Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

o-Semiquinone radical anion isolated as an amorphous porous solid

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1 COMPUTATIONAL DETAILS OF THE G TENSOR

In the course of this work, the atomic contributions to the principal components of the **g** tensor were estimated. The g_{rs} components of the **g** tensor can be expressed as a sum of four contributions[1–5]:

$$g_{rs} = \delta_{rs} g_e + \delta_{rs} \Delta g^{RMC} + \Delta g_{rs}^{DSO} + \Delta g_{rs}^{PSO},$$

in which g_e = 2,002319 is of the free electron g-value, δ_{rs} is the Kronecker delta ensuring that g_e and Δg^{RMC}, that is the contribution to g_{rs} stemming from the relativistic mass correction, contribute only to the diagonal elements of the g matrix. The Δg^{DSO} and Δg^{PSO} contributions are the diamagnetic spin-orbit term (previously referred to as "gauge correction") and the paramagnetic spin-orbit term (or orbital Zeeman/spin-orbit coupling cross term). The exact definitions of Δg^{RMC}, Δg^{DSO} and Δg^{PSO} can be found in literature[1–5]. Δg^{RMC} and Δg^{DSO} tend to be of minor magnitude. Moreover, in the case of semiquinones their opposite signs lead to the mutual cancellation of these two terms (Table S3), whereby Δg^{PSO} determines the observed values of g_{rs}. Appropriate approximation of the atomic contributions to the **g** tensor can be thus obtained through the breakdown of the Δg^{PSO} term into contributions from each of the atoms. The mean-field approximation to the molecular spin-orbit coupling operator employed in this work [RI-SOMF(1X)][6] takes into account the multicenter terms (except for the exchange part), therefore these multicenter terms were neglected to obtain the atomic contributions. Considering that such an omission may cause significant errors[6,7], the Δg^{PSO} values calculated in the one-center approximation were compared with those calculated when taking the multicenter terms into account. The comparison (Table S3) revealed only slight deviations.

References

1 I. Ciofini, R. Reviakine, A. Arbuznikov and M. Kaupp, *Theor. Chem. Acc.*, 2004, **111**, 132–140.

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3 F. Neese, *J. Chem. Phys.*, 2001, **115**, 11080–11096.

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5 M. Kaupp, M. Bühl and V. G. Malkin, Eds., *Calculation of NMR and EPR Parameters. Theory and Applications*, Wiley-VCH, Weinheim, 2004.

6 F. Neese, *J. Chem. Phys.*, 2005, **122**, 034107.

7 M. Witwicki, *ChemPhysChem*, 2015, **16**, 1912–1925.

2 SUPPORTING FIGURES

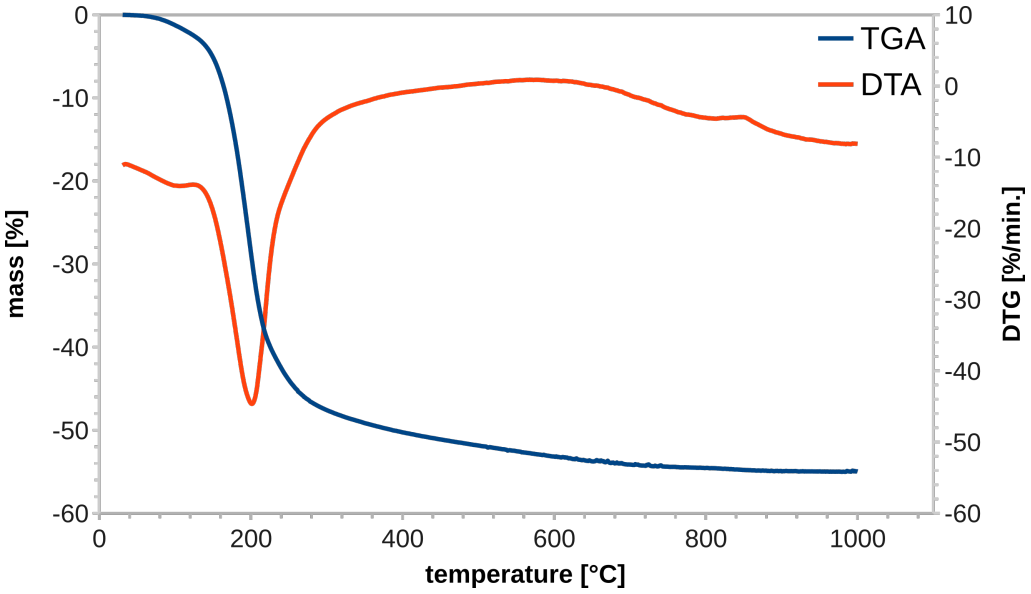


Fig. S1 Thermograms of TGA and DTA for **1**.

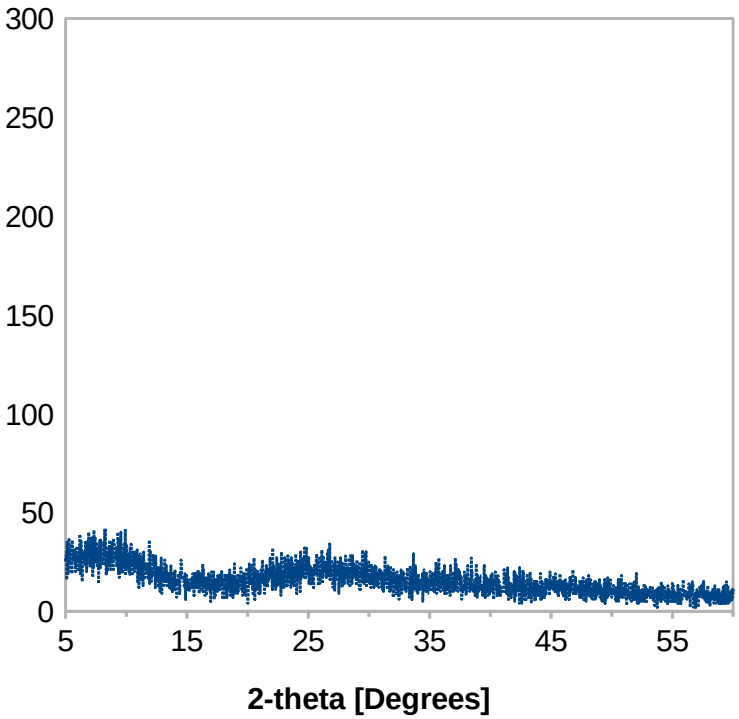


Fig. S2 Powder X-ray diffraction for **1**.

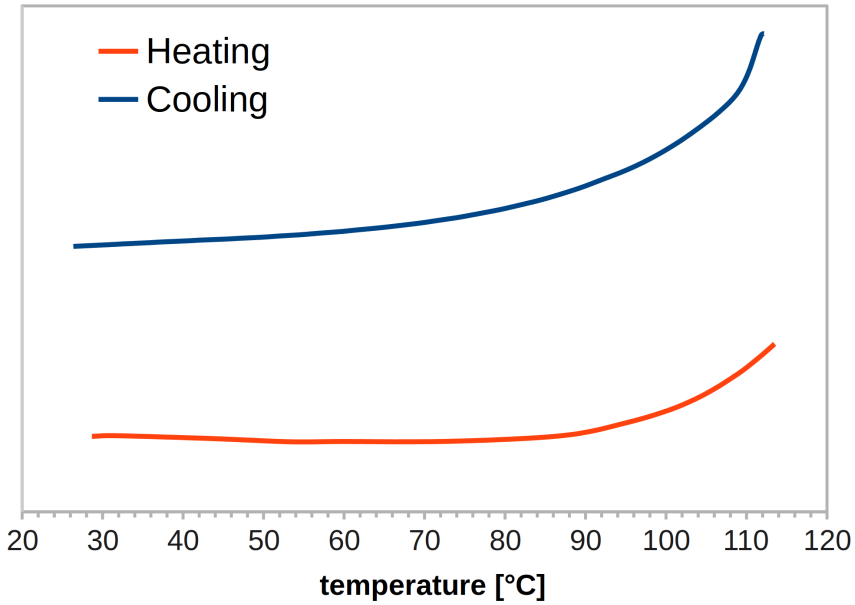


Fig. S3 DSC traces for **1** during the cooling and heating scans (rate 10 K/min).

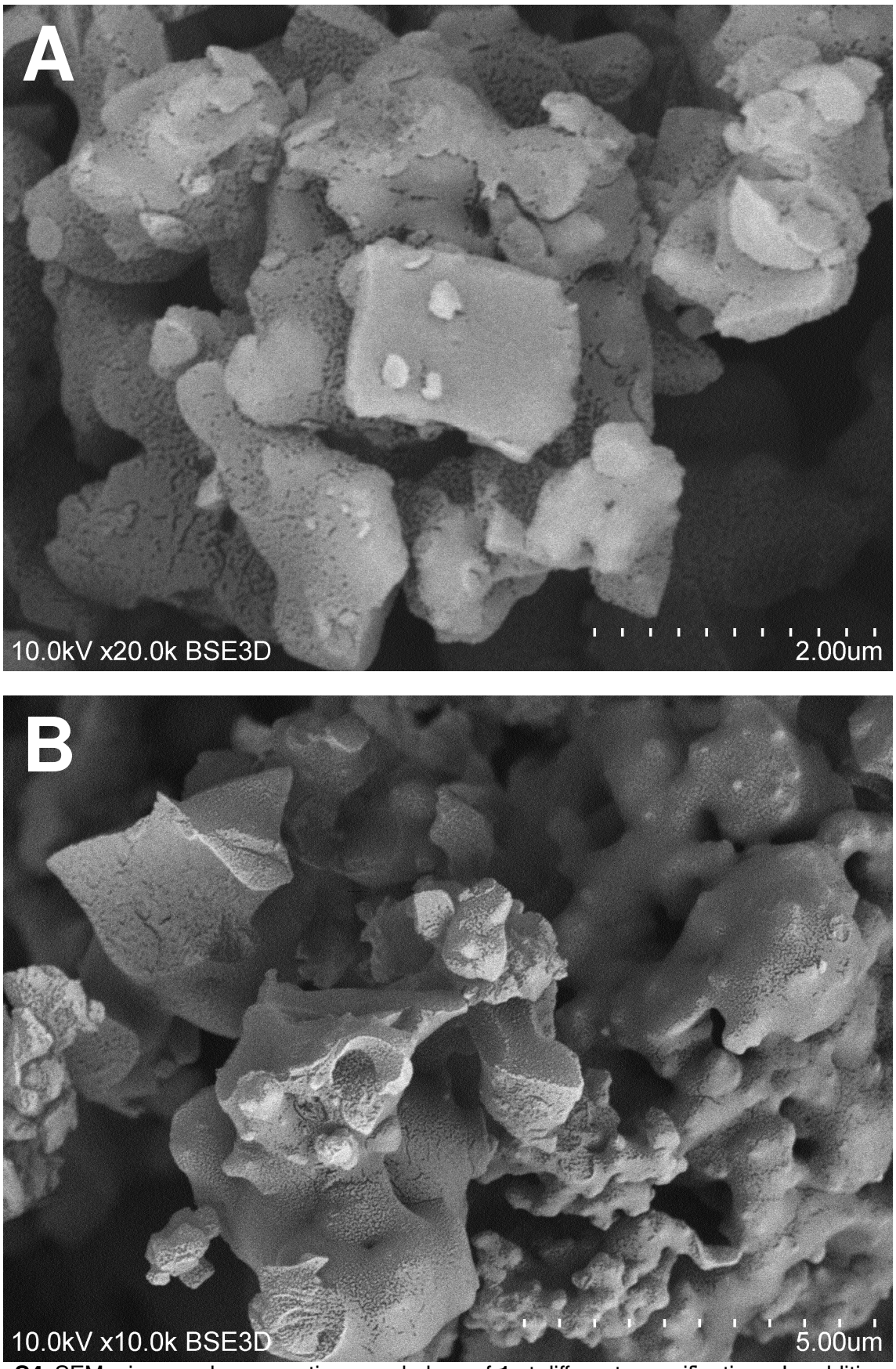


Fig. S4. SEM micrographs presenting morphology of **1** at different magnifications. In addition, the sizes of pour diameters are shown.

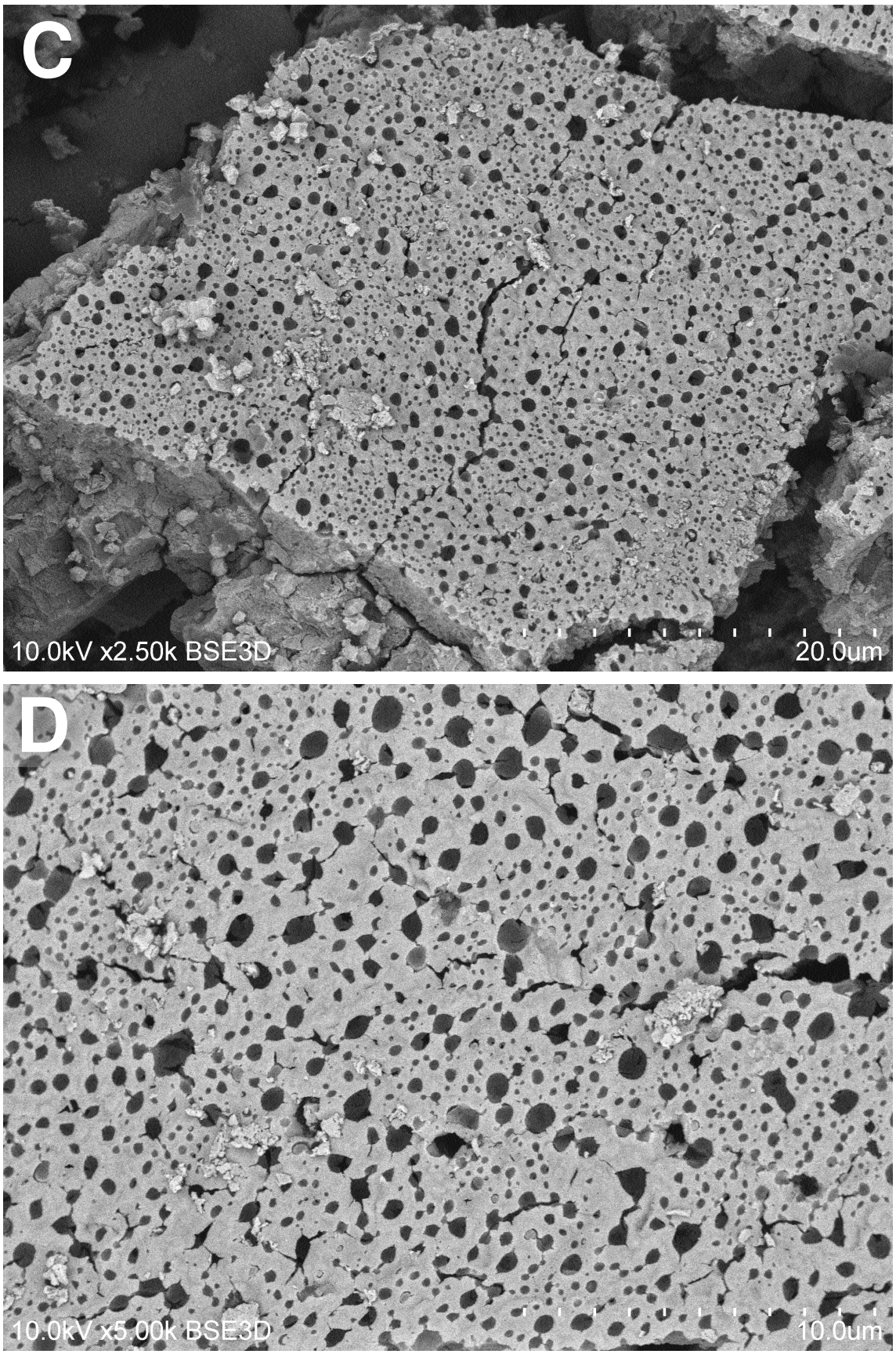
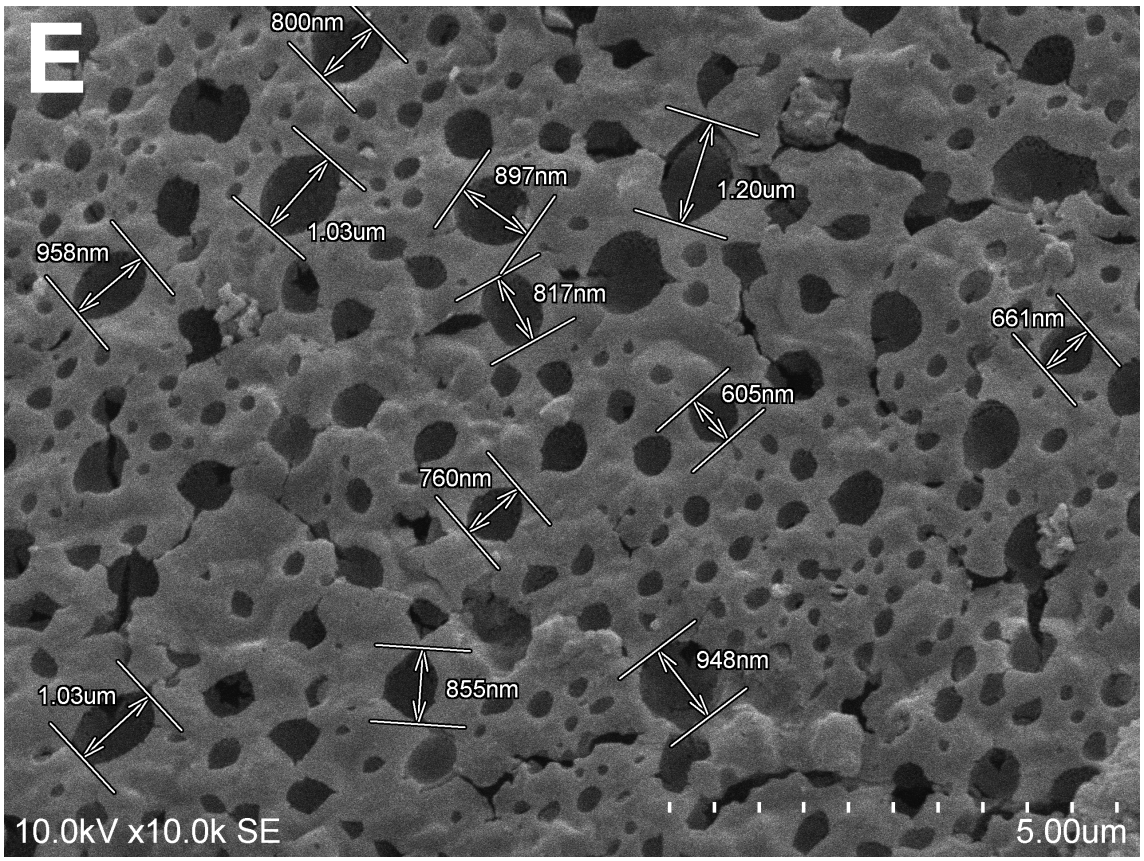
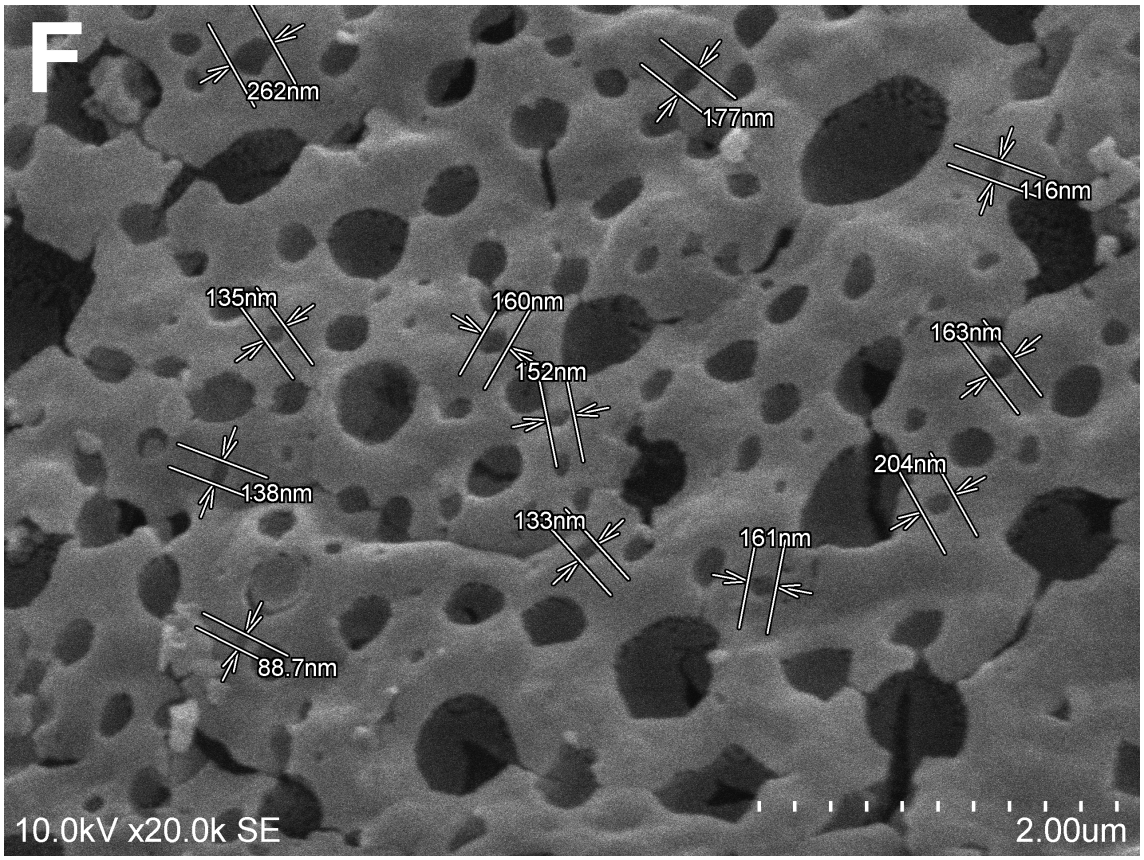


Fig. S4 Continued.





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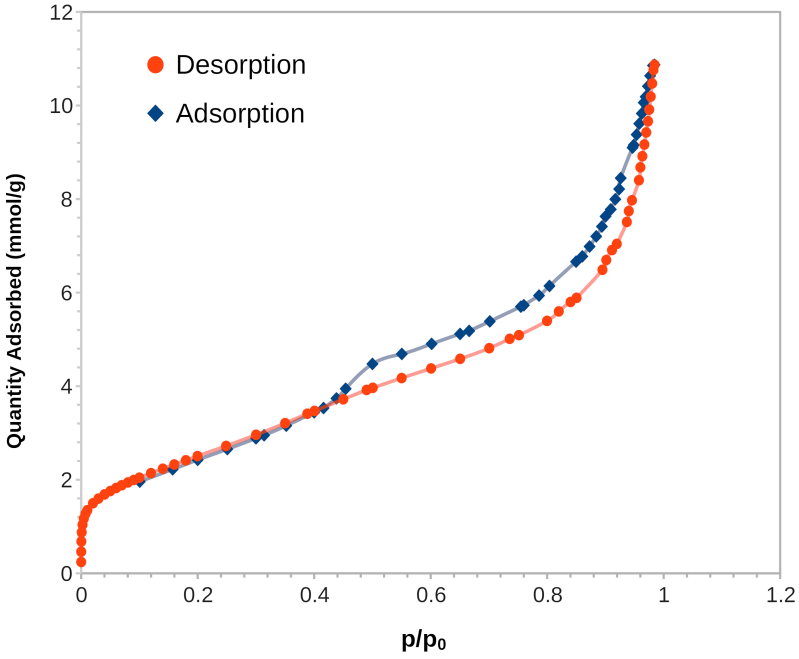


Fig. S5 N_2 adsorption isotherms measured at 77 K for **1**.

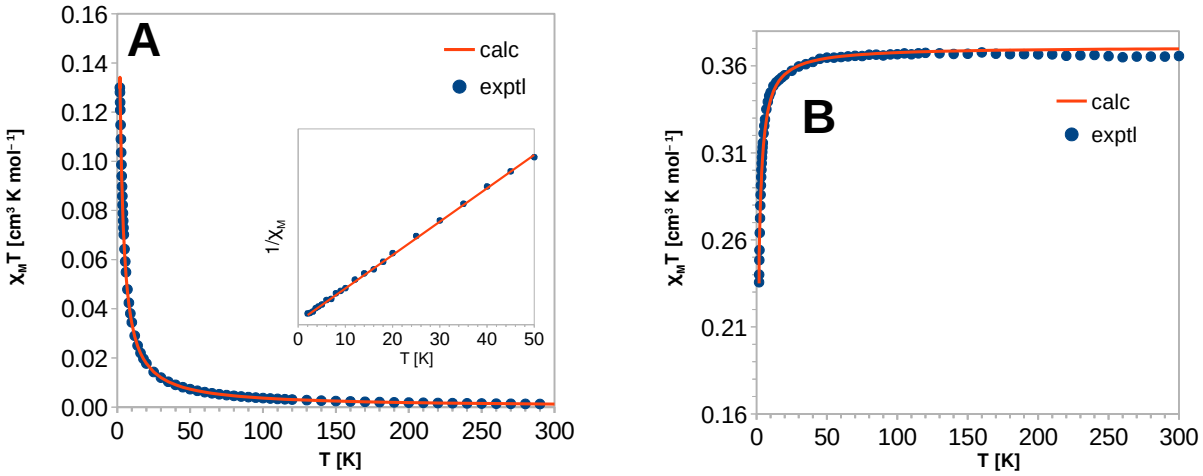


Fig. S6 Temperature dependence of χ_M for **1**, the inset shows $1/\chi_M$ (A) and the product $\chi_M T$ with a fit to the Curie-Weiss law (B).

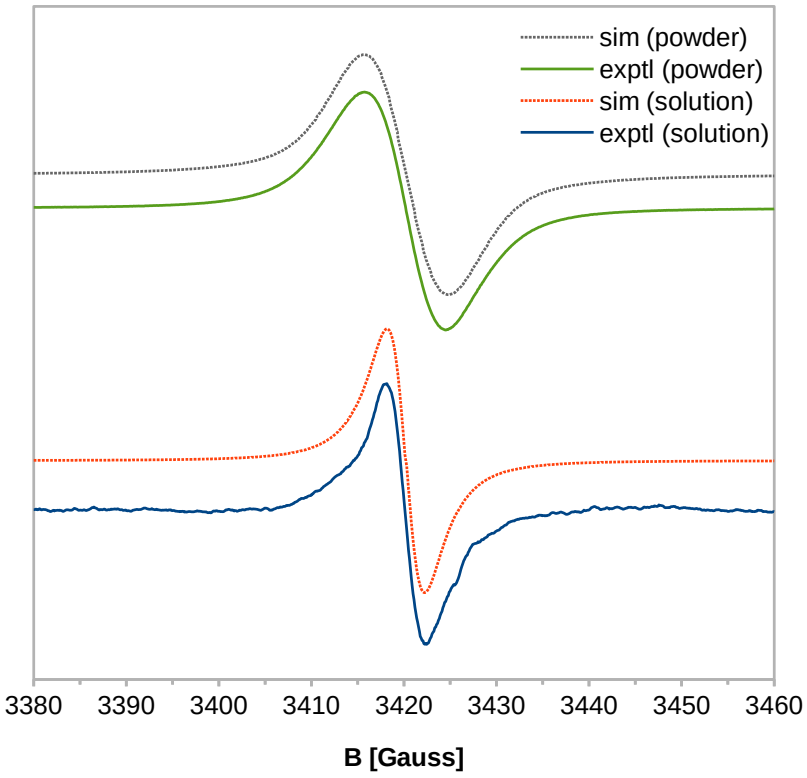


Fig. S7 X-band (~9.7 GHz) EPR spectra of **1** recorded at 77 K for powder (green) and frozen methanol solution (blue).

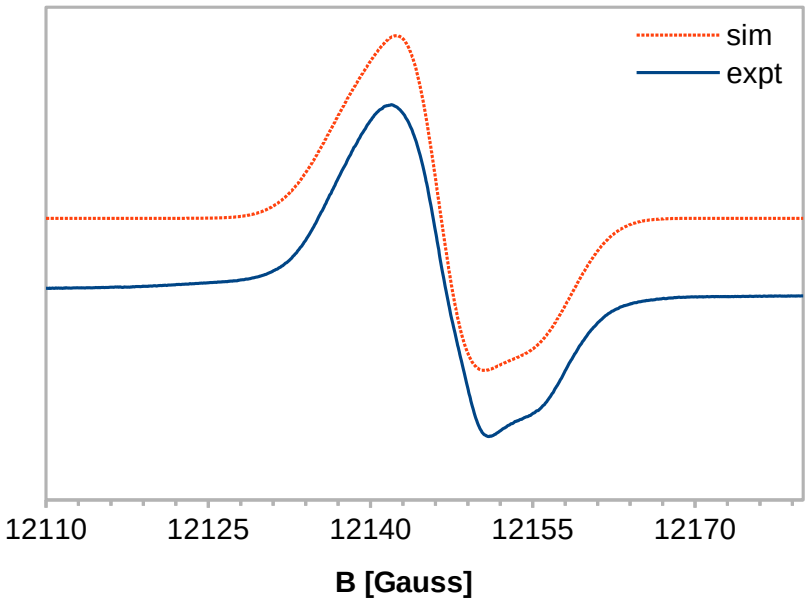


Fig. S8 Q-band (~34 GHz) EPR spectra of **1** recorded at 110 K for powder.

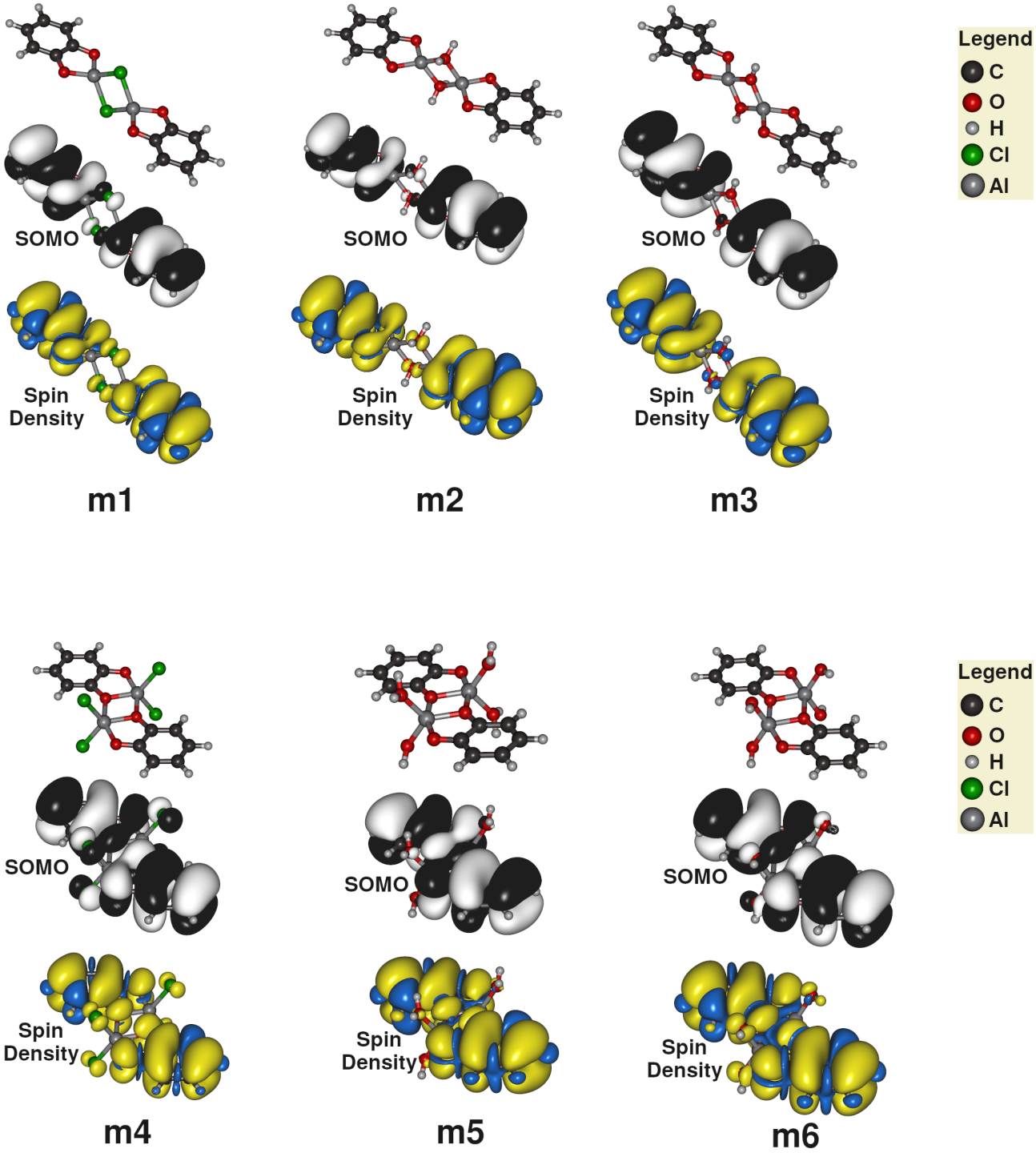
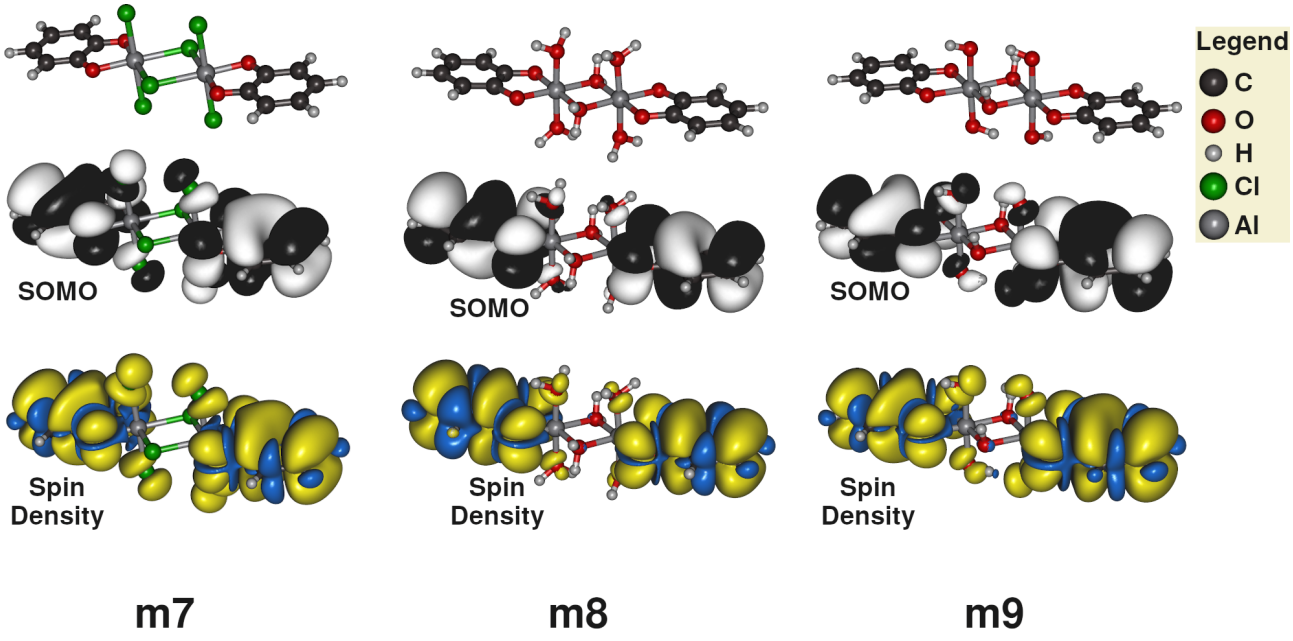
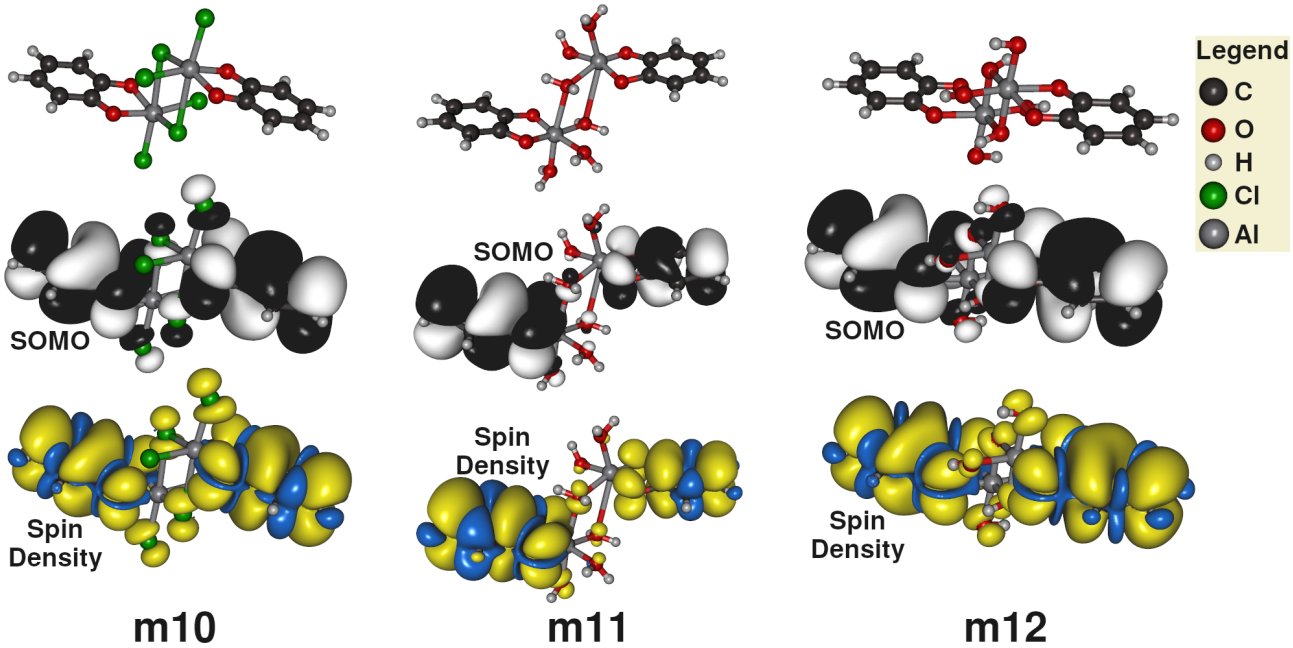


Fig. S9 Molecular models of the Al radical complex (**1**) optimized at the BP86/def2-TZVP level. Singly-occupied molecular orbitals (contoured at isovalue 10^{-2}) and spin density (contoured at isovalue 10^{-4}) calculated at the B3LYP/IGLO-III level.





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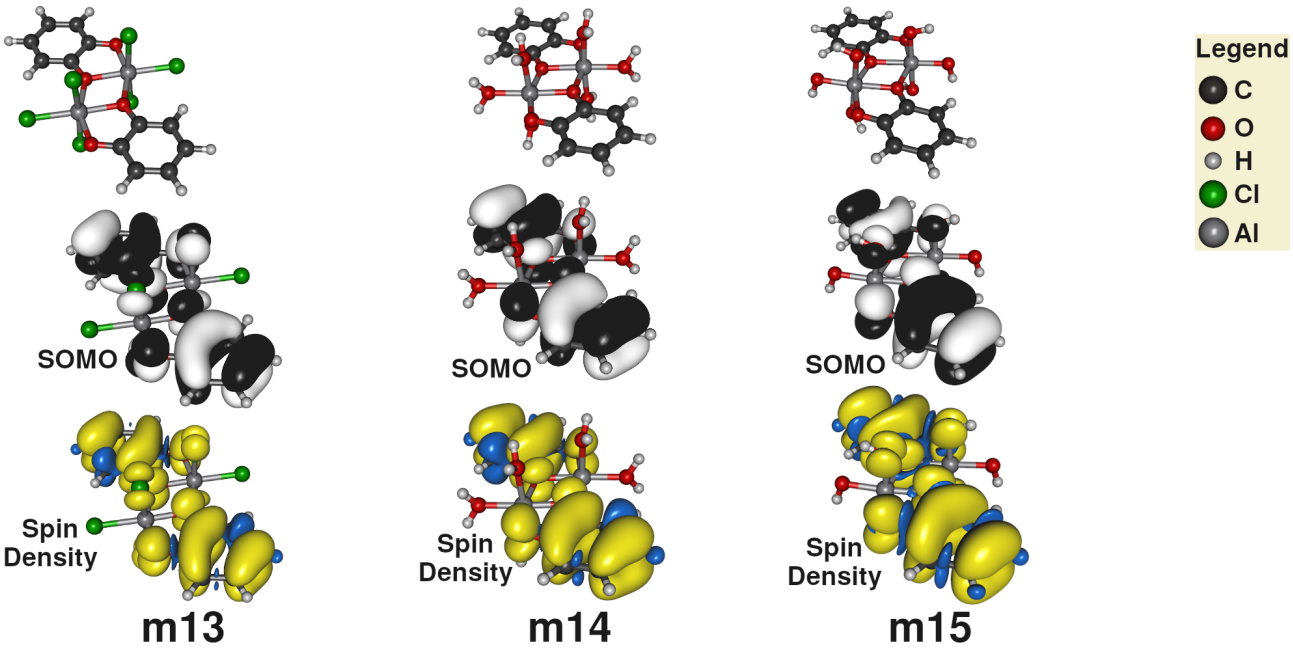

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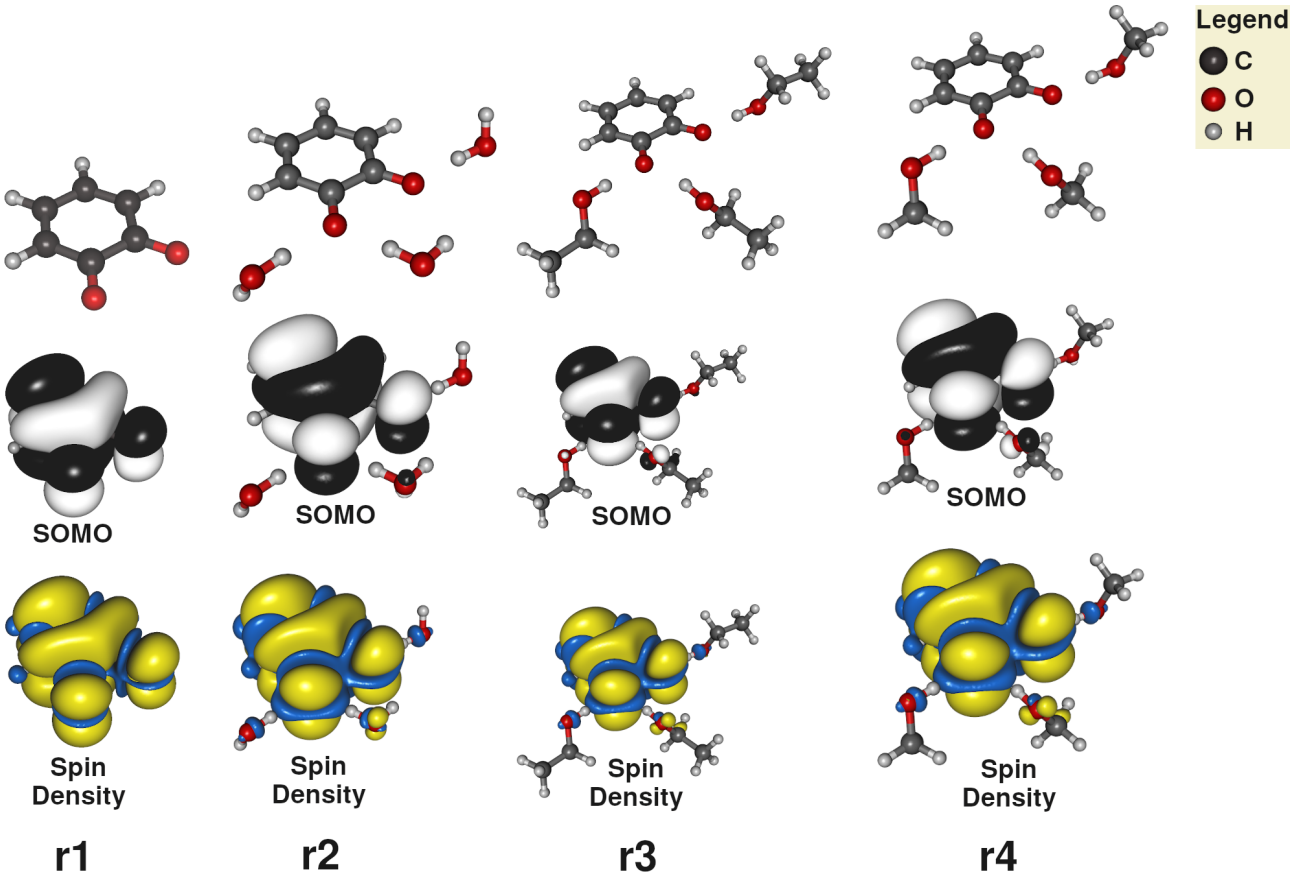

Fig. S10 Molecular models of o-semiquinone with hydrogen bonded solvent molecules optimized at the BP86/def2-TZVP level. Singly-occupied molecular orbitals (contoured at isovalue 10^{-2}) and spin density (contoured at isovalue 10^{-4}) calculated at the B3LYP/IGLO-III level.

3 SUPPORTING TABLES

Table S1 The principal components of the g tensors calculated at the DFT level.

model	c.n.	composition	basis set	UB3LYP				UPBE0				TPSS0			
				g_z	g_y	g_x	g_{iso}	g_z	g_y	g_x	g_{iso}	g_z	g_y	g_x	g_{iso}
m1	4	$[Al_2(sq)(ct)(Cl)_2]^{\bullet,+}$	IGLO-II	2.00116	2.00484	2.00488	2.00363	2.00122	2.00483	2.00484	2.00363	2.00131	2.00464	2.00472	2.00356
			IGLO-III	2.00104	2.00480	2.00491	2.00358	2.00111	2.00476	2.00490	2.00359	2.00121	2.00458	2.00480	2.00353
m2	4	$[Al_2(sq)(ct)(H_2O)_2]^{\bullet,3+}$	IGLO-II	2.00224	2.00440	2.00441	2.00368	2.00230	2.00412	2.00425	2.00356	2.00231	2.00392	2.00415	2.00346
			IGLO-III	2.00225	2.00429	2.00448	2.00367	2.00230	2.00405	2.00434	2.00357	2.00230	2.00387	2.00424	2.00347
m3	4	$[Al_2(sq)(ct)(OH)_2]^{\bullet,+}$	IGLO-II	2.00210	2.00465	2.00503	2.00393	2.00212	2.00464	2.00500	2.00392	2.00213	2.00455	2.00480	2.00383
			IGLO-III	2.00208	2.00478	2.00493	2.00393	2.00209	2.00478	2.00490	2.00392	2.00211	2.00469	2.00471	2.00384
m4	5	$[Al_2(sq)(ct)(Cl)_4]^{\bullet,-}$	IGLO-II	2.00466	2.00493	2.00559	2.00506	2.00460	2.00466	2.00556	2.00494	2.00439	2.00452	2.00534	2.00475
			IGLO-III	2.00470	2.00475	2.00538	2.00494	2.00446	2.00471	2.00535	2.00484	2.00423	2.00461	2.00516	2.00466
m5	5	$[Al_2(sq)(ct)(H_2O)_4]^{\bullet,3+}$	IGLO-II	2.00246	2.00434	2.00496	2.00392	2.00246	2.00433	2.00492	2.00390	2.00245	2.00423	2.00475	2.00381
			IGLO-III	2.00246	2.00439	2.00485	2.00390	2.00241	2.00425	2.00471	2.00379	2.00238	2.00408	2.00453	2.00366
m6	5	$[Al_2(sq)(ct)(OH)_4]^{\bullet,-}$	IGLO-II	2.00267	2.00483	2.00610	2.00453	2.00252	2.00482	2.00596	2.00443	2.00240	2.00471	2.00560	2.00424
			IGLO-III	2.00263	2.00491	2.00587	2.00447	2.00242	2.00489	2.00568	2.00433	2.00235	2.00477	2.00537	2.00416
m7	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	IGLO-II	2.00013	2.00570	2.00993	2.00525	2.00052	2.00557	2.00786	2.00465	2.00077	2.00527	2.00730	2.00445
			IGLO-III	2.00012	2.00546	2.01021	2.00526	2.00051	2.00533	2.00828	2.00471	2.00076	2.00505	2.00770	2.00451
m8	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	IGLO-II	2.00229	2.00503	2.00662	2.00465	2.00232	2.00506	2.00608	2.00449	2.00233	2.00477	2.00585	2.00432
			IGLO-III	2.00230	2.00520	2.00641	2.00464	2.00232	2.00506	2.00608	2.00449	2.00233	2.00494	2.00574	2.00434
m9	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	IGLO-II	2.00172	2.00591	2.00704	2.00489	2.00196	2.00544	2.00686	2.00475	2.00201	2.00528	2.00650	2.00460
			IGLO-III	2.00186	2.00586	2.00676	2.00482	2.00197	2.00565	2.00669	2.00477	2.00152	2.00591	2.00674	2.00472
m10	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	IGLO-II	2.00176	2.00613	2.00645	2.00478	2.00173	2.00579	2.00607	2.00453	2.00179	2.00544	2.00580	2.00434
			IGLO-III	2.00175	2.00613	2.00661	2.00483	2.00172	2.00559	2.00645	2.00459	2.00178	2.00528	2.00614	2.00440
m11	6	$[Al_2(sq)(ct)(H_2O)_6]^{3+}$	IGLO-II	2.00233	2.00476	2.00516	2.00408	2.00231	2.00474	2.00501	2.00402	2.00231	2.00463	2.00475	2.00389
			IGLO-III	2.00232	2.00489	2.00505	2.00408	2.00231	2.00485	2.00491	2.00403	2.00231	2.00466	2.00474	2.00390
m12	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	IGLO-II	2.00215	2.00542	2.00716	2.00491	2.00223	2.00526	2.00687	2.00479	2.00224	2.00513	2.00651	2.00463
			IGLO-III	2.00215	2.00559	2.00694	2.00489	2.00222	2.00546	2.00669	2.00479	2.00223	2.00533	2.00635	2.00464
m13	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	IGLO-II	2.00283	2.00768	2.00868	2.00639	2.00286	2.00745	2.00777	2.00603	2.00270	2.00648	2.00748	2.00555
			IGLO-III	2.00277	2.00764	2.00788	2.00610	2.00258	2.00651	2.00811	2.00573	2.00222	2.00589	2.00762	2.00524
m14	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	IGLO-II	2.00237	2.00456	2.00524	2.00406	2.00238	2.00455	2.00519	2.00404	2.00237	2.00445	2.00501	2.00394
			IGLO-III	2.00237	2.00462	2.00515	2.00404	2.00237	2.00460	2.00511	2.00403	2.00236	2.00450	2.00494	2.00393
m15	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	IGLO-II	2.00257	2.00554	2.00736	2.00516	2.00253	2.00552	2.00734	2.00513	2.00238	2.00539	2.00683	2.00487
			IGLO-III	2.00246	2.00561	2.00706	2.00504	2.00234	2.00561	2.00688	2.00494	2.00225	2.00548	2.00643	2.00472
		experimental for complex (1)		***2.00204***	***2.00377***	***2.00455***	***2.00367***	***2.00204***	***2.00377***	***2.00455***	***2.00367***	***2.00204***	***2.00377***	***2.00455***	***2.00367***
r1	–	$sq^{\bullet,-}$	IGLO-II	2.00219	2.00639	2.00728	2.00529	2.00219	2.00642	2.00730	2.00530	2.00217	2.00618	2.00689	2.00508
	–		IGLO-III	2.00219	2.00620	2.00703	2.00514	2.00219	2.00623	2.00705	2.00516	2.00218	2.00601	2.00667	2.00495
r2	–	$sq^{\bullet,-} \times 3H_2O$	IGLO-II	2.00220	2.00595	2.00655	2.00490	2.00220	2.00594	2.00654	2.00489	2.00219	2.00574	2.00623	2.00472
	–		IGLO-III	2.00220	2.00583	2.00637	2.00480	2.00220	2.00583	2.00636	2.00480	2.00219	2.00563	2.00608	2.00463
r3	–	$sq^{\bullet,-} \times 3EtOH$	IGLO-II	2.00223	2.00589	2.00658	2.00490	2.00223	2.00587	2.00658	2.00489	2.00222	2.00568	2.00626	2.00472
	–		IGLO-III	2.00224	2.00587	2.00650	2.00487	2.00224	2.00586	2.00649	2.00486	2.00222	2.00567	2.00619	2.00469
r4	–	$sq^{\bullet,-} \times 3MeOH$	IGLO-II	2.00224	2.00592	2.00659	2.00491	2.00223	2.00590	2.00658	2.00491	2.00222	2.00571	2.00627	2.00473
	–		IGLO-III	2.00224	2.00587	2.00649	2.00487	2.00223	2.00586	2.00648	2.00486	2.00222	2.00567	2.00618	2.00469
		experimental for uncomplexed radical (2)		***2.00233***	***2.00534***	***2.00573***	***2.00469***	***2.00233***	***2.00534***	***2.00573***	***2.00469***	***2.00233***	***2.00534***	***2.00573***	***2.00469***

Table S2 The total Löwdin spin populations for selected groups of atoms calculated at the B3LYP/IGLO-III level.

model	c.n.	composition	On both Al atoms	On all O atoms	On O atoms in sq and ct	On O atoms in H_2O	On O atoms in OH^-	On Cl atoms	On O atoms in H-bonded molecules
m1	4	$[Al_2(sq)(ct)(Cl)_2]^{\bullet,+}$	0.004	0.293	0.293	–	–	0.007	–
m2	4	$[Al_2(sq)(ct)(H_2O)_2]^{\bullet,3+}$	0.009	0.255	0.252	0.003	–	–	–
m3	4	$[Al_2(sq)(ct)(OH)_2]^{\bullet,+}$	0.021	0.253	0.254	–	-0.002	–	–
m4	5	$[Al_2(sq)(ct)(Cl)_4]^{\bullet,-}$	0.000	0.355	0.355	–	–	0.015	–
m5	5	$[Al_2(sq)(ct)(H_2O)_4]^{\bullet,3+}$	0.005	0.285	0.284	0.001	–	–	–
m6	5	$[Al_2(sq)(ct)(OH)_4]^{\bullet,-}$	-0.001	0.400	0.390	–	0.010	–	–
m7	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	-0.007	0.456	0.456	–	–	0.048	–
m8	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	0.002	0.396	0.387	0.009	–	–	–
m9	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	-0.005	0.515	0.480	–	0.036	–	–
m10	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	0.000	0.416	0.416			0.022	–
m11	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	0.006	0.318	0.310	0.008	–	–	–
m12	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	-0.004	0.489	0.469	–	0.020	–	–
m13	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	-0.005	0.431	0.431	–	–	0.057	–
m14	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	0.005	0.320	0.320	0.000	–	–	–
m15	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	-0.011	0.548	0.486	–	0.063	–	–
r1	–	$sq^{\bullet,-}$	–	0.505	–	–	–	–	–
r2	–	$sq^{\bullet,-} \times 3H_2O$	–	0.486	–	–	–	–	0.000
r3	–	$sq^{\bullet,-} \times 3EtOH$	–	0.483	–	–	–	–	0.000
r4	–	$sq^{\bullet,-} \times 3MeOH$	–	0.482	–	–	–	–	0.000

Table S3 Various contributions to the principal components of the g tensor calculated at the UB3LYP/IGLO-III level.

model	c.n.	composition			g_z	g_y	g_x
m1	4	$[Al_2(sq)(ct)(Cl)_2]^{\bullet,+}$			2.00104	2.00480	2.00491
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00021	-0.00021	-0.00021
			Δg^{DSO}		0.00031	0.00015	0.00035
			Δg^{PSO}		-0.00138	0.00254	0.00245
			Δg^{PSO} /1-center/	*total*	-0.00137	0.00242	0.00238
				Al atoms	0.00001	-0.00005	-0.00010
				O atoms in sq and ct	0.00000	0.00265	0.00192
				C atoms	-0.00003	-0.00020	0.00049
				H atoms	0.00000	0.00000	0.00000
				Cl atoms	-0.00135	0.00001	0.00007
m2	4	$[Al_2(sq)(ct)(H_2O)_2]^{\bullet,3+}$			2.00225	2.00429	2.00448
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00020	-0.00020	-0.00020
			Δg^{DSO}		0.00028	0.00014	0.00032
			Δg^{PSO}		-0.00015	0.00203	0.00203
			Δg^{PSO} /1-center/	*total*	-0.00015	0.00191	0.00190
				Al atoms	0.00001	-0.00007	-0.00011
				O atoms in sq and ct	-0.00001	0.00219	0.00155
				C atoms	-0.00004	-0.00020	0.00048
				H atoms	0.00000	0.00000	0.00000
				O atoms in H_2O	-0.00011	0.00000	-0.00002
m3	4	$[Al_2(sq)(ct)(OH)_2]^{\bullet,+}$			2.00208	2.00478	2.00493
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00021	-0.00021	-0.00021
			Δg^{DSO}		0.00027	0.00031	0.00015
			Δg^{PSO}		-0.00030	0.00236	0.00267
			Δg^{PSO} /1-center/	*total*	-0.00032	0.00228	0.00256
				Al atoms	0.00001	-0.00009	-0.00005
				O atoms in sq and ct	0.00000	0.00190	0.00281
				C atoms	-0.00003	0.00049	-0.00019
				H atoms	0.00000	0.00000	0.00000
				O atoms in OH^-	-0.00030	-0.00001	0.00000

Table S3 Continued.

model	c.n.	composition			g_z	g_y	g_x
m4	5	$[Al_2(sq)(ct)(Cl)_4]^{\bullet,-}$			2.00470	2.00475	2.00538
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00022	-0.00022	-0.00022
			Δg^{DSO}		0.00032	0.00034	0.00017
			Δg^{PSO}		0.00228	0.00231	0.00310
			Δg^{PSO} /1-center/	*total*	0.00227	0.00232	0.00310
				Al atoms	0.00002	0.00000	-0.00001
				O atoms in sq and ct	0.00014	0.00181	0.00307
				C atoms	-0.00001	0.00032	0.00006
				H atoms	0.00000	0.00000	0.00000
				Cl atoms	0.00213	0.00019	-0.00001
m5	5	$[Al_2(sq)(ct)(H_2O)_4]^{\bullet,3+}$			2.00246	2.00439	2.00485
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00020	-0.00020	-0.00020
			Δg^{DSO}		0.00028	0.00032	0.00016
			Δg^{PSO}		0.00006	0.00196	0.00258
			Δg^{PSO} /1-center/	*total*	0.00006	0.00198	0.00240
				Al atoms	0.00001	-0.00001	-0.00001
				O atoms in sq and ct	0.00000	0.00170	0.00239
				C atoms	-0.00003	0.00030	0.00002
				H atoms	0.00000	0.00000	0.00000
				O atoms in H_2O	0.00008	0.00000	0.00001
m6	5	$[Al_2(sq)(ct)(OH)_4]^{\bullet,-}$			2.00263	2.00491	2.00587
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00022	-0.00022	-0.00022
			Δg^{DSO}		0.00027	0.00028	0.00019
			Δg^{PSO}		0.00027	0.00254	0.00358
			Δg^{PSO} /1-center/	*total*	0.00026	0.00252	0.00349
				Al atoms	0.00002	0.00000	0.00000
				O atoms in sq and ct	0.00001	0.00201	0.00363
				C atoms	-0.00002	0.00046	-0.00014
				H atoms	0.00000	0.00000	0.00000
				O atoms in OH^-	0.00026	0.00005	-0.00001

Table S3 Continued.

model	c.n.	composition			g_z	g_y	g_x
m7	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$			2.00012	2.00546	2.01021
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00024	-0.00024	-0.00024
			Δg^{DSO}		0.00042	0.00020	0.00045
			Δg^{PSO}		-0.00238	0.00319	0.00768
			Δg^{PSO} /1-center/	*total*	-0.00237	0.00306	0.00771
				Al atoms	0.00002	-0.00001	-0.00001
				O atoms in sq and ct	0.00002	0.00453	0.00254
				C atoms	-0.00002	-0.00018	0.00038
				H atoms	0.00000	0.00000	0.00000
				Cl atoms	-0.00238	-0.00128	0.00480
m8	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$			2.00230	2.00520	2.00641
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00022	-0.00022	-0.00022
			Δg^{DSO}		0.00034	0.00037	0.00016
			Δg^{PSO}		-0.00014	0.00273	0.00415
			Δg^{PSO} /1-center/	*total*	-0.00015	0.00269	0.00403
				Al atoms	0.00001	-0.00005	-0.00006
				O atoms in sq and ct	0.00001	0.00220	0.00434
				C atoms	-0.00003	0.00045	-0.00017
				H atoms	0.00000	0.00000	0.00000
				O atoms in H_2O	-0.00014	0.00008	-0.00008
m9	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$			2.00186	2.00586	2.00676
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00024	-0.00024	-0.00024
			Δg^{DSO}		0.00032	0.00035	0.00018
			Δg^{PSO}		-0.00054	0.00343	0.00449
			Δg^{PSO} /1-center/	*total*	-0.00100	0.00350	0.00437
				Al atoms	0.00001	0.00001	0.00001
				O atoms in sq and ct	0.00001	0.00273	0.00472
				C atoms	-0.00003	0.00041	-0.00016
				H atoms	0.00000	0.00000	0.00000
				O atoms in OH^-	-0.00099	0.00035	-0.00020

Table S3 Continued.

model	c.n.	composition			g_z	g_y	g_x
m10	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$			2.00175	2.00613	2.00661
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00023	-0.00023	-0.00023
			Δg^{DSO}		0.00033	0.00022	0.00037
			Δg^{PSO}		-0.00067	0.00381	0.00414
			Δg^{PSO} /1-center/	*total*	-0.00066	0.00373	0.00406
				Al atoms	0.00000	-0.00005	-0.00003
				O atoms in sq and ct	0.00001	0.00395	0.00199
				C atoms	-0.00002	-0.00015	0.00040
				H atoms	0.00000	0.00000	0.00000
				Cl atoms	-0.00065	-0.00002	0.00170
m11	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$			2.00232	2.00489	2.00505
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00021	-0.00021	-0.00021
			Δg^{DSO}		0.00030	0.00033	0.00018
			Δg^{PSO}		-0.00009	0.00245	0.00275
			Δg^{PSO} /1-center/	*total*	-0.00009	0.00228	0.00265
				Al atoms	-0.00001	-0.00008	-0.00010
				O atoms in sq and ct	-0.00001	0.00185	0.00297
				C atoms	-0.00003	0.00043	-0.00018
				H atoms	0.00000	0.00000	0.00000
				O atoms in H_2O	-0.00004	0.00008	-0.00005
m12	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$			2.00215	2.00559	2.00694
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00023	-0.00023	-0.00023
			Δg^{DSO}		0.00029	0.00032	0.00020
			Δg^{PSO}		-0.00023	0.00319	0.00466
			Δg^{PSO} /1-center/	*total*	-0.00022	0.00322	0.00460
				Al atoms	0.00000	0.00001	0.00000
				O atoms in sq and ct	0.00002	0.00263	0.00469
				C atoms	-0.00002	0.00042	-0.00014
				H atoms	0.00000	0.00000	0.00000
				O atoms in OH^-	-0.00023	0.00016	0.00004

Table S3 Continued.

model	c.n.	composition			g_z	g_y	g_x
m13	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$			2.00277	2.00764	2.00788
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00024	-0.00024	-0.00024
			Δg^{DSO}		0.00035	0.00024	0.00034
			Δg^{PSO}		0.00034	0.00532	0.00545
			Δg^{PSO} /1-center/	*total*	0.00024	0.00520	0.00553
				Al atoms	0.00001	0.00000	0.00002
				O atoms in sq and ct	0.00001	0.00264	0.00305
				C atoms	-0.00002	0.00036	-0.00003
				H atoms	0.00000	0.00000	0.00000
				Cl atoms	0.00024	0.00220	0.00249
m14	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$			2.00237	2.00462	2.00515
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00021	-0.00021	-0.00021
			Δg^{DSO}		0.00031	0.00034	0.00016
			Δg^{PSO}		-0.00005	0.00217	0.00287
			Δg^{PSO} /1-center/	*total*	-0.00005	0.00224	0.00264
				Al atoms	0.00001	-0.00001	0.00000
				O atoms in sq and ct	0.00000	0.00189	0.00268
				C atoms	-0.00003	0.00034	-0.00004
				H atoms	0.00000	0.00000	0.00000
				O atoms in H_2O	-0.00004	0.00002	0.00000
m15	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$			2.00246	2.00561	2.00706
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00025	-0.00025	-0.00025
			Δg^{DSO}		0.00028	0.00027	0.00024
			Δg^{PSO}		-0.00019	0.00359	0.00459
			Δg^{PSO} /1-center/	*total*	0.00013	0.00316	0.00465
				Al atoms	0.00001	0.00002	0.00001
				O atoms in sq and ct	0.00004	0.00246	0.00451
				C atoms	-0.00002	0.00040	-0.00013
				H atoms	0.00000	0.00000	0.00000
				O atoms in OH^-	0.00010	0.00027	0.00026

Table S3 Continued.

model	c.n.	composition			g_z	g_y	g_x
r1	–	$sq^{\bullet,-}$			2.00219	2.00620	2.00703
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00023	-0.00023	-0.00023
			Δg^{DSO}		0.00013	0.00018	0.00015
			Δg^{PSO}		-0.00003	0.00393	0.00479
			Δg^{PSO} /1-center/	*total*	-0.00001	0.00380	0.00466
				O atoms in sq	-0.00001	0.00354	0.00485
				C atoms	0.00000	0.00026	-0.00019
				H atoms	0.00000	0.00000	0.00000
r2	–	$sq^{\bullet,-} \times 3H_2O$			2.00220	2.00583	2.00637
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00023	-0.00023	-0.00023
			Δg^{DSO}		0.00012	0.00017	0.00015
			Δg^{PSO}		-0.00001	0.00358	0.00413
			Δg^{PSO} /1-center/	*total*	0.00000	0.00345	0.00407
				O atoms in sq	-0.00001	0.00328	0.00419
				C atoms	-0.00001	0.00021	-0.00010
				H atoms	0.00000	0.00000	0.00000
				O atoms in H_2O	0.00001	-0.00004	-0.00002
r3	–	$sq^{\bullet,-} \times 3$EtOH			2.00224	2.00587	2.00650
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00023	-0.00023	-0.00023
			Δg^{DSO}		0.00013	0.00018	0.00015
			Δg^{PSO}		0.00002	0.00360	0.00426
			Δg^{PSO} /1-center/	*total*	0.00003	0.00350	0.00422
				O atoms in sq	0.00000	0.00327	0.00434
				C atoms	-0.00001	0.00025	-0.00010
				H atoms	0.00000	0.00000	0.00000
				O atoms in EtOH	0.00004	-0.00002	-0.00002
r4	–	$sq^{\bullet,-} \times 3$MeOH			2.00224	2.00587	2.00649
			g_e		2.00232	2.00232	2.00232
			Δg^{RMC}		-0.00023	-0.00023	-0.00023
			Δg^{DSO}		0.00012	0.00017	0.00015
			Δg^{PSO}		0.00002	0.00360	0.00425
			Δg^{PSO} /1-center/	*total*	0.00003	0.00348	0.00419
				O atoms in sq	0.00000	0.00327	0.00432
				C atoms	-0.00001	0.00023	-0.00011
				H atoms	0.00000	0.00000	0.00000
				O atoms in MeOH	0.00004	-0.00002	-0.00003

Table S4 The isotropic hyperfine coupling constant due to ^{27}Al (a_{Al}) calculated at the DFT and DLPNO-CCSD level. The values are given in MHz.

model	c.n.	composition	basis set	B3LYP	PBE0	TPSS0	wB97X	B2PLYP	mPW2PLYP	DSD-BLYP	DLPNO-CCSD
m1	4	$[Al_2(sq)(ct)(Cl)_2]^{\bullet,+}$	IGLO-II	-8.28	-8.39	-7.13	-6.17	-8.29	-8.64	-6.58	-9.27
			IGLO-III	-7.84	-7.98	-6.80	-5.79	-7.78	-8.13	-6.13	–
m2	4	$[Al_2(sq)(ct)(H_2O)_2]^{\bullet,3+}$	IGLO-II	-8.21	-5.94	-4.58	-6.44	-6.10	-6.32	-6.45	-4.49
			IGLO-III	-7.26	-5.51	-4.26	-6.13	-5.66	-5.89	-6.07	–
m3	4	$[Al_2(sq)(ct)(OH)_2]^{\bullet,+}$	IGLO-II	-7.68	-7.71	-6.75	-6.03	-5.80	-5.99	-6.22	-0.22
			IGLO-III	-7.14	-7.17	-6.29	-5.60	-5.39	-5.57	-5.73	–
m4	5	$[Al_2(sq)(ct)(Cl)_4]^{\bullet,-}$	IGLO-II	-6.61	-6.75	-5.82	-6.28	-5.93	-6.00	-5.53	-6.66
			IGLO-III	-6.27	-6.41	-5.52	-5.84	-5.61	-5.72	-5.24	–
m5	5	$[Al_2(sq)(ct)(H_2O)_4]^{\bullet,3+}$	IGLO-II	-5.38	-4.87	-4.09	-4.53	-4.39	-4.48	-4.04	-3.21
			IGLO-III	-5.12	-4.47	-3.82	-4.24	-4.15	-4.24	-3.80	–
m6	5	$[Al_2(sq)(ct)(OH)_4]^{\bullet,-}$	IGLO-II	-5.98	-6.18	-5.46	-5.80	-5.67	-5.72	-5.17	-7.07
			IGLO-III	-5.63	-5.70	-5.02	-5.30	-5.26	-5.32	-4.85	–
m7	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	IGLO-II	-9.89	-9.18	-7.92	-9.34	-8.79	-8.92	-10.15	-11.14
			IGLO-III	-9.22	-8.48	-7.31	-8.56	-8.19	-8.29	-9.35	–
m8	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	IGLO-II	-7.19	-6.35	-5.56	-6.55	-7.11	-7.11	-7.15	-6.56
			IGLO-III	-5.78	-5.92	-5.20	-6.05	-6.59	-6.59	-6.67	–
m9	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	IGLO-II	-9.06	-6.36	-5.62	-5.99	-5.62	-5.71	-6.06	-7.50
			IGLO-III	-8.04	-5.70	-5.05	-5.37	-5.12	-5.20	-5.59	–
m10	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	IGLO-II	-7.18	-6.36	-5.37	-6.57	-6.12	-6.29	-6.40	-6.44
			IGLO-III	-6.73	-5.97	-5.03	-6.08	-5.77	-5.92	-6.09	–
m11	6	$[Al_2(sq)(ct)(H_2O)_6]^{3+}$	IGLO-II	-6.57	-5.88	-4.87	-6.00	-6.06	-6.17	-6.79	-4.99
			IGLO-III	-6.03	-5.53	-4.60	-5.69	-5.74	-5.83	-6.34	–
m12	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	IGLO-II	-5.35	-4.90	-4.32	-4.69	-4.31	-4.41	-4.76	-4.80
			IGLO-III	-4.79	-4.47	-3.93	-4.28	-3.97	-4.81	-4.37	–
m13	6	$[Al_2(sq)(ct)(Cl)_6]^{\bullet,3-}$	IGLO-II	-8.25	-8.43	-7.43	-8.99	-8.26	-8.37	-7.74	-7.15
			IGLO-III	-7.72	-7.97	-6.93	-8.25	-7.70	-7.79	-7.27	–
m14	6	$[Al_2(sq)(ct)(H_2O)_6]^{\bullet,3+}$	IGLO-II	-6.97	-6.96	-6.21	-6.21	-5.97	-6.09	-5.67	-6.60
			IGLO-III	-6.61	-6.61	-5.91	-5.78	-5.61	-5.72	-5.33	–
m15	6	$[Al_2(sq)(ct)(OH)_6]^{\bullet,3-}$	IGLO-II	-6.81	-7.00	-6.01	-6.56	-6.16	-6.24	-6.30	-5.39
			IGLO-III	-6.20	-6.28	-5.47	-5.90	-5.61	-5.69	-5.72	–
		experimental for complex 1		*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*

Table S4 The isotropic hyperfine coupling constant due to ^{1}H calculated at the DFT and DLPNO-CCSD level. The values are given in MHz.

model	basis set	B3LYP		PBE0		TPSS0		wB97X		B2PLYP		mPW2PLYP		DSD-BLYP		DLPNO-CCSD	
		H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2	H1	H2
m1	IGLO-II	-0.51	-0.90	-0.81	-1.05	-0.85	-1.16	-0.91	-1.05	-0.25	-0.95	-0.42	-1.00	-0.32	-1.06	-0.79	-1.14
	IGLO-III	-0.43	-0.86	-0.66	-1.00	-0.64	-1.06	-0.73	-0.93	-0.06	-0.88	-0.23	-0.92	-0.28	-1.00	–	–
m2	IGLO-II	-0.54	-1.13	-0.93	-1.33	-1.08	-1.41	-0.98	-1.42	-0.22	-1.02	-0.46	-1.13	-0.28	-0.91	-0.90	-0.99
	IGLO-III	-0.43	-0.86	-0.77	-0.86	-0.72	-1.20	-0.87	-0.96	-0.01	-0.99	-0.23	-1.12	-0.38	-0.85	–	–
m3	IGLO-II	-0.37	-0.73	-0.55	-0.82	-0.61	-0.98	-0.66	-0.89	-0.15	-0.80	-0.30	-0.82	-0.19	-0.87	-0.53	-0.90
	IGLO-III	-0.26	-0.72	-0.49	-0.85	-0.39	-0.89	-0.48	-0.74	0.02	-0.69	-0.12	-0.78	-0.15	-0.78	–	–
m4	IGLO-II	-0.42	-1.03	-0.69	-1.16	-0.76	-1.32	-0.88	-1.15	-0.16	-1.10	-0.35	-1.11	-0.31	-1.21	-0.71	-1.27
	IGLO-III	-0.43	-1.01	-0.57	-1.10	-0.56	-1.17	-0.72	-1.02	-0.02	-1.06	-0.15	-1.01	-0.24	-1.15	–	–
m5	IGLO-II	-0.45	-0.90	-0.56	-0.91	-0.62	-1.01	-0.73	-1.04	-0.14	-0.89	-0.26	-1.05	-0.24	-1.18	-0.57	-1.13
	IGLO-III	-0.62	-0.99	-0.96	-1.19	-0.95	-0.95	-0.83	-1.04	0.05	-1.12	-0.21	-1.28	-0.25	-1.08	–	–
m6	IGLO-II	-0.37	-0.75	-0.57	-0.99	-0.67	-1.01	-0.70	-0.97	-0.12	-0.90	-0.25	-0.88	-0.23	-0.92	-0.62	-1.02
	IGLO-III	-0.34	-0.77	-0.50	-0.91	-0.52	-0.96	-0.50	-0.84	-0.05	-0.80	-0.15	-0.81	-0.21	-0.91	–	–
m7	IGLO-II	-0.49	-0.72	-0.76	-0.81	-0.80	-0.92	-0.84	-0.86	-0.22	-0.82	-0.41	-0.86	-0.25	-0.83	-0.74	-0.96
	IGLO-III	-0.38	-0.67	-0.65	-0.78	-0.59	-0.88	-0.66	-0.73	-0.06	-0.77	-0.16	-0.75	-0.22	-0.78	–	–
m8	IGLO-II	-0.47	-0.80	-0.83	-1.01	-0.84	-1.22	-0.87	-1.26	-0.21	-1.27	-0.33	-0.94	-0.34	-1.00	-0.82	-1.05
	IGLO-III	-0.28	-0.77	-0.71	-1.22	-0.51	-1.02	-0.74	-1.14	-0.08	-1.21	-0.23	-1.15	-0.25	-1.20	–	–
m9	IGLO-II	-0.39	-0.60	-0.53	-0.69	-0.58	-0.78	-0.67	-0.72	-0.14	-0.65	-0.22	-0.69	-0.20	-0.74	-0.53	-0.75
	IGLO-III	-0.30	-0.62	-0.46	-0.68	-0.48	-0.69	-0.50	-0.62	-0.07	-0.61	-0.15	-0.61	-0.22	-0.67	–	–
m10	IGLO-II	-0.54	-0.95	-0.80	-1.15	-0.89	-1.26	-0.89	-1.16	-0.21	-1.04	-0.38	-1.05	-0.30	-1.12	-0.79	-1.24
	IGLO-III	-0.38	-0.91	-0.63	-1.02	-0.62	-1.12	-0.74	-1.04	-0.03	-0.96	-0.22	-1.06	-0.28	-1.02	–	–
m11	IGLO-II	-0.55	-1.01	-0.79	-1.41	-1.00	-1.36	-0.92	-1.43	-0.17	-1.19	-0.47	-1.29	-0.37	-1.30	-0.82	-1.41
	IGLO-III	-0.48	-0.99	-0.68	-1.29	-0.78	-1.50	-0.73	-1.10	0.05	-0.99	-0.25	-1.26	-0.32	-1.35	–	–
m12	IGLO-II	-0.33	-0.56	-0.47	-0.67	-0.59	-0.77	-0.56	-0.66	-0.16	-0.65	-0.28	-0.63	-0.16	-0.71	-0.49	-0.78
	IGLO-III	-0.26	-0.60	-0.40	-0.64	-0.38	-0.68	-0.47	-0.63	-0.01	-0.60	-0.13	-0.63	-0.13	-0.65	–	–
m13	IGLO-II	-0.48	-0.95	-0.78	-1.13	-0.79	-1.23	-0.92	-1.05	-0.17	-1.00	-0.34	-1.09	-0.26	-1.07	-0.82	-1.17
	IGLO-III	-0.41	-0.92	-0.66	-0.98	-0.62	-1.13	-0.69	-1.02	-0.08	-0.90	-0.20	-1.01	-0.22	-1.06	–	–
m14	IGLO-II	-0.62	-1.17	-0.79	-1.26	-0.90	-1.57	-1.02	-1.29	-0.14	-1.06	-0.52	-1.18	-0.26	-1.16	-1.00	-1.28
	IGLO-III	-0.23	-0.36	-0.26	-0.43	-0.24	-0.39	-0.33	-0.38	0.00	-0.30	-0.06	-0.35	-0.08	-0.33	–	–
m15	IGLO-II	-0.36	-0.61	-0.58	-0.64	-0.63	-0.77	-0.61	-0.65	-0.10	-0.57	-0.25	-0.67	-0.20	-0.67	-0.55	-0.76
	IGLO-III	-0.25	-0.56	-0.44	-0.64	-0.41	-0.66	-0.50	-0.62	-0.06	-0.60	-0.10	-0.65	-0.18	-0.60	–	–
r1	IGLO-II	-4.55	-8.06	-4.68	-8.54	-4.99	-9.21	-4.55	-8.13	-4.92	-9.37	-4.79	-9.37	-4.93	-10.31	-3.19	-9.86
	IGLO-III	-3.61	-8.12	-3.61	-8.64	-3.99	-9.05	-3.47	-7.83	-4.02	-9.31	-3.87	-9.33	-4.80	-10.29	–	–
r2	IGLO-II	-2.94	-8.56	-2.83	-9.17	-3.08	-9.96	-2.60	-8.79	-3.47	-9.65	-3.22	-9.75	-2.52	-10.97	-1.95	-10.28
	IGLO-III	-2.42	-8.53	-2.23	-9.15	-2.59	-9.65	-2.05	-8.37	-3.04	-9.49	-2.79	-9.60	-2.07	-10.87	–	–
r3	IGLO-II	-3.15	-8.51	-3.07	-9.10	-3.37	-9.85	-2.85	-8.72	-3.58	-9.72	-3.35	-9.80	-2.48	-10.65	-2.25	-10.28
	IGLO-III	-2.68	-8.44	-2.51	-9.05	-2.90	-9.52	-2.33	-8.26	-3.18	-9.54	-2.96	-9.63	-2.27	-10.64	–	–
r4	IGLO-II	-3.09	-8.53	-3.01	-9.13	-3.30	-9.89	-2.79	-8.75	-3.53	-9.73	-3.30	-9.82	-2.26	-10.75	-2.22	-10.29
	IGLO-III	-2.61	-8.47	-2.45	-9.09	-2.83	-9.56	-2.27	-8.29	-3.14	-9.56	-2.91	-9.65	-2.16	-10.71	–	–
experimental for uncomplexed radical		***2.1***	***10.3***	***2.1***	***10.3***	***2.1***	***10.3***	***2.1***	***10.3***	***2.1***	***10.3***	***2.1***	***10.3***	***2.1***	***10.3***	***2.1***	***10.3***

Table S5 The principal components of the g tensors calculated at the DFT level for the S = 1 counterparts of **m2**, **m5**, **m8**, **m11** and **m14**.

model	c.n.	composition	basis set	UB3LYP				UPBE0				TPSS0			
				g_z	g_y	g_x	g_{iso}	g_z	g_y	g_x	g_{iso}	g_z	g_y	g_x	g_{iso}
m2(S=1)	4	$[Al_2(sq)_2(H_2O)_2]^{\bullet\bullet,4+}$	IGLO-II	2.00231	2.00412	2.00421	2.00355	2.00232	2.00403	2.00419	2.00351	2.00232	2.00385	2.00410	2.00342
			IGLO-III	2.00231	2.00406	2.00431	2.00356	2.00232	2.00397	2.00429	2.00353	2.00231	2.00380	2.00419	2.00344
m5(S=1)	5	$[Al_2(sq)_2(H_2O)_4]^{\bullet\bullet,4+}$	IGLO-II	2.00236	2.00414	2.00479	2.00377	2.00236	2.00410	2.00473	2.00373	2.00236	2.00398	2.00455	2.00363
			IGLO-III	2.00235	2.00416	2.00469	2.00373	2.00236	2.00410	2.00463	2.00370	2.00235	2.00397	2.00448	2.00360
m8(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet\bullet,4+}$	IGLO-II	2.00231	2.00490	2.00641	2.00454	2.00232	2.00487	2.00628	2.00449	2.00232	2.00477	2.00592	2.00434
			IGLO-III	2.00231	2.00509	2.00629	2.00456	2.00232	2.00506	2.00616	2.00451	2.00232	2.00495	2.00582	2.00436
m11(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet\bullet,4+}$	IGLO-II	2.00234	2.00461	2.00490	2.00395	2.00235	2.00458	2.00478	2.00390	2.00235	2.00447	2.00454	2.00379
			IGLO-III	2.00235	2.00471	2.00482	2.00396	2.00235	2.00466	2.00472	2.00391	2.00235	2.00446	2.00458	2.00380
m14(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet\bullet,4+}$	IGLO-II	2.00235	2.00452	2.00502	2.00396	2.00236	2.00447	2.00495	2.00393	2.00236	2.00435	2.00474	2.00382
			IGLO-III	2.00235	2.00456	2.00491	2.00394	2.00235	2.00450	2.00484	2.00390	2.00235	2.00436	2.00467	2.00379
		experimental for complex (1)		***2.00204***	***2.00377***	***2.00455***	***2.00367***	***2.00204***	***2.00377***	***2.00455***	***2.00367***	***2.00204***	***2.00377***	***2.00455***	***2.00367***

Table S6 The isotropic hyperfine coupling constant due to ^{27}Al (a_{Al}) calculated at the DFT and DLPNO-CCSD level for the S = 1 counterparts of **m2**, **m5**, **m8**, **m11** and **m14**. The values are given in MHz.

model	c.n.	composition	basis set	B3LYP	PBE0	TPSS0	wB97X	B2PLYP	mPW2PLYP	DSD-BLYP	DLPNO-CCSD
m2(S=1)	4	$[Al_2(sq)_2(H_2O)_2]^{\bullet\bullet,4+}$	IGLO-II	-7.06	-6.30	-6.08	-7.27	-6.63	-6.93	-7.17	-6.26
			IGLO-III	-6.66	-5.93	-5.79	-6.96	-6.66	-6.61	-7.17	–
m5(S=1)	5	$[Al_2(sq)_2(H_2O)_4]^{\bullet\bullet,4+}$	IGLO-II	-7.29	-7.05	-6.78	-7.36	-6.98	-7.16	-6.54	-6.75
			IGLO-III	-6.86	-6.61	-6.58	-6.89	-6.86	-6.74	-6.54	–
m8(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet\bullet,4+}$	IGLO-II	-8.53	-8.42	-8.27	-8.68	-8.44	-8.57	-8.70	-8.11
			IGLO-III	-7.96	-7.84	-8.06	-8.01	-7.96	-7.96	-8.70	–
m11(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet\bullet,4+}$	IGLO-II	-6.83	-6.39	-7.72	-6.70	-6.65	-6.85	-7.54	-6.11
			IGLO-III	-6.44	-6.01	-7.43	-6.35	-6.44	-6.47	-7.54	–
m14(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet\bullet,4+}$	IGLO-II	-7.98	-7.85	-7.79	-8.12	-7.76	-7.93	-7.37	-7.75
			IGLO-III	-7.52	-7.37	-7.53	-7.56	-7.52	-7.45	-7.37	–
		experimental for complex 1		*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*	*±2.5*

Table S7 The isotropic hyperfine coupling constant due to ^{1}H calculated at the DFT and DLPNO-CCSD level for the S = 1 counterparts of **m2**, **m5**, **m8**, **m11** and **m14**. The values are given in MHz.

model	c.n.	composition	basis set	B3LYP		PBE0		TPSS0		wB97X	
				H1	H2	H1	H2	H1	H2	H1	H2
m2(S=1)	4	$[Al_2(sq)_2(H_2O)_2]^{\bullet,\bullet,4+}$	IGLO-II	-1.51	-7.49	-2.11	-8.32	-2.26	-9.28	-2.41	-8.23
			IGLO-III	-1.24	-7.12	-1.75	-7.84	-1.73	-8.51	-1.96	-7.42
m5(S=1)	5	$[Al_2(sq)_2(H_2O)_4]^{\bullet,\bullet,4+}$	IGLO-II	-0.02	-6.82	-0.31	-7.49	-0.21	-8.21	-0.31	-7.29
			IGLO-III	-0.07	-6.54	-0.22	-7.13	-0.05	-7.62	-0.24	-6.66
m8(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet,\bullet,4+}$	IGLO-II	-0.73	-5.72	-1.15	-6.31	-1.23	-7.01	-1.43	-6.24
			IGLO-III	-0.57	-5.53	-0.93	-6.06	-0.86	-6.56	-1.13	-5.76
m11(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet,\bullet,4+}$	IGLO-II	-1.23	-6.89	-1.78	-7.66	-1.91	-8.55	-2.09	-7.62
			IGLO-III	-1.00	-6.60	-1.46	-7.27	-1.44	-7.90	-1.69	-6.93
m14(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet,\bullet,4+}$	IGLO-II	-0.36	-6.48	-0.72	-7.12	-0.68	-7.82	-0.82	-6.95
			IGLO-III	-0.25	-6.23	-0.57	-6.79	-0.43	-7.27	-0.64	-6.36

Table S7 Continued.

model	c.n.	composition	basis set	B2PLYP		mPW2PLYP		DSD-BLYP		DLPNO-CCSD	
				H1	H2	H1	H2	H1	H2	H1	H2
m2(S=1)	4	$[Al_2(sq)_2(H_2O)_2]^{\bullet,\bullet,4+}$	IGLO-II	-0.63	-7.60	-1.07	-7.93	-0.78	-7.27	-2.19	-8.88
			IGLO-III	-0.27	-7.15	-0.68	-7.44	-0.71	-7.03	–	–
m5(S=1)	5	$[Al_2(sq)_2(H_2O)_4]^{\bullet,\bullet,4+}$	IGLO-II	-0.28	-8.05	-0.06	-8.14	-0.68	-8.92	-0.11	-8.33
			IGLO-III	-0.46	-7.61	-0.23	-7.69	-0.61	-8.50	–	–
m8(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet,\bullet,4+}$	IGLO-II	-0.08	-5.88	-0.44	-6.16	-0.81	-7.89	-1.17	-6.69
			IGLO-III	-0.21	-5.61	-0.13	-5.86	-0.80	-7.64	–	–
m11(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet,\bullet,4+}$	IGLO-II	-0.33	-6.93	-0.75	-7.26	-1.22	-6.41	-1.84	-8.08
			IGLO-III	-0.01	-6.58	-0.40	-6.88	-1.13	-6.08	–	–
m14(S=1)	6	$[Al_2(sq)_2(H_2O)_6]^{\bullet,\bullet,4+}$	IGLO-II	-0.19	-7.59	-0.44	-7.72	-0.59	-7.68	-0.66	-7.87
			IGLO-III	-0.07	-7.18	-0.17	-7.29	-0.51	-7.38	–	–