34
Reflections collected	19891	25351	45680
Independent reflections (*R*(int))	8737 (0.0267)	11251 (0.0226)	11969 (0.0367)
Completeness to θ = 32.50°	98.6 %	98.7 %	99.6 %
Max. and min. transmission	0.8856 and 0.7063	0.8439 and 0.7527	0.9320 and 0.7631
Data / restraints / parameters	8737 / 0 / 354	11251 / 0 / 416	11969 / 0 / 448
Goodness-of-fit on F^2	1.046	1.078	1.088
*R*1, *wR*2 indices ($I > 2\sigma(I)$)	0.0254, 0.0543	0.0264, 0.0622	0.0375, 0.0913
*R*1, *wR*2 indices (all data)	0.0293, 0.0561	0.0302, 0.0645	0.0504, 0.1003
Largest diff. peak and hole / e.Å^{-3}	0.741 and -0.601	1.828 and -0.706	2.056 and -1.050

Table S2. Selected bond distances (Å) and angles (°) for complexes **1–3**.

Complex	**1**	**2**	**3**
Dy-O1	2.4524(17)	2.4203(16)	2.320(2)
Dy-O2	2.3903(16)	2.3956(15)	2.312(2)
Dy-O3	2.4657(16)	2.4357(16)	2.370(2)
Dy-O4	2.4177(16)	2.3923(16)	2.287(2)
Dy-N1	2.4490(17)	2.4938(17)	2.583(3)
Dy-N3	2.4599(18)	2.4747(16)	2.554(2)
Dy-N4	2.4184(17)	2.4547(16)	2.565(2)
Dy-N5	2.4412(19)	2.4795(16)	2.536(2)
Dy-N7	2.4939(18)	2.5018(18)	2.696(3)
N1-Dy-N3	65.09(6)	64.57(6)	61.89(8)
N3-Dy-N4	65.35(6)	65.08(5)	62.11(8)
N4-Dy-N5	66.11(6)	65.16(5)	62.10(8)
N5-Dy-N7	65.01(6)	64.24(6)	59.59(8)
N1-Dy-N7	102.95(6)	104.98(6)	127.77(8)

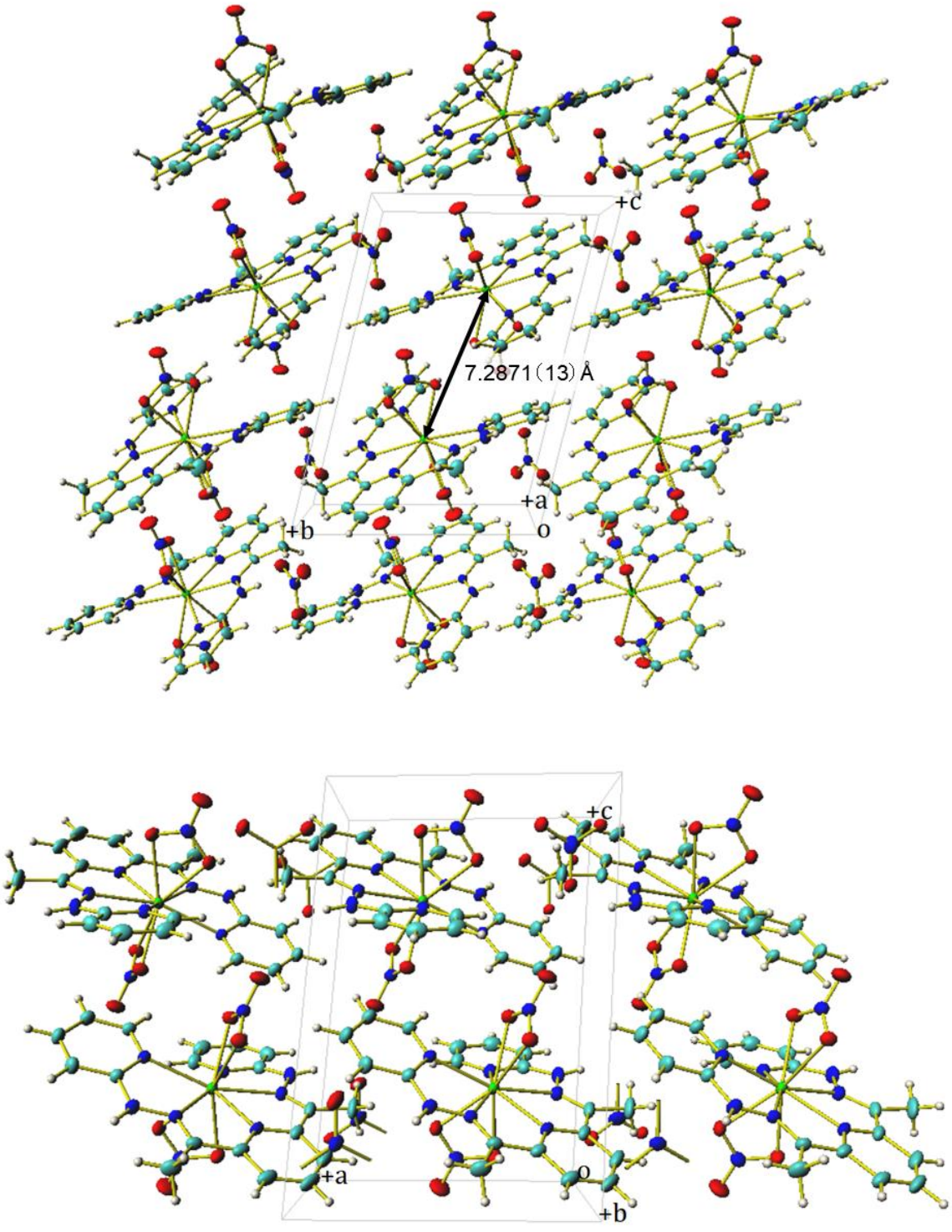


Figure S2. Crystal packing of **1**.

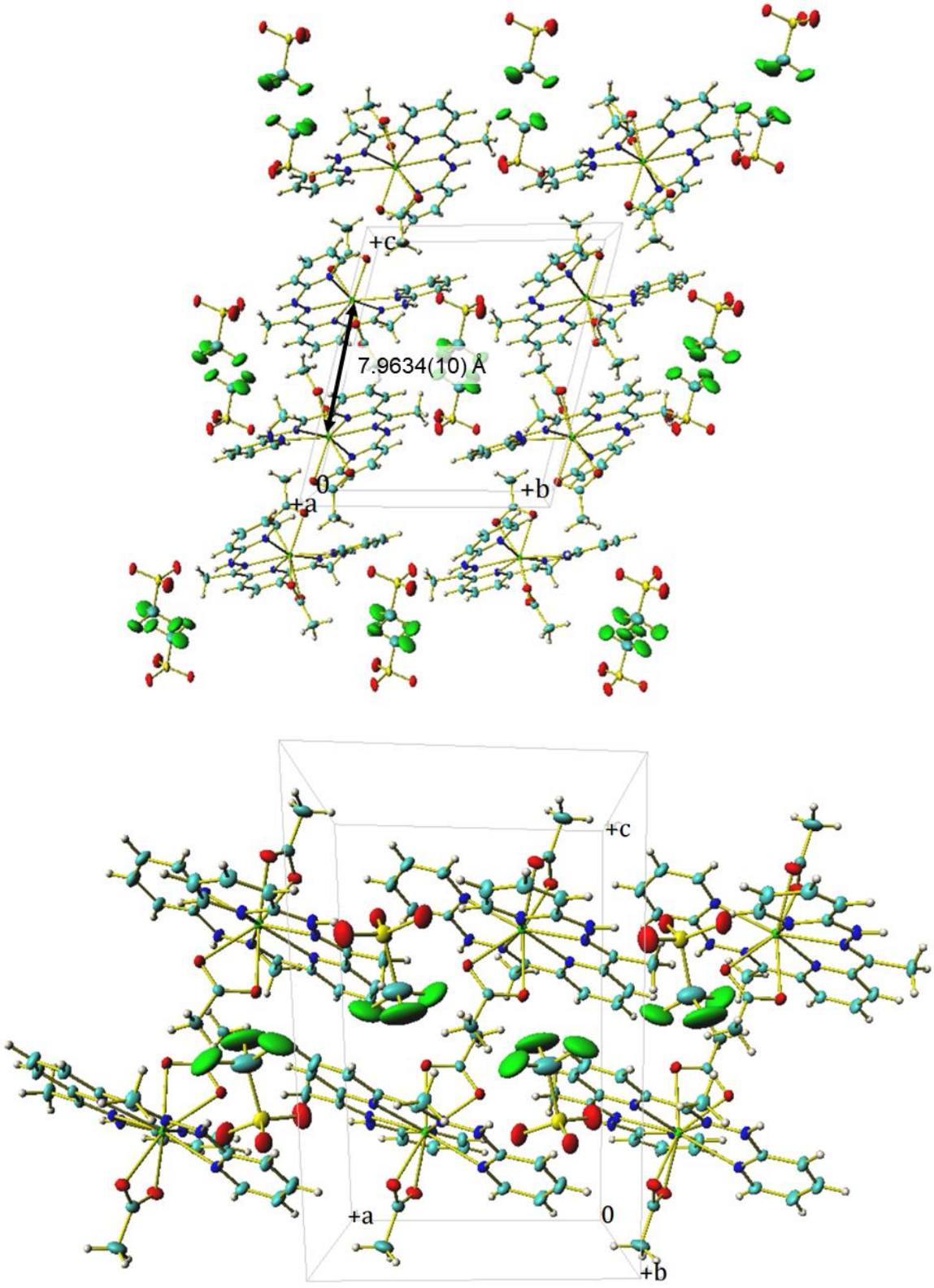


Figure S3. Crystal packing of **2**.

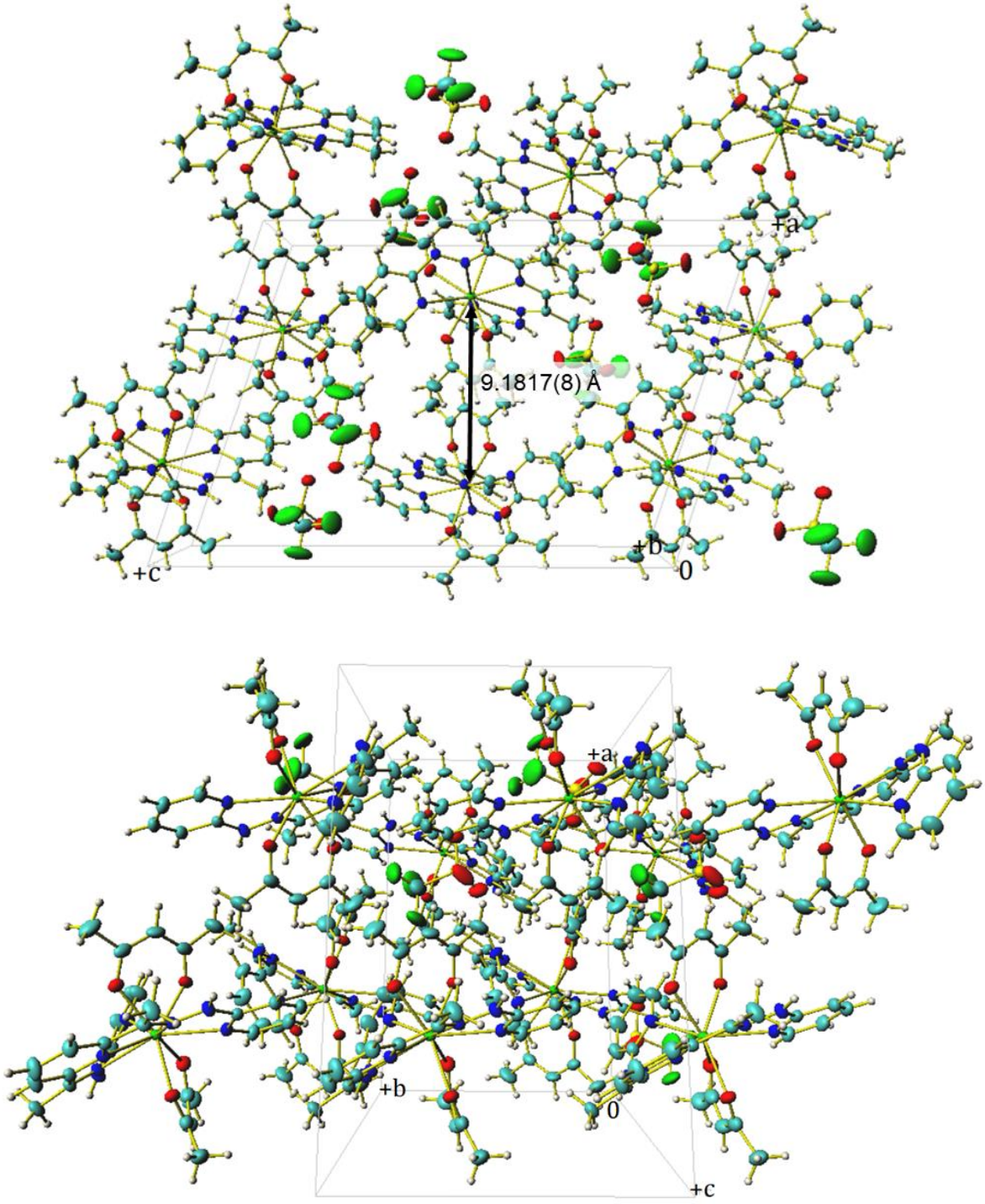


Figure S4. Crystal packing of **3**.

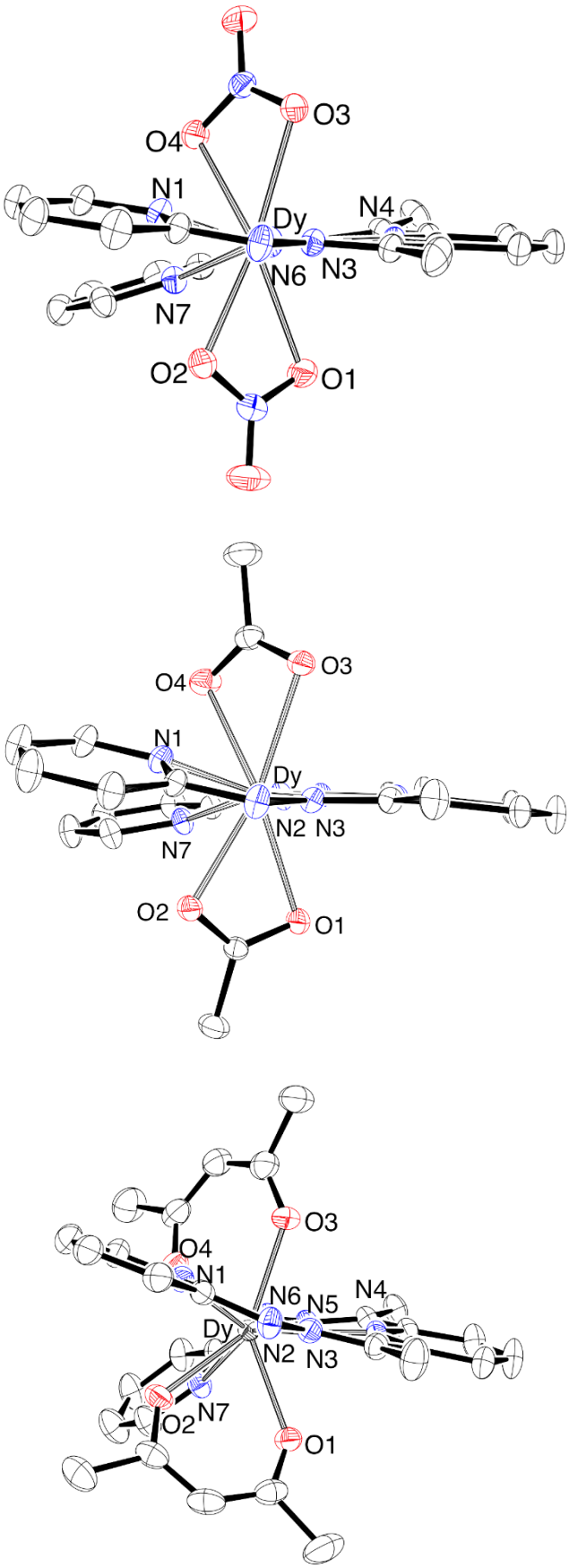


Figure S5. ORTEP drawing of the cationic part of **1** (top), **2** (middle), and **3** (bottom) at the 50% probability level.

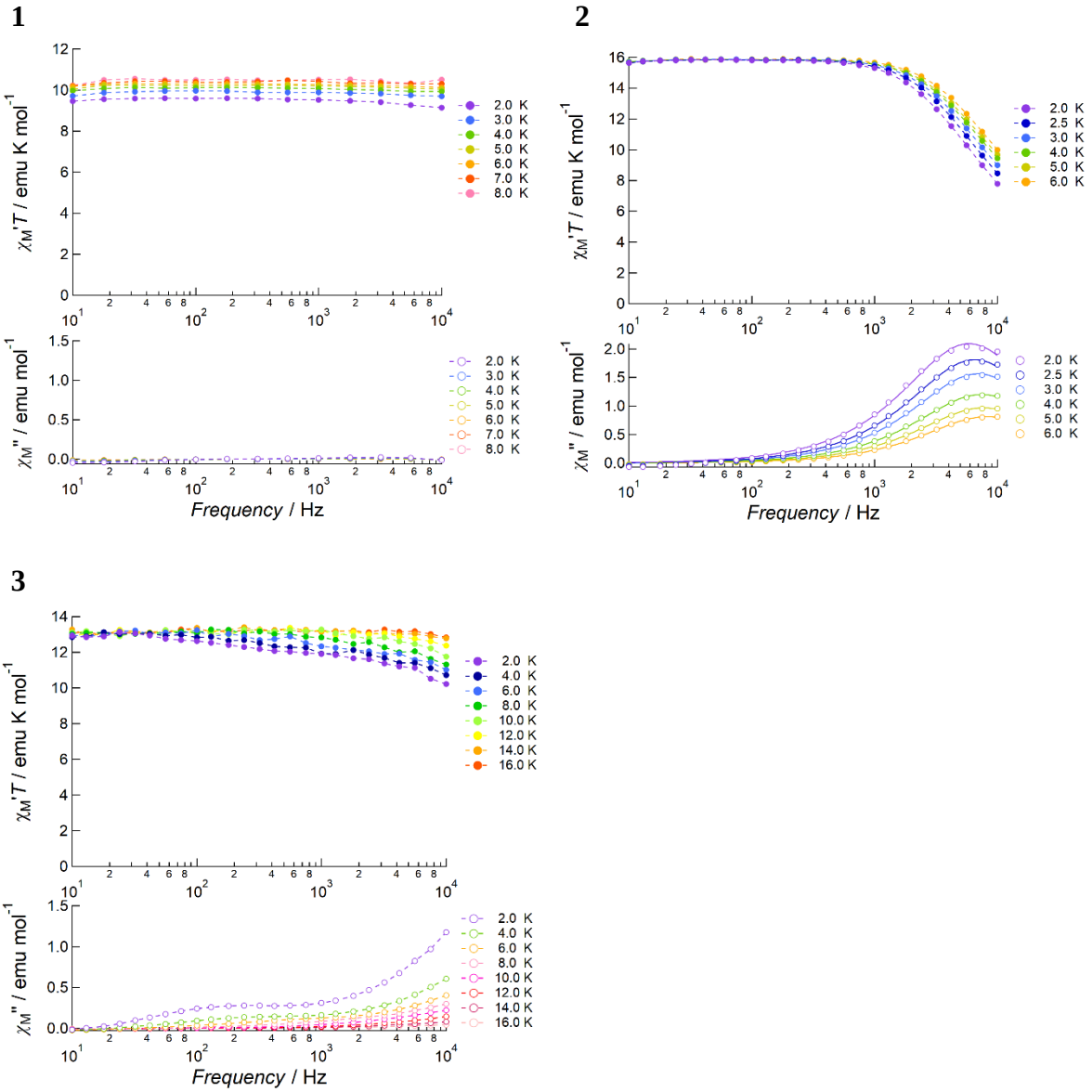


Figure S6. Frequency dependence of $\chi_M'T$ (closed circles) and χ_M'' (open circles) of **1**–**3** measured under an oscillating field of 3 Oe and zero dc field. For **2**, frequency dependence of the out-of-phase susceptibilities were analyzed on the basis of the equation 1, and the results were depicted as solid curves. Estimated best fit parameters were below.

	2.0 K	2.5 K	3.0 K	4.0 K	5.0 K	6.0 K
$\chi_T - \chi_S$	4.7(1)	4.01(8)	3.46(7)	2.65(6)	2.13(5)	1.76(4)
τ / 10^{-5} s	2.70(9)	2.44(7)	2.29(7)	2.15(7)	2.07(7)	1.94(7)
α	0.076(15)	0.065(13)	0.064(13)	0.063(13)	0.060(14)	0.051(13)

Table S3. Best fitted parameters on the basis of the Cole-Cole equation for **1** measured under 1000 Oe dc field.

T/K	χ_T / emu mol^{-1}	χ_S / emu mol^{-1}	τ / s	α
2.0	5.80(4)	0.44(3)	0.00068(1)	0.20(1)
2.2	5.65(4)	0.39(4)	0.00048(1)	0.17(1)
2.4	5.51(3)	0.35(4)	0.000336(7)	0.17(1)
2.6	5.41(3)	0.32(5)	0.000233(5)	0.14(1)
2.8	5.32(2)	0.28(5)	0.000163(3)	0.13(1)
3.0	5.20(2)	0.28(5)	0.000115(2)	0.109(9)
3.2	5.05(1)	0.25(4)	0.000082(1)	0.10(1)
3.4	4.883(8)	0.25(5)	0.000060(1)	0.091(6)
3.6	4.707(5)	0.30(4)	0.0000446(6)	0.075(5)
3.8	4.539(5)	0.30(6)	0.0000332(6)	0.070(6)
4.0	4.379(4)	0.29(7)	0.0000251(6)	0.070(6)
4.2	4.208(4)	0.3(1)	0.0000191(7)	0.069(7)

Table S4. Best fitted parameters on the basis of the Cole-Cole equation for **2** measured under 1000 Oe dc field.

T/K	χ_T / emu mol^{-1}	χ_S / emu mol^{-1}	τ / s	α
2.0	10(2)	0.228(5)	0.05(2)	0.219(6)
2.2	9(1)	0.212(5)	0.037(7)	0.199(7)
2.4	8.1(7)	0.198(5)	0.028(3)	0.181(6)
2.6	7.5(4)	0.188(4)	0.021(1)	0.161(6)
2.8	7.4(2)	0.179(5)	0.0161(7)	0.145(5)
3.0	7.1(1)	0.171(4)	0.0120(3)	0.129(5)
3.2	6.82(9)	0.165(5)	0.0089(2)	0.115(5)
3.4	6.55(6)	0.160(6)	0.0066(1)	0.103(4)
3.6	6.34(4)	0.154(6)	0.00493(5)	0.095(4)
3.8	6.11(3)	0.150(7)	0.00368(3)	0.086(4)
4.0	5.90(2)	0.144(7)	0.00278(2)	0.083(4)
4.2	5.69(2)	0.138(7)	0.00210(1)	0.080(4)
4.4	5.48(1)	0.131(7)	0.001600(9)	0.079(3)
4.6	5.27(1)	0.126(7)	0.001221(7)	0.076(3)
4.8	5.08(1)	0.119(7)	0.000935(5)	0.077(3)
5.0	4.901(8)	0.110(7)	0.000719(3)	0.078(3)
5.2	4.727(8)	0.102(7)	0.000555(3)	0.080(3)
5.4	4.563(7)	0.094(8)	0.000429(2)	0.083(3)
5.6	4.410(7)	0.08(1)	0.000331(2)	0.090(4)
5.8	4.266(7)	0.07(1)	0.000255(2)	0.096(4)
6.0	4.128(7)	0.06(1)	0.000197(2)	0.104(4)
6.2	3.995(7)	0.05(2)	0.000151(1)	0.114(5)
6.4	3.871(6)	0.04(2)	0.000115(1)	0.128(5)
6.6	3.738(6)	0*	0.0000877(5)	0.143(3)
6.8	3.622(7)	0*	0.0000663(5)	0.159(4)
7.0	3.506(7)	0*	0.0000504(4)	0.173(5)
7.2	3.395(7)	0*	0.0000382(3)	0.189(5)
7.4	3.287(7)	0*	0.0000289(3)	0.204(6)
7.6	3.178(6)	0*	0.0000218(2)	0.221(7)
7.8	3.055(6)	0*	0.0000166(2)	0.238(7)

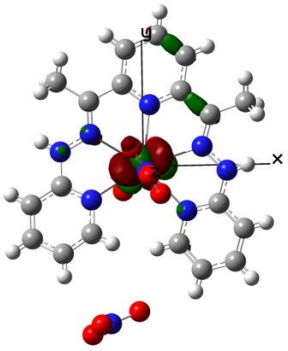
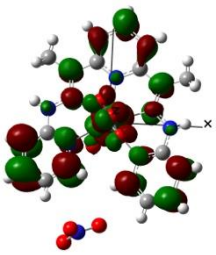
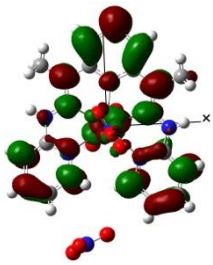
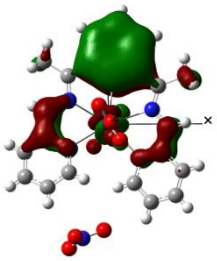
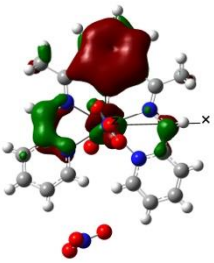
* fixed at 0 emu mol^{-1}

Table S5. Best fitted parameters on the basis of the Cole-Davidson equation for **3** measured under 1000 Oe dc field.

T/K	χ_T / emu mol^{-1}	χ_S / emu mol^{-1}	τ / s	β
2.0	2.3(2)	0.37(1)	0.026(8)	0.45(1)
3.0	1.97(4)	0.274(5)	0.0143(8)	0.526(8)
4.0	2.32(3)	0.193(7)	0.0121(6)	0.529(8)
4.5	2.42(3)	0.15(1)	0.0103(5)	0.51(1)
5.0	2.39(2)	0.11(1)	0.0079(4)	0.49(1)
5.5	2.27(1)	0.079(1)	0.0056(2)	0.48(1)
6.0	2.13(1)	0.05(1)	0.0039(1)	0.47(1)
6.5	1.997(7)	0.02(2)	0.00272(9)	0.45(1)
7.0	1.866(5)	0.01(1)	0.00187(5)	0.45(1)
7.5	1.753(4)	0*	0.00132(2)	0.443(3)
8.0	1.649(4)	0*	0.00094(2)	0.444(4)
8.5	1.555(3)	0*	0.00068(1)	0.444(3)
9.0	1.471(3)	0*	0.00050(2)	0.442(4)
9.5	1.396(3)	0*	0.000378(7)	0.440(4)
10.0	1.328(3)	0*	0.000288(7)	0.438(5)
10.5	1.266(2)	0*	0.000222(5)	0.436(5)
11.0	1.209(2)	0*	0.000173(4)	0.432(6)
11.5	1.157(2)	0*	0.000136(4)	0.427(7)
12.0	1.110(2)	0*	0.000108(3)	0.421(8)
12.5	1.066(2)	0*	0.000085(4)	0.41(1)
13.0	1.026(2)	0*	0.000068(3)	0.41(1)
13.5	0.989(2)	0*	0.000055(3)	0.39(2)
14.0	0.954(2)	0*	0.000045(3)	0.38(2)

* fixed at 0 emu mol^{-1}

Figure S7. Kohn-Sham orbitals of *f* orbitals for models **m1** – **m3**. Numbers in parentheses are corresponding orbital energies (in eV), and unoccupied orbitals are indicated in red. Some *f* orbitals are difficult to distinguish a dominant molecular orbital, so that possible molecular orbitals are put in one grid.

<table>
<tr><td colspan="2">m1 (HOMO level : α –3.923 eV, β –3.689eV)</td></tr>
<tr><td>Alpha orbital</td><td>Beta orbital</td></tr>
<tr><td> 
HOMO-38 (-12.6)</td><td> 
LUMO+11
(-1.1)
 
LUMO+10
(-1.16)</td></tr>
<tr><td> 
HOMO-39
(-12.9)
 
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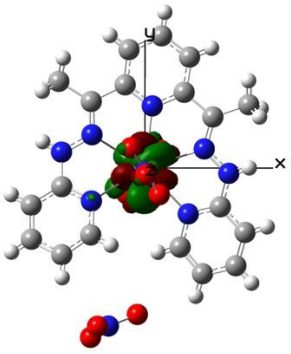
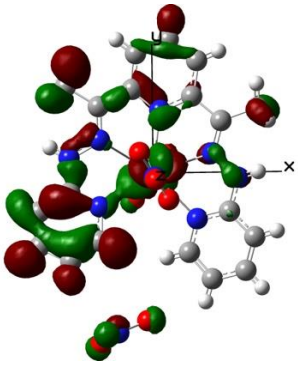
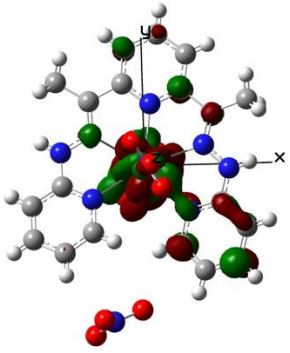
(-13.0)</td><td> 
LUMO+5 (-1.9)</td></tr>
<tr><td> 
HOMO-46 (-13.4)</td><td> 
LUMO+4 (-2.0)</td></tr>
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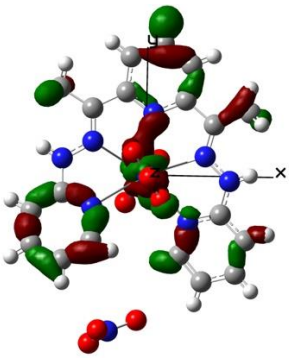
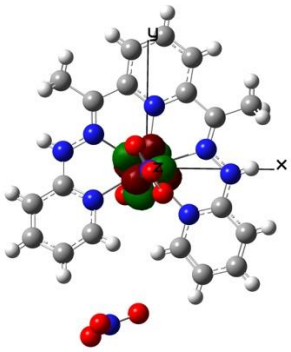
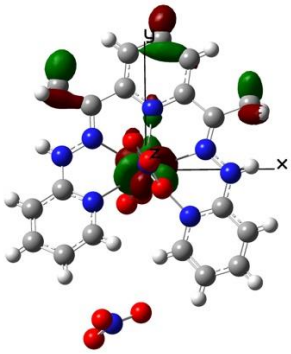
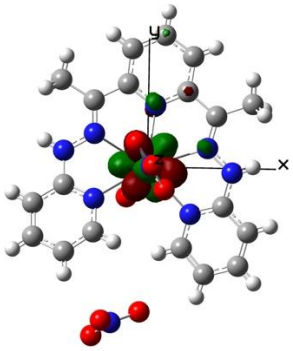
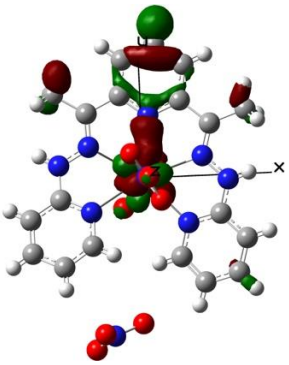
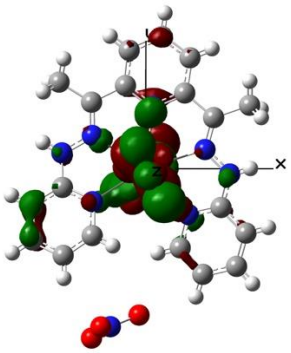
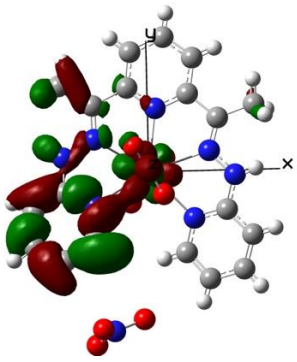
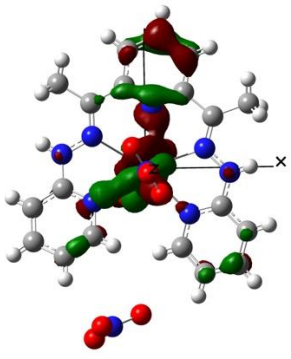
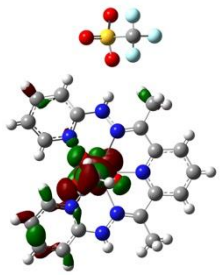
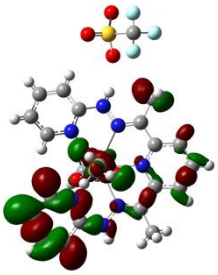
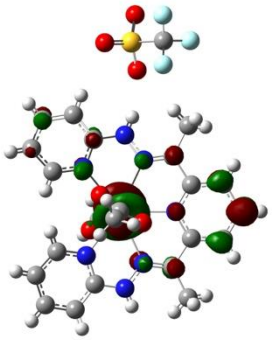
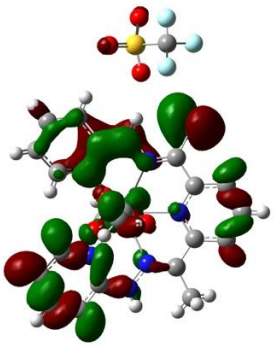
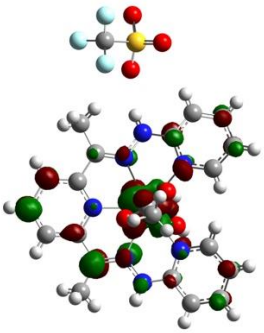
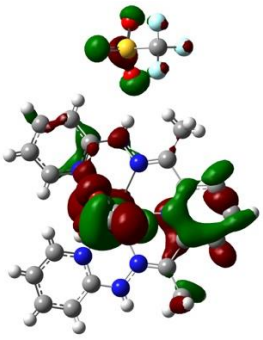
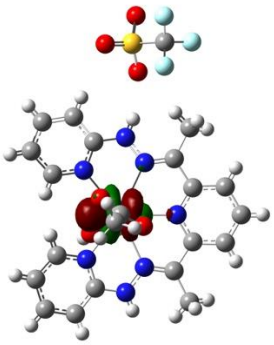
 HOMO-50 (-13.9)	 LUMO+3 (-2.7)
 HOMO-52 (-13.9)	 LUMO+2 (-2.7)
 HOMO-53 (-14.0)	 HOMO-21 (-9.5)
 HOMO-54 (-14.0)	 HOMO-22 (-9.7)

Figure S7, continue

m2 (HOMO level : α –4.923 eV, β –4.923 eV)	
Alpha orbital	Beta orbital
  HOMO-42 (-11.8) or HOMO-43 (-11.9)	 LUMO+10 (-0.4)
 HOMO-44 (-11.9)	 LUMO+8 (-0.6)
 HOMO-52 (-12.6)	 LUMO+5 (-1.5)

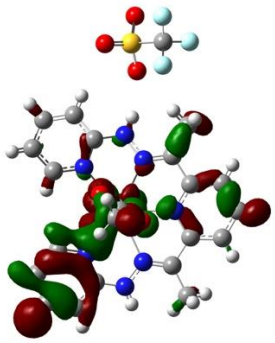
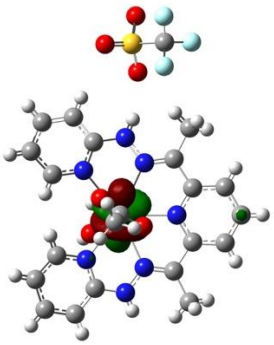
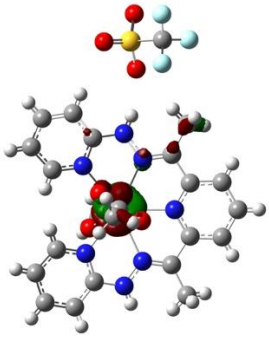
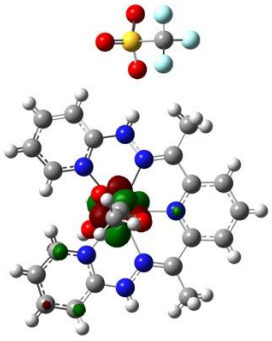
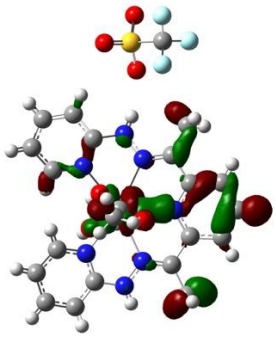
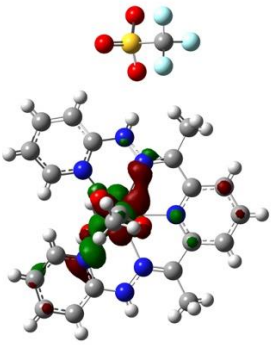
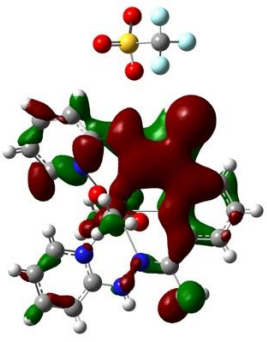
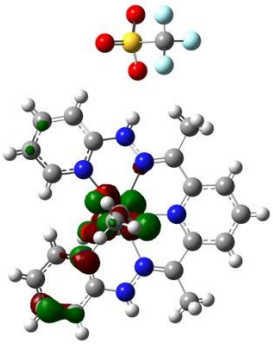
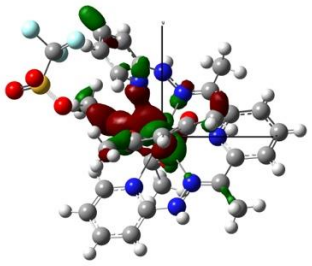
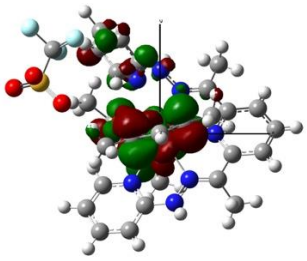
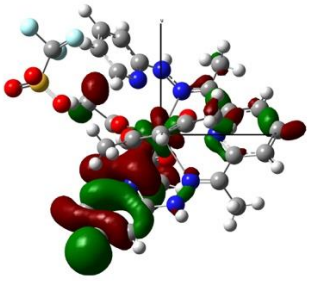
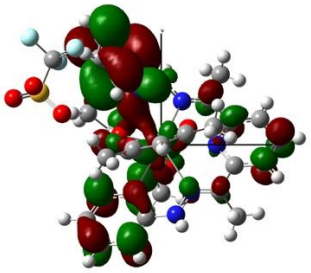
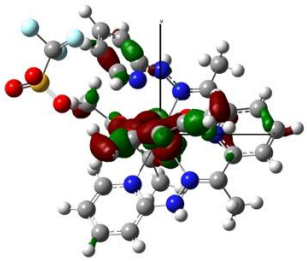
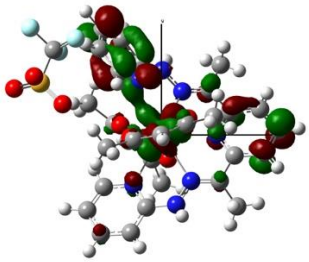
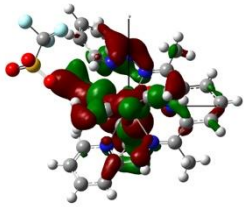
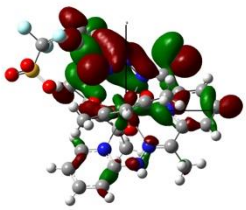
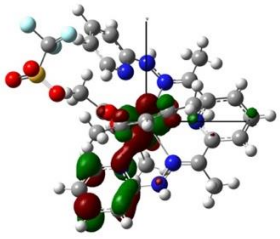
 HOMO-59 (-13.0)	 LUMO+4 (-1.5)
 HOMO-63 (-13.2)	 LUMO+2 (-2.0)
 HOMO-64 (-13.3)	 HOMO-18 (-8.7)
 HOMO-65 (-13.3)	 HOMO-19 (-8.8)

Figure S7, continue

m3 (HOMO level : α –3.588 eV, β –3.588 eV)	
Alpha orbital	Beta orbital
 HOMO-52 (-12.0)	 LUMO+12 (-0.4)
 HOMO-55 (-12.3)	 LUMO+6 (-1.3)
 HOMO-60 (-12.8)	 LUMO+5 (-1.5)
  HOMO-66 (-13.1) or HOMO-67 (-13.2)	 LUMO+3 (-2.0)

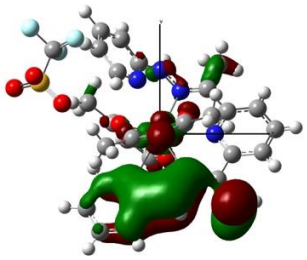
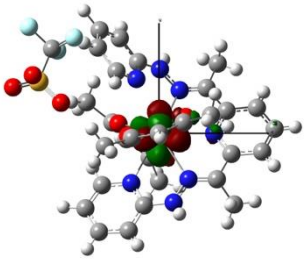
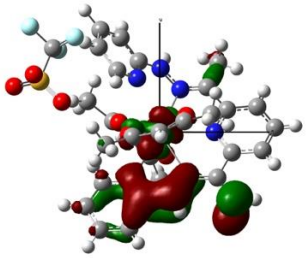
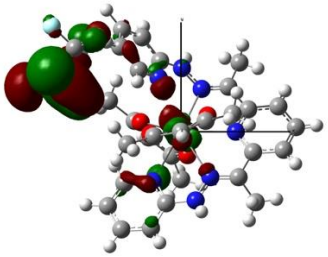
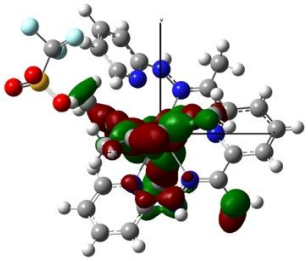
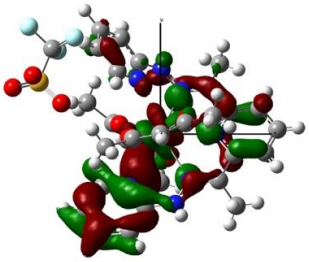
 HOMO-69 (-13.3)	 LUMO+2 (-2.1)
 HOMO-70 (-13.4)	 HOMO-23 (-8.9)
 HOMO-71 (-13.5)	 HOMO-24 (-9.0)

Table S7. Cartesian coordinates of **m1**–**m3** for DFT calculations (in Å)

	m1				**m2**				**m3**		
	x	*y*	*z*		*x*	*y*	*z*		*x*	*y*	*z*
Dy	0.00000	0.00000	0.00000	Dy	0.00000	0.00000	0.00000	Dy	0.00000	0.00000	0.00000
C	-2.11707	-2.56948	0.83416	O	0.99227	-0.49003	2.15567	O	1.21679	0.74138	1.83237
C	-3.24882	-3.34558	0.79371	O	-0.84676	0.71578	2.12806	O	-1.40187	-0.11564	1.84404
C	-4.43081	-2.77087	0.29688	C	0.00000	0.00000	2.75785	C	2.36789	0.81778	3.89482
C	-4.43564	-1.46366	-0.09321	C	-0.21521	-0.30507	4.20897	H	3.12691	0.30915	3.54399
C	-3.24373	-0.73187	0.00803	H	-0.85294	-1.01744	4.29414	H	2.21574	0.57613	4.83255
C	-3.36218	3.35670	-0.54194	H	-0.54836	0.47763	4.65293	H	2.55954	1.77730	3.83156
C	-2.09373	2.57665	-0.42531	H	0.61649	-0.56991	4.60661	C	1.12543	0.49677	3.08184
C	-0.77117	3.23176	-0.38403	O	-1.28009	-0.80031	-1.85843	C	0.00000	0.00000	3.72946
C	-0.62280	4.60144	-0.54875	O	0.44859	0.44962	-2.35342	H	0.06654	-0.21183	4.65312
C	0.65270	5.14221	-0.49329	C	-0.55250	-0.22328	-2.72140	C	-1.23409	-0.20846	3.07721
C	1.74067	4.32677	-0.26279	C	-0.88773	-0.35144	-4.17628	C	-2.45840	-0.57510	3.89965
C	1.53213	2.95711	-0.09592	H	-1.57317	-1.01303	-4.29054	H	-3.04917	0.20205	3.96801
C	2.65252	2.00952	0.13679	H	-0.10406	-0.61508	-4.66359	H	-2.17773	-0.85208	4.79696
C	4.05190	2.50098	0.28054	H	-1.20081	0.49368	-4.50760	H	-2.93515	-1.31160	3.46440
C	2.94642	-1.50044	0.26568	N	-1.56952	1.91834	-0.34356	O	0.29733	-1.07387	-2.10907
C	3.91101	-2.48663	0.52730	N	0.22574	3.32854	0.11208	O	-1.84301	0.43612	-1.28263
C	3.55459	-3.79636	0.40787	H	0.55053	4.10910	0.26672	C	0.00794	-2.17366	-4.19455
C	2.25490	-4.13202	0.00140	N	1.04846	2.24428	-0.02874	H	0.94299	-2.43176	-4.04738
C	1.38248	-3.11103	-0.26701	N	2.44018	0.00000	-0.28751	H	-0.08778	-1.78931	-5.09118
H	-3.98507	0.99529	-0.55770	N	1.03653	-2.25745	-0.12777	H	-0.56485	-2.96412	-4.11533
H	4.07168	0.04689	0.64808	N	0.23143	-3.33898	-0.01394	C	-0.42103	-1.09613	-3.10752
H	-1.32922	-2.95231	1.14543	H	0.52651	-4.12596	-0.19423	C	-1.47208	-0.26156	-3.47503
H	-3.23251	-4.22778	1.08692	N	-1.45329	-1.91650	0.72239	H	-1.74772	-0.20288	-4.38292
H	-5.20719	-3.28054	0.23405	C	-2.91062	1.74596	-0.47227	C	-2.11678	0.49340	-2.48021
H	-5.21172	-1.06785	-0.41949	H	-3.22340	0.90535	-0.71512	C	-3.29059	1.41656	-2.90909
H	-4.00981	3.00966	0.07540	C	-3.82836	2.74338	-0.26206	H	-3.97878	1.41587	-2.21033
H	-3.19026	4.27979	-0.34145	H	-4.73771	2.59111	-0.37461	H	-3.67726	1.08678	-3.74739
H	-3.70297	3.28158	-1.43764	C	-3.35071	3.99496	0.12696	H	-2.95820	2.32879	-3.03894
H	-1.36267	5.14492	-0.69314	H	-3.94942	4.68295	0.30916	N	-1.25599	-2.25934	0.20322
H	0.77464	6.05601	-0.61178	C	-2.00583	4.21281	0.24080	N	0.66967	-3.14383	1.14063

H	2.59953	4.68307	-0.22004	H	-1.67552	5.05165	0.47099	H	0.94110	-3.66240	1.41074
H	4.54289	2.30745	-0.52227	C	-1.13929	3.13910	-0.00017	N	1.34447	-2.08075	0.64539
H	4.04551	3.44910	0.43148	C	2.99519	3.74650	-0.31896	N	2.51031	0.00000	-0.51145
H	4.47117	2.06189	1.02432	H	2.36837	4.39554	-0.64646	N	0.94528	1.95780	-1.30082
H	4.77555	-2.25104	0.77601	H	3.73605	3.67967	-0.92704	N	0.04706	2.91113	-1.66989
H	4.17256	-4.46616	0.59627	H	3.31530	4.01781	0.54524	H	0.21049	3.35204	-2.40482
H	1.99333	-5.02043	-0.08282	C	2.32079	2.41348	-0.20531	N	-1.02445	2.46890	0.34510
H	0.52482	-3.32937	-0.55499	C	3.12076	1.16446	-0.28427	C	-2.59071	-2.34917	-0.00960
N	-2.09090	-1.26489	0.44153	C	4.51660	1.20150	-0.33189	H	-3.01923	-1.56881	-0.45828
N	-3.25243	0.60078	-0.33717	H	4.97028	2.01266	-0.34266	C	-3.34387	-3.39956	0.39931
N	-2.06529	1.28086	-0.31997	C	5.20805	0.00197	-0.36329	H	-4.34230	-3.34635	-0.07491
N	0.28731	2.42252	-0.16173	H	6.13858	0.00258	-0.35888	C	-2.72384	-4.46843	1.04539
N	2.31599	0.76235	0.19297	C	4.51649	-1.19717	-0.39872	H	-3.25179	-5.25333	1.41068
N	3.27616	-0.18217	0.41645	H	4.97043	-2.00765	-0.44908	C	-1.37402	-4.40872	1.27372
N	1.69800	-1.80184	-0.13716	C	3.12108	-1.16306	-0.35866	H	-0.96890	-5.08303	1.61515
N	0.00000	0.00000	2.87659	C	2.31118	-2.41096	-0.32851	C	-0.67831	-3.27452	0.86269
O	0.54985	-0.91258	2.18077	C	2.97975	-3.74471	-0.42384	C	3.41884	-3.22468	1.28719
O	0.00572	-0.01834	4.09363	H	3.22333	-4.04394	0.45534	H	3.26912	-3.25720	2.25506
O	-0.56439	0.92787	2.21089	H	3.76838	-3.66879	-0.96557	H	4.37368	-3.09373	1.10895
N	-0.03923	-0.36989	-2.83008	H	2.37775	-4.37569	-0.82177	H	3.12366	-4.06696	0.88195
O	-0.69862	-1.12188	-2.01946	C	-1.07442	-3.15294	0.39913	C	2.63563	-2.07975	0.69503
O	-0.04469	-0.55138	-4.02798	C	-1.93400	-4.26095	0.46546	C	3.30205	-0.93025	0.06037
O	0.61560	0.56806	-2.28023	H	-1.63334	-5.11125	0.23846	C	4.70039	-0.83050	0.01126
N	-1.43099	-6.09403	1.48992	C	-3.22789	-4.05619	0.87286	H	5.24729	-1.47230	0.44858
O	-1.86281	-6.03449	2.65727	H	-3.82619	-4.76883	0.91042	C	5.26182	0.20947	-0.67752
O	-2.11844	-6.59253	0.58324	C	-3.64016	-2.77175	1.22911	H	6.20743	0.28332	-0.73337
O	-0.29726	-5.65499	1.22187	H	-4.50779	-2.61195	1.52156	C	4.45848	1.15837	-1.29585
				C	-2.72588	-1.74564	1.13720	H	4.76665	1.87219	-1.69116
				H	-3.00082	-0.89008	1.37421	C	3.07512	1.02281	-1.17618
				S	0.50932	7.36698	0.67181	C	2.17011	2.05690	-1.72171
				O	0.67444	8.56407	-0.11868	C	2.67577	3.16439	-2.58474
				O	0.76012	6.15326	-0.06337	H	2.01492	3.36337	-3.28173
				O	-0.64972	7.34621	1.50233	H	3.51968	2.89258	-3.00377
				F	3.07068	7.44069	1.15025	H	2.82546	3.96268	-2.03757
				F	1.89559	6.39626	2.64224	C	-0.95154	3.23329	-0.75663

F	1.88044	8.55057	2.54275	C	-1.78005	4.31885	-0.99971
C	1.90884	7.43575	1.80655	H	-1.71788	4.80616	-1.81292
				C	-2.69743	4.67541	-0.02740
				H	-3.40314	5.56422	-0.13793
				C	-2.77766	3.88993	1.13687
				H	-3.40389	4.09819	1.81934
				C	-1.92843	2.81261	1.26731
				H	-1.99084	2.28470	2.05427
				S	-5.47196	2.35149	6.09754
				O	-6.63705	2.08708	5.30777
				O	-4.45250	1.38796	5.87481
				O	-5.73641	2.63474	7.48000
				C	-4.86122	3.83747	5.45929
				F	-4.62875	3.75999	4.13179
				F	-3.86541	4.34898	5.96360
				F	-5.91167	4.83033	5.57573