Complete Ref. 12.

12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. l.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A. J.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, revision A.11.3*; Gaussian, Inc.: Pittsburgh, PA, 1998.

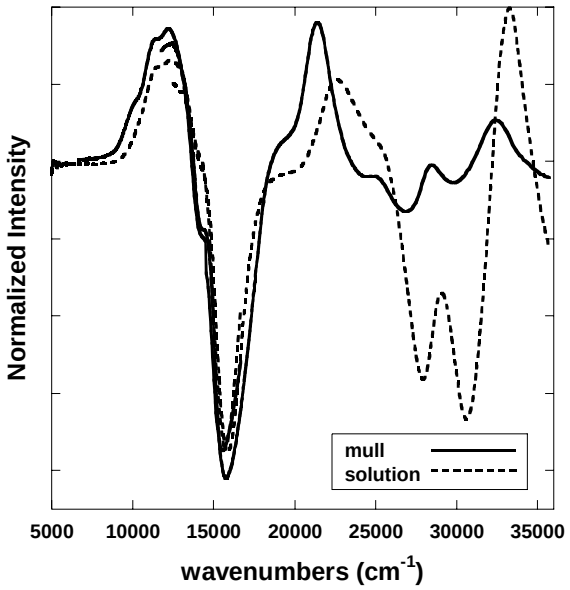

Figure S1. Comparison of the mull (solid curves) and the solution (dotted curves) MCD spectra of the μ_3O complex.

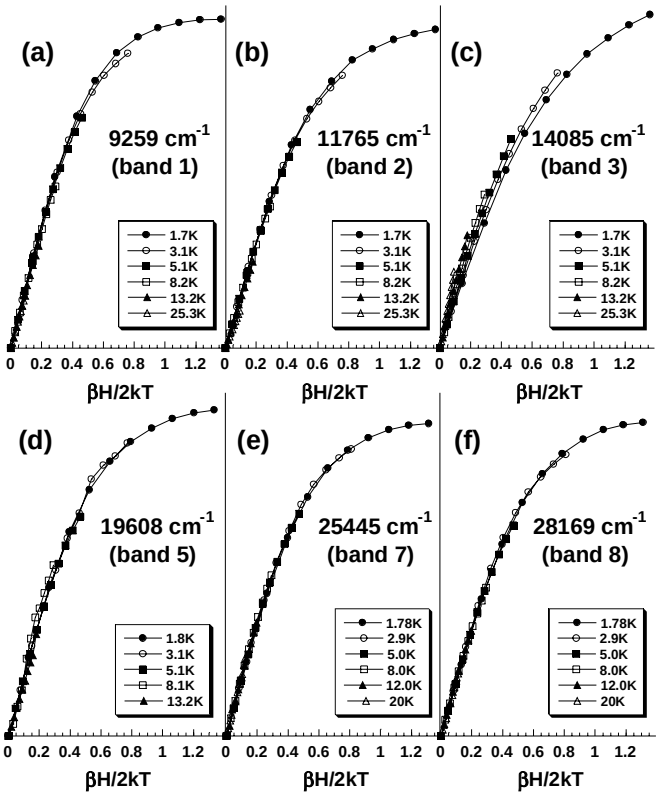

Figure S2. VTVH MCD plots of the TrisOH mull sample: (a) 9259 cm^{-1} (1080 nm, band 1), (b) 11765 cm^{-1} (850 nm, band 2), (c) 14085 cm^{-1} (710 nm, band 3), (d) 19608 cm^{-1} (510 nm, band 5), (e) 25445 cm^{-1} (393 nm, band 7) and (f) 28169 cm^{-1} (355 nm, band 8).

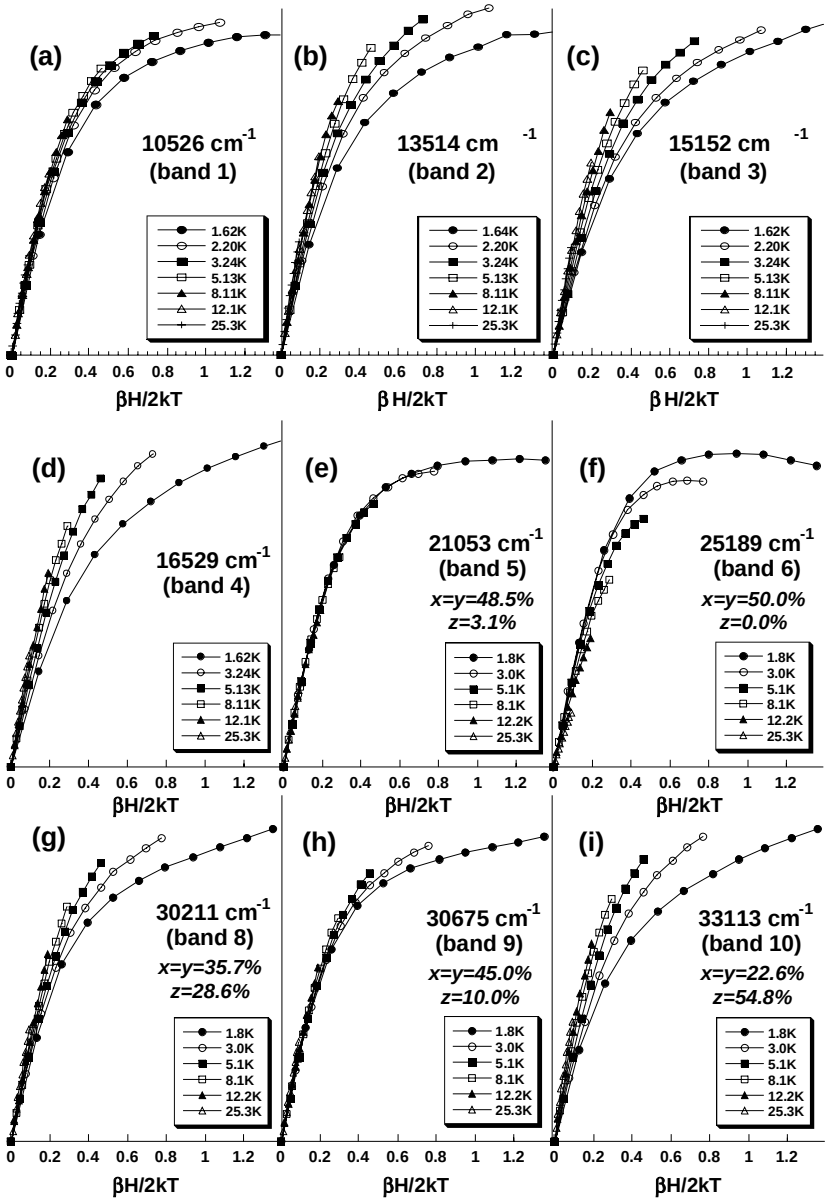

Figure S3. VTVH MCD plots of the μ_3O solution: (a) 10526 cm^{-1} (950 nm, band 1), (b) 13514 cm^{-1} (740 nm, band 2), (c) 15152 cm^{-1} (660 nm, band 3), (d) 16529 cm^{-1} (605 nm, band 4), (e) 21053 cm^{-1} (475 nm, band 5), (f) 25189 cm^{-1} (397 nm, band 6), (g) 30211 cm^{-1} (331 nm, band 8), (h) 30675 cm^{-1} (326 nm, band 9) and (i) 33113 cm^{-1} (302 nm, band 10). From (e) to (i), polarizations obtained from orientation-averaged simulations are indicated.

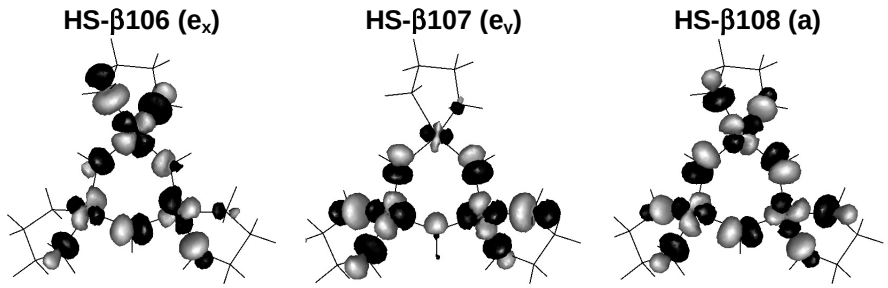

Figure S4. Contours of the metal-based, unoccupied acceptor MOs of TrisOH in the S_{tot} = 3/2 state.

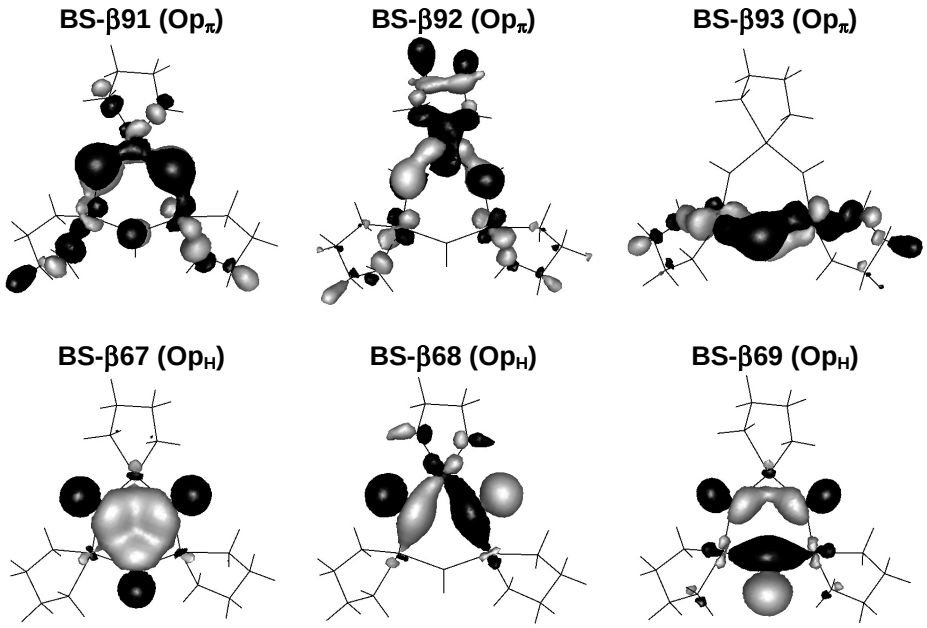

Figure S5. Contours of the OH-based Op_H (based on the in-plane O *p*-orbitals along the O-H bond) and Op_π (based on the out-of-plane O *p*-orbitals) MOs of TrisOH in the broken-symmetry $|\alpha_1\beta_2\alpha_3>$ state.

Table S1. Coordinates of TrisOH Model Used in the DFT Calculations.

	x	y	z
Cu	-2.1076231121	-0.3278842891	0.0000000000
O	-0.6244225915	-1.6134194575	0.0000000000
H	-0.9777512878	-2.5263707216	0.0000000000
N	-3.7735579084	0.3802803872	-1.0078414709
N	-3.4796921769	-1.5086731921	1.0078414709
C	-5.0200589960	-0.0529174957	-0.2612262915
C	-4.7988835438	-1.4746217421	0.2612262915
H	-3.7391285730	-0.0620096268	-1.9363737452
H	-3.7786749995	1.3928912268	-1.1662961315
H	-3.5812528059	-1.0768268319	1.9363737452
H	-3.1769474703	-2.4749819062	1.1662961315
H	-5.9024700228	-0.0128014964	-0.9090935037
H	-5.1787995763	0.6491146960	0.5648307037
H	-5.6274044297	-1.7809085231	0.9090935037
H	-4.7368523442	-2.1916990793	-0.5648307037
Cu	0.7698554287	1.9891972981	0.0000000000
O	-1.0850509393	1.3474755578	0.0000000000
H	-1.6990255827	2.1099428196	0.0000000000
N	2.2161114343	3.0778568140	-1.0078414709
N	0.4332967795	3.7678384187	1.0078414709
C	2.4642016034	4.3739573624	-0.2612262915
C	1.1223818817	4.8932659319	0.2612262915
H	1.8158623693	3.2691851506	-1.9363737452
H	3.0956166854	2.5759829362	-1.1662961315
H	0.8580670112	3.6398693261	1.9363737452
H	-0.5549234732	3.9888081797	1.1662961315
H	2.9401485742	5.1180896855	-0.9090935037
H	3.1515496040	4.1604146464	0.5648307037
H	1.2713902045	5.7639294620	0.9090935037
H	0.4703590930	5.1980839974	-0.5648307037
Cu	1.3377676797	-1.6613130096	0.0000000000
O	1.7094735377	0.2659439054	0.0000000000
H	2.6767768722	0.4164279077	0.0000000000
N	1.5574464757	-3.4581372055	-1.0078414709
N	3.0463954011	-2.2591652256	1.0078414709
C	2.5558573943	-4.3210398697	-0.2612262915
C	3.6765016584	-3.4186441836	0.2612262915
H	1.9232662053	-3.2071755143	-1.9363737452
H	0.6830583158	-3.9688741567	-1.1662961315
H	2.7231857910	-2.5630424880	1.9363737452
H	3.7318709451	-1.5138262672	1.1662961315
H	2.9623214238	-5.1052882257	-0.9090935037
H	2.0272499739	-4.8095293414	0.5648307037
H	4.3560142744	-3.9830209538	0.9090935037
H	4.2664932481	-3.0063849276	-0.5648307037

Table S2. Energies (eV) and Compositions (%) of Cu, O $2p_{xy}$ and O $2p_z$ in α-MO's from a Mulliken Population Analysis of the unrestricted broken-symmetry DFT Calculation on the TrisOH Model.

α-MO #	E (eV)	Cu_1	Cu_2	Cu_3	O_{12}		O_{23}		O_{13}	
					$2p_{xy}$	$2p_z$	$2p_{xy}$	$2p_z$	$2p_{xy}$	$2p_z$
x'^2-y'^2										
108 (LUMO)	*-13.52*	2.1	51.9	2.1	6.0	1.6	6.0	1.6	0.5	0.1
107 (HOMO)	*-14.48*	19.8	5.2	19.7	0.9	0.1	0.9	0.1	13.2	4.5
106	*-14.73*	17.4	16.3	17.6	7.9	0.3	8.0	0.2	1.0	0.0
Op_π										
93	*-16.80*	19.7	16.1	19.7	0.3	7.8	0.3	7.9	0.1	0.0
92	*-16.86*	11.2	6.1	11.2	0.6	21.6	0.6	21.6	0.3	7.4
91	*-16.89*	26.4	0.3	26.4	0.1	0.0	0.1	0.0	0.4	23.5
Op_σ										
81	*-18.48*	7.4	8.7	7.6	16.1	0.0	16.7	0.0	11.8	0.1
80	*-18.58*	7.0	7.0	6.8	17.1	0.1	16.6	0.1	0.3	0.0
79	*-18.73*	13.6	3.6	13.6	7.1	0.0	7.1	0.0	24.2	0.0
Op_H										
69	*-20.23*	4.6	3.3	4.6	29.5	0.0	29.5	0.0	0.1	0.0
68	*-20.26*	7.5	1.3	7.5	8.7	0.0	8.7	0.0	37.8	0.0
67	*-20.87*	3.7	3.5	3.7	20.4	0.0	20.5	0.0	18.9	0.0

Table S3. Energies (eV) and Compositions (%) of Cu, O $2p_{xy}$ and O $2p_z$ in β-MO's from a Mulliken Population Analysis of the unrestricted broken-symmetry DFT Calculation on the TrisOH Model.

β-MO #	E (eV)	Cu_1	Cu_2	Cu_3	O_{12}		O_{23}		O_{13}	
					$2p_{xy}$	$2p_z$	$2p_{xy}$	$2p_z$	$2p_{xy}$	$2p_z$
x'^2-y'^2										
108	*-13.36*	25.9	2.1	25.7	3.1	0.7	3.1	0.7	8.9	2.6
107 (LUMO)	*-13.82*	29.4	1.9	29.6	3.3	1.1	3.3	1.1	1.0	0.0
106 (HOMO)	*-14.52*	6.3	35.1	6.3	6.1	1.5	6.1	1.5	2.8	0.6
Op_π										
93	*-16.68*	26.5	0.1	26.7	0.1	0.1	0.1	0.1	0.6	29.2
92	*-16.79*	7.1	38.7	7.4	0.2	9.6	0.2	10.5	0.1	0.0
91	*-16.80*	7.6	10.7	7.1	0.8	22.1	0.7	21.2	0.1	5.8
Op_σ										
81	*-18.29*	13.1	0.3	13.1	0.1	0.0	0.1	0.0	48.2	0.2
80	*-18.45*	5.2	10.4	5.1	21.1	0.1	20.7	0.1	0.0	0.0
79	*-18.59*	5.1	18.6	5.2	20.1	0.0	20.4	0.0	0.3	0.0
Op_H										
69	*-20.08*	4.1	1.7	4.1	8.2	0.0	8.2	0.0	44.8	0.0
68	*-20.23*	2.0	9.8	2.0	28.8	0.0	28.8	0.0	0.2	0.0
67	*-20.84*	3.4	4.1	3.4	22.4	0.0	22.4	0.0	15.3	0.0

Table S4. Energies (eV) and Compositions (%) of Cu, O $2p_{xy}$ and O $2p_z$ in β-MO's from a Mulliken Population Analysis of the DFT Calculation on the TrisOH Model with S = 3/2.

β-MO #	E (eV)	Cu_1	Cu_2	Cu_3	O_{12}		O_{23}		O_{13}	
					$2p_{xy}$	$2p_z$	$2p_{xy}$	$2p_z$	$2p_{xy}$	$2p_z$
x'^2-y'^2										
108	*-13.19*	17.7	17.7	17.7	5.4	1.4	5.4	1.4	5.4	1.4
107	*-13.76*	30.9	2.5	26.6	3.5	1.2	4.0	1.4	0.9	0.0
106 (LUMO)	*-13.76*	9.1	37.5	13.4	2.1	0.5	1.6	0.3	4.7	1.7
Op_π										
93	*-16.69*	9.8	36.3	11.6	0.3	10.0	0.3	10.7	0.1	0.0
92	*-16.69*	28.7	2.1	26.9	0.2	3.9	0.1	3.2	0.3	13.6
91	*-16.70*	6.8	6.7	6.7	0.7	19.8	0.7	19.8	0.7	20.0
Op_σ										
81	*-18.27*	11.8	11.8	11.8	19.4	0.0	19.4	0.0	19.4	0.0
80	*-18.33*	6.0	9.8	5.2	23.3	0.2	19.4	0.2	0.2	0.0
79	*-18.33*	8.0	4.2	8.8	5.3	0.0	9.2	0.1	28.4	0.2
Op_H										
69	*-20.08*	2.0	4.2	3.7	14.9	0.0	39.8	0.0	6.5	0.0
68	*-20.08*	4.6	2.4	2.9	25.9	0.0	1.0	0.0	34.3	0.0
67	*-20.80*	3.6	3.6	3.6	20.0	0.0	20.0	0.0	20.0	0.0