Double-malate bridging tri-lanthanoid cluster encapsulated arsenotungstates: syntheses, structures, luminescence and magnetic properties

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Table S1 Selected bond distances of **1Dy**–**5Sm**.

1Dy		2Tb		3Gd		4Eu		5Sm	
Dy(1)-O(15)	2.333(14)	Tb(1)-O(15)	2.307(17)	Gd(1)-O(15)	2.372(19)	Eu(1)-O(15)	2.356(11)	Sm(1)-O(15)	2.348(12)
Dy(1)-O(42)	2.356(15)	Tb(1)-O(74)	2.352(17)	Gd(1)-O(48)	2.374(16)	Eu(1)-O(48)	2.394(11)	Sm(1)-O(42)	2.400(12)
Dy(1)-O(48)	2.363(13)	Tb(1)-O(48)	2.375(17)	Gd(1)-O(42)	2.399(17)	Eu(1)-O(42)	2.411(10)	Sm(1)-O(48)	2.418(12)
Dy(1)-O(74)	2.385(15)	Tb(1)-O(42)	2.397(17)	Gd(1)-O(74)	2.508(14)	Eu(1)-O(74)	2.414(11)	Sm(1)-O(74)	2.428(11)
Dy(1)-O(2W)	2.422(16)	Tb(1)-O(2W)	2.428(17)	Gd(1)-O(2W)	2.469(16)	Eu(1)-O(2W)	2.482(12)	Sm(1)-O(1W)	2.496(13)
Dy(1)-O(1W)	2.432(15)	Tb(1)-O(1W)	2.452(18)	Gd(1)-O(1W)	2.459(17)	Eu(1)-O(1W)	2.482(12)	Sm(1)-O(2W)	2.509(13)
Dy(1)-O(3W)	2.548(13)	Tb(1)-O(3W)	2.527(16)	Gd(1)-O(3W)	2.577(15)	Eu(1)-O(3W)	2.585(10)	Sm(1)-O(3W)	2.580(10)
Dy(1)-O(43)	2.563(13)	Tb(1)-O(43)	2.559(15)	Gd(1)-O(43)	2.597(16)	Eu(1)-O(43)	2.585(11)	Sm(1)-O(43)	2.595(11)
Dy(1)-O(23)	2.615(14)	Tb(1)-O(23)	2.600(16)	Gd(1)-O(23)	2.620(16)	Eu(1)-O(23)	2.604(11)	Sm(1)-O(23)	2.624(12)
Dy(2)-O(73)	2.264(14)	Tb(2)-O(73)	2.294(18)	Gd(2)-O(73)	2.317(19)	Eu(2)-O(73)	2.301(11)	Sm(2)-O(73)	2.318(12)
Dy(2)-O(42)	2.324(13)	Tb(2)-O(42)	2.322(15)	Gd(2)-O(42)	2.399(17)	Eu(2)-O(35)	2.364(10)	Sm(2)-O(42)	2.379(11)
Dy(2)-O(35)	2.344(14)	Tb(2)-O(35)	2.341(16)	Gd(2)-O(35)	2.370(16)	Eu(2)-O(42)	2.371(10)	Sm(2)-O(35)	2.390(11)
Dy(2)-O(39)A	2.372(15)	Tb(2)-O(39)A	2.406(18)	Gd(2)-O(39)A	2.376(15)	Eu(2)-O(39)A	2.402(12)	Sm(2)-O(39)A	2.418(12)
Dy(2)-O(5W)	2.400(15)	Tb(2)-O(5W)	2.415(19)	Gd(2)-O(5W)	2.452(17)	Eu(2)-O(5W)	2.453(12)	Sm(2)-O(5W)	2.480(13)
Dy(2)-O(3W)	2.400(14)	Tb(2)-O(3W)	2.468(16)	Gd(2)-O(3W)	2.485(17)	Eu(2)-O(3W)	2.470(10)	Sm(2)-O(3W)	2.491(11)
Dy(2)-O(4W)	2.446(16)	Tb(2)-O(4W)	2.473(18)	Gd(2)-O(4W)	2.486(14)	Eu(2)-O(4W)	2.500(12)	Sm(2)-O(4W)	2.505(12)
Dy(2)-O(74)	2.489(14)	Tb(2)-O(74)	2.490(15)	Gd(2)-O(74)	2.508(14)	Eu(2)-O(74)	2.506(10)	Sm(2)-O(74)	2.501(11)
Dy(3)-O(56)	2.268(14)	Tb(3)-O(56)	2.285(18)	Gd(3)-O(56)	2.319(17)	Eu(3)-O(56)	2.320(11)	Sm(3)-O(56)	2.340(12)
Dy(3)-O(48)	2.305(13)	Tb(3)-O(30)	2.301(17)	Gd(3)-O(48)	2.353(14)	Eu(3)-O(48)	2.351(11)	Sm(3)-O(48)	2.355(11)
Dy(3)-O(30)	2.321(14)	Tb(3)-O(48)	2.336(17)	Gd(3)-O(30)	2.385(18)	Eu(3)-O(30)	2.354(11)	Sm(3)-O(30)	2.361(12)
Dy(3)-O(74)	2.385(13)	Tb(3)-O(8W)	2.38(2)	Gd(3)-O(74)	2.424(13)	Eu(3)-O(74)	2.411(10)	Sm(3)-O(74)	2.435(11)
Dy(3)-O(7W)	2.386(17)	Tb(3)-O(74)	2.412(15)	Gd(3)-O(8W)	2.425(17)	Eu(3)-O(8W)	2.427(14)	Sm(3)-O(8W)	2.436(15)
Dy(3)-O(8W)	2.398(19)	Tb(3)-O(6W)	2.46(2)	Gd(3)-O(7W)	2.446(16)	Eu(3)-O(7W)	2.456(12)	Sm(3)-O(7W)	2.479(13)
Dy(3)-O(6W)	2.455(16)	Tb(3)-O(7W)	2.454(18)	Gd(3)-O(6W)	2.506(17)	Eu(3)-O(6W)	2.515(13)	Sm(3)-O(6W)	2.513(15)
Dy(3)-O(23)	2.532(14)	Tb(3)-O(23)	2.523(17)	Gd(3)-O(23)	2.577(17)	Eu(3)-O(23)	2.545(11)	Sm(3)-O(23)	2.578(12)

Table S2 BVS values of selected oxygens atoms in **1Dy–5Sm**.

atom	BVS					protonation
	1Dy	**2Tb**	**3Gd**	**4Eu**	**5Sm**	
O(74)	–0.976	–1.069	–1.068	–1.112	–1.118	monoprotonated
O(1W)	–0.312	–0.321	–0.345	–0.332	–0.332	diprotonated
O(2W)	–0.321	–0.343	–0.336	–0.332	–0.321	diprotonated
O(3W)	–0.568	–0.570	–0.572	–0.594	–0.601	diprotonated
O(4W)	–0.300	–0.304	–0.321	–0.316	–0.324	diprotonated
O(5W)	–0.340	–0.355	–0.351	–0.359	–0.347	diprotonated
O(6W)	–0.293	–0.315	–0.304	–0.304	–0.317	diprotonated
O(7W)	–0.353	–0.320	–0.357	–0.356	–0.348	diprotonated
O(8W)	–0.342	–0.390	–0.378	–0.385	–0.390	diprotonated

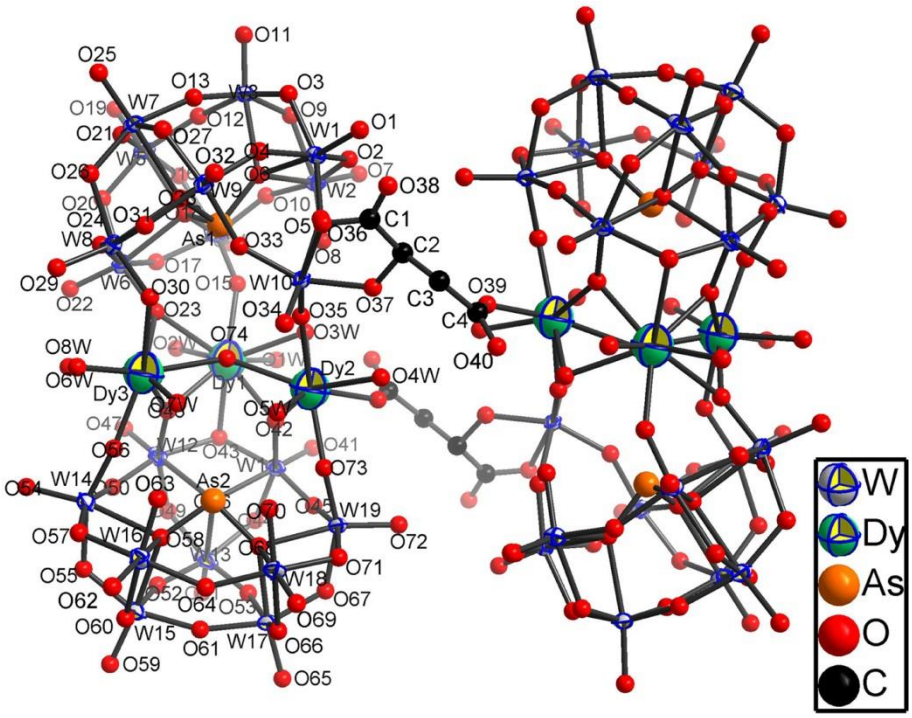

Fig. S1 Ball-and-stick representation of dimeric polyanion for **1Dy**.

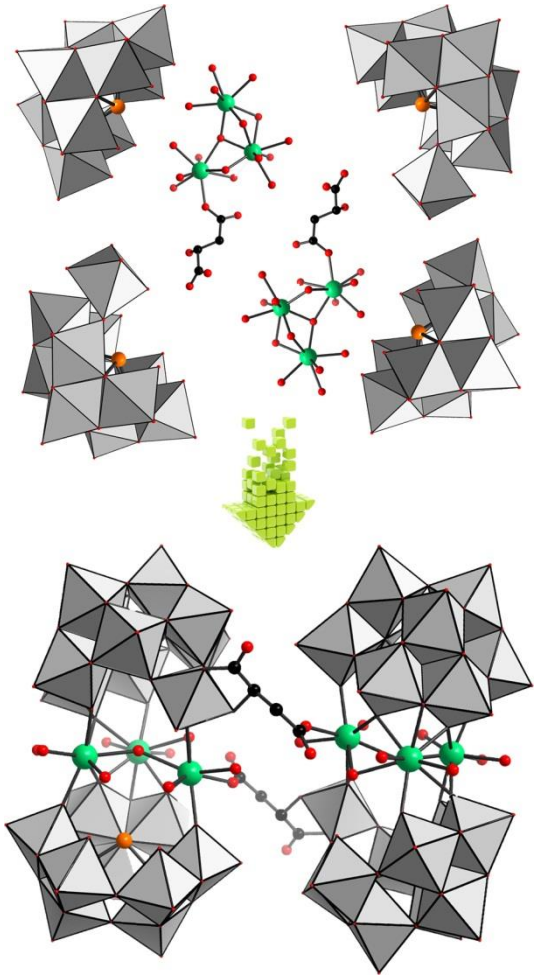

Fig. S2 Representation of the dimeric polyanion is assembled by the $[AsW_9O_{33}]^{9-}$ and $[AsW_{10}O_{35}]^{7-}$ subunits together with trinuclear $[Dy_3(\mu_3\text{-}OH)(H_2O)_8(mal)]^{6+}$ cluster groups for **1Dy**.

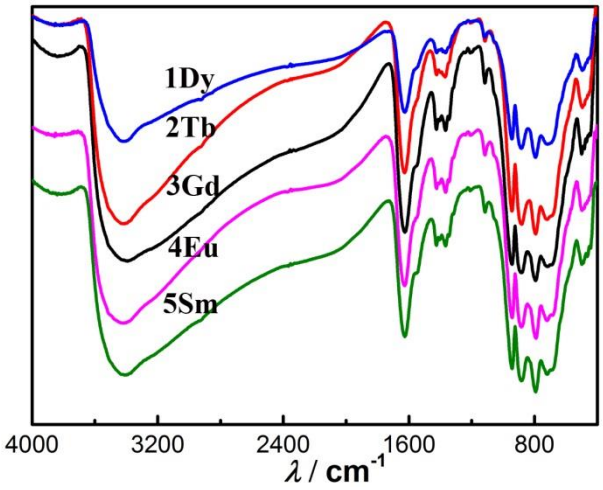

Fig. S3. IR spectra of **1Dy–5Sm**.

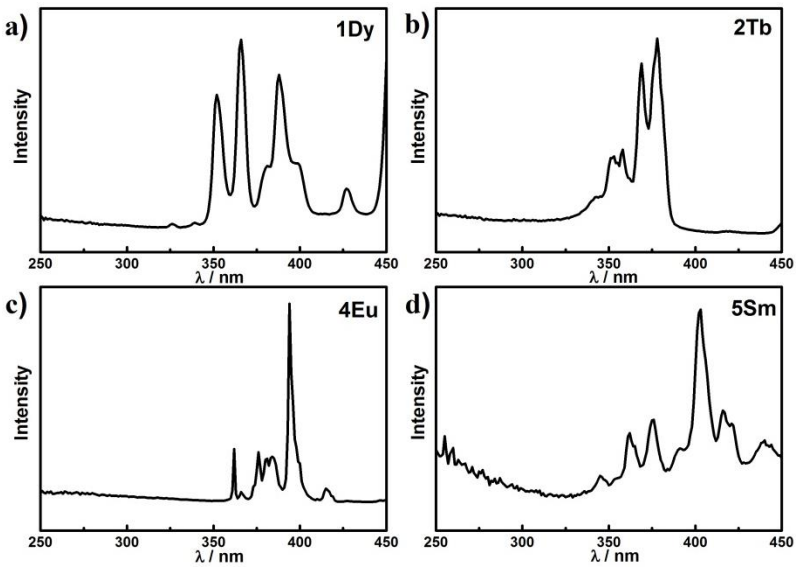

Fig. S4 The excitation spectra of **1Dy** (a), **2Tb** (b), **4Eu** (c), and **5Sm** (d) in the solid state at room temperature.

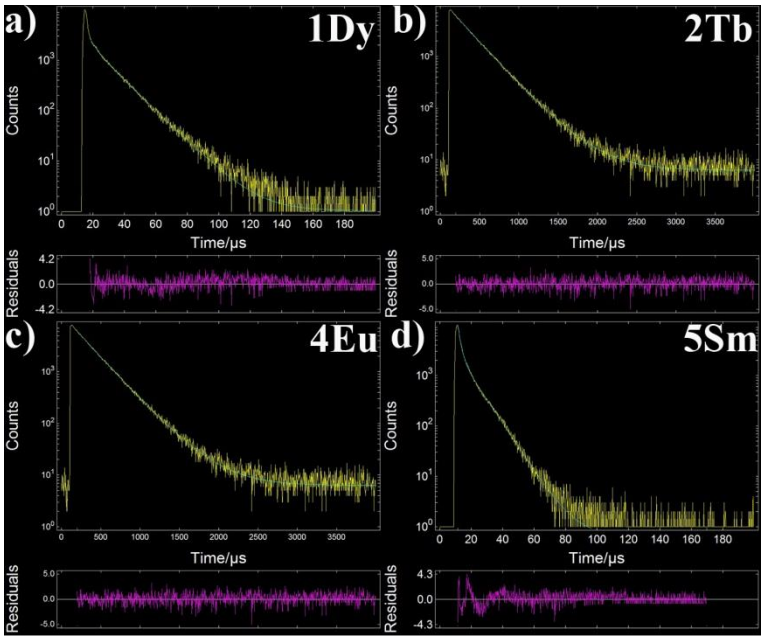

Fig. S5 Decay curves of **1Dy** (a), **2Tb** (b), **4Eu** (c) and **5Sm** (d).

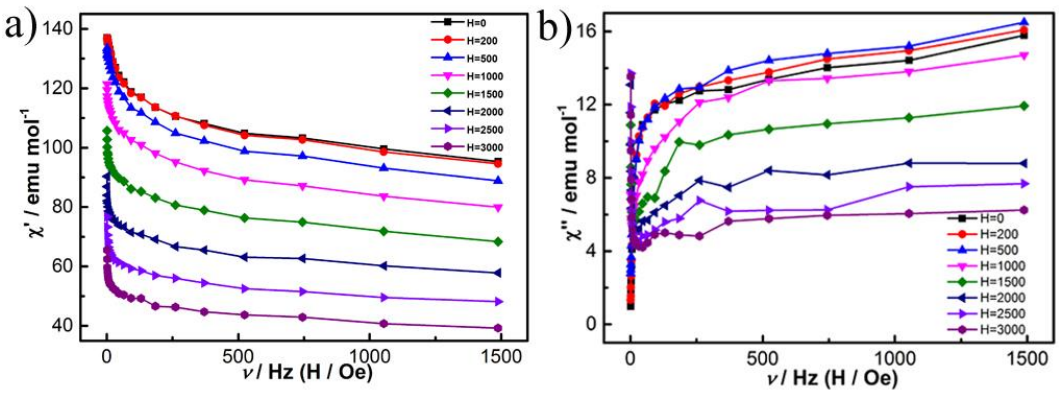

Fig. S6 Frequency dependency of the in-phase (χ') (a) and out-of-phase (χ'') (b) signals from ac susceptibility measurements of **1Dy** under different static field in the range of 0–3000 Oe.

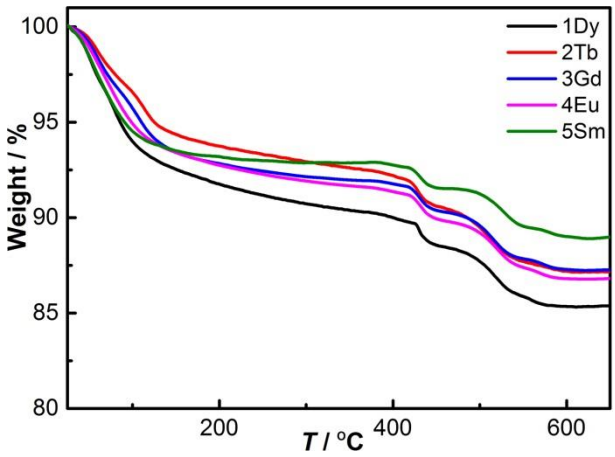

Fig. S7 TG curves of **1Dy–5Sm**.

The thermal behaviors of the five compounds have been analyzed upon heating to 650 °C. The TG curves show three mass losses stages (Fig. S7). The first stage occurring below 200 °C can be ascribed to the loss of the surface adsorbed water and seventeen lattice water molecules. The second weight loss of about 1.2% in the range of 380–470 °C could be attributed to the sublimation of one As_2O_3 group. The third weight loss of about 2.8% up to 600 °C, corresponding to the removal of one hydroxyl ion, eight coordinated water molecules, and two malate ligands. The oxidation of organic ligands together with the collapse of the POMs framework occurs in this process.