## Supporting information for

## Lanthanide-ion-tuned magnetic properties in a series of three-dimensional cyano-bridged Ln<sup>III</sup>W<sup>V</sup> assemblies

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	4	5	6	7	2a
formula	$C_{10}H_{10}N_9O_4NdW$	$C_{10}H_{10}N_9O_4SmW$	$C_{10}H_{10}N_9O_4EuW$	$C_{10}H_{10}N_9O_4GdW$	$C_8H_{10}N_8O_5CeW$
$M(g \text{ mol}^{-1})$	648.36	654.47	656.08	661.37	622.21
crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	tetragonal
space group	Стса	Стса	Стса	Стса	P4/ncc
<i>a</i> (Å)	16.462(2)	16.5021(15)	16.4652(15)	16.4265(18)	11.1891(6)
<i>b</i> (Å)	14.6853(16)	14.435(2)	14.4351(14)	14.3441(16)	11.1891(6)
<i>c</i> (Å)	14.8818(17)	14.8641(12)	14.8544(19)	14.8343(12)	14.0286(14)
$\alpha$ (°)	90.00	90.00	90.00	90.00	90.00
$V(\text{\AA}^3)$	3597.6(7)	3540.7(7)	3530.5(7)	3495.3(6)	1756.3(2)
Ζ	8	8	8	8	4
$\rho (\text{g cm}^{-3})$	2.394	2.455	2.469	2.514	2.353
$\mu (\mathrm{mm}^{-1})$	9.279	9.812	10.067	10.375	9.137
observed $[I > 2\sigma(I)]$	1131	1425	1326	1396	871
GOF on $F^2$	1.035	1.090	1.078	1.061	1.023
$R_1, \omega R_2 [I > 2\sigma(I)]$	0.0307, 0.0489	0.0335, 0.0827	0.0379, 0.0952	0.0348, 0.1049	0.0161, 0.0616
$R_1, \omega R_2$ (all data)	0.0498, 0.0514	0.0446, 0.0859	0.0520, 0.1023	0.0488, 0.1123	0.0315, 0.0755

Table S1 Crystallographic data and structural refinement for compounds 4-7 and 2a

Table S2 Selected bond distances (Å) and angles (°) for compounds 4-7 and 2a

	4	5	6	7		2a
W1-C1	2.222(6)	2.127(7)	2.123(8)	2.184(8)	W1-C1	2.183(6)
W1-C2	2.150(6)	2.146(7)	2.149(8)	2.137(7)	W1-C2	2.156(5)
W1-C3	2.197(6)	2.205(8)	2.160(10)	2.129(9)	Ce1-O1	2.540(6)
W1-C4	2.149(6)	2.207(7)	2.193(8)	2.184(8)	Ce1-O2A	2.588(15)
C1-N1	1.133(7)	1.152(9)	1.150(10)	1.090(10)	Ce1-O2B	2.511(6)
C2-N2	1.205(7)	1.170(8)	1.166(9)	1.183(9)	Ce1-N1	2.626(5)
C3-N3	1.122(7)	1.036(9)	1.048(11)	1.070(11)	C1-N1	1.123(7)
C4-N4	1.165(7)	1.134(9)	1.150(10)	1.169(10)	C2-N2	1.157(6)
Ln1-N1	2.523(5)	2.613(6)	2.617(8)	2.584(6)	W1-C1-N1	174.5(5)
Ln1-N5	2.664(7)	2.627(7)	2.622(9)	2.608(9)	W1-C2-N2	169.2(4)
Ln1-O1	2.531(6)	2.265(6)	2.260(7)	2.266(8)	Ce1-N1-C1	168.1(4)
Ln1-O2	2.552(5)	2.412(5)	2.410(6)	2.390(6)		
Ln1-O3	2.434(4)	2.541(6)	2.545(7)	2.512(7)		
W1-C1-N1	169.5(5)	172.1(6)	172.3(7)	172.3(7)		
W1-C2-N2	172.4(5)	173.2(6)	174.3(7)	175.6(7)		
W1-C3-N3	175.9(5)	174.7(7)	173.5(9)	174.5(8)		
W1-C4-N4	176.5(5)	171.0(6)	171.3(6)	173.2(7)		
Ln1-N1-C1	164.5(5)	161.3(5)	160.1(6)	164.0(7)		



Figure S1 TG curve of the precursor  $[HN(n-C_4H_9)_3]_3[W(CN)_8]$ .



(b)



Figure S2 Powder XRD patterns of as-synthesized (1-7) and simulated from single crystal XRD data.





**Figure S3** IR spectra of compounds (*a*) **1**, (*b*) **2**, (*c*) **3**, (*d*) **4**, (*e*) **5**, (*f*) **6** and (*g*) **7** in the range of 4000~400 cm<sup>-1</sup>, 2300~2000 cm<sup>-1</sup>, and 1600~700 cm<sup>-1</sup>. IR spectra of compounds **1-7** exhibit characteristic  $v_{C=N}$  stretches at 2200-2100 cm<sup>-1</sup>. The lower energy stretches are reasonably assigned to the terminal CN ligands, while the presence of strong peaks at higher frequencies as compared to the precursor [HN(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>3</sub>[W(CN)<sub>8</sub>] confirms the predominant existence of bridging CN groups. The shifts toward higher frequencies of CN peaks are caused mainly by the electron-density withdrawal from the sp  $\sigma^*$  molecular orbital of the CN ligands by metal centers and kinematics coupling in the Ln<sup>III</sup>-NC-W<sup>V</sup> unit. The incorporation of pyrazine is detected by the presence of sharp bands below 1500 cm<sup>-1</sup>.



(*c*)





**Figure S4** TG curves of compounds (*a*) **1**, (*b*) **2**, (*c*) **3**, (*d*) **4**, (*e*) **5**, (*f*) **6** and (*g*) **7**, which show that the stage of weight loss at low temperatures can be attributed to the partial loss of coordinated pyrazine. Upon further heating, the frameworks collapsed.







Figure S5 EDS spectra of compounds (*a*) 1, (*b*) 2, (*c*) 3, (*d*) 4, (*e*) 5, (*f*) 6 and (*g*) 7, which show the presence of Ln and W atoms in the products. The absence of hydrogen and nitrogen atoms can be attributed to difficulties of the EDS instruction detecting above two atoms.

![](_page_10_Figure_3.jpeg)

**Figure S6** Field dependence of the magnetization for compounds 2 (2.0 K), 4 (1.8 K) and 5 (2.0 K).

![](_page_11_Figure_1.jpeg)

Figure S7 Temperature dependence of the ac susceptibility for compound 5 at different frequencies under  $H_{ac} = 3.5$  Oe and  $H_{dc} = 0$  Oe.

![](_page_11_Figure_3.jpeg)

Figure S8 Temperature dependence of the ac susceptibility for compound 2a at different frequencies under  $H_{ac} = 3.5$  Oe and  $H_{dc} = 0$  Oe.

![](_page_12_Figure_1.jpeg)

Figure S9 Powder XRD patterns of as-synthesized (5), simulated from single-crystal data of

![](_page_12_Figure_3.jpeg)

compounds 5 and 5a.

Figure S10 Field dependence of the magnetization for compounds 3 and 6 at 1.8 K.

![](_page_13_Figure_1.jpeg)

Figure S11 Temperature dependence of the ac susceptibility for compound 3 at different frequencies under  $H_{ac} = 3.5$  Oe and  $H_{dc} = 0$  Oe.

![](_page_13_Figure_3.jpeg)

Figure S12 Temperature dependence of the ac susceptibility for compound 6 at 1 Hz under  $H_{ac} = 3.5$  Oe and  $H_{dc} = 0$  Oe.

![](_page_14_Figure_1.jpeg)

**Figure S13** Temperature dependence of  $1/\chi_M$  for compound **7**. The red solid line represents the fit obtained by the Curie-Weiss law.

![](_page_14_Figure_3.jpeg)

Figure S14 Temperature dependence of the ac susceptibility for compound 7 at different frequencies under  $H_{ac} = 3.5$  Oe and  $H_{dc} = 0$  Oe.

![](_page_15_Figure_1.jpeg)

Figure S15 Temperature dependence of zfc and fc for compound 7 with H = 30 Oe.

![](_page_15_Figure_3.jpeg)

Figure S16 The hysteresis loop measured at 2.0 K for compound 7.