Electronic Supplementary Information

Heteropentanuclear metal string complex $[Mo_2NiMo_2(tpda)_4(NCS)_2]$ with two linearly aligned quadruply bonded Mo_2 units connected by a Ni ion and a meso configuration of the complex

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X-ray Structure Determinations:

For compound **1**, crystallographic data were collected on a NONIUS Kappa CCD diffractometer using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Cell parameters were retrieved and refined using DENZO-SMN software on all observed reflections. Data reduction was performed with the DENZO-SMN software. An empirical absorption was based on the symmetry-equivalent reflection and absorption corrections were applied with the SORTAV program. The structures were solved and refined with SHELX programs. There are also some difficulties in the refinement of anion and solvent molecule. The hydrogen atoms were included in calculated positions and refined using a riding mode.

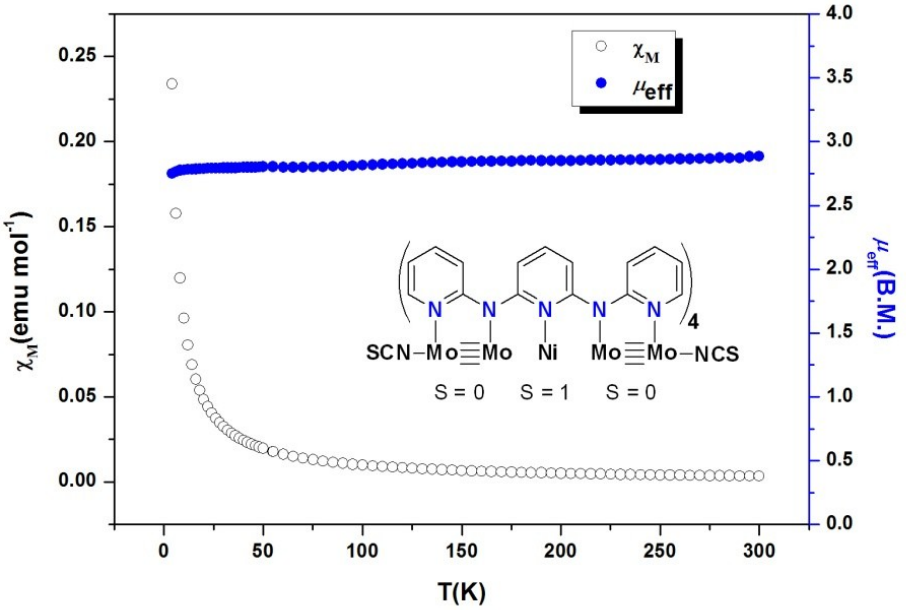

Fig. S1 Molar magnetic susceptibility χ_M (○) and effective magnetic moment (μ_{eff}) (●) for $[Mo_2NiMo_2(tpda)_4(NCS)_2]$ (**1**).

X-ray absorption Experiment section

Soft X-ray absorption $L_{2,3}$ edge measurement was carried out at beamline BL20A1, NSRRC. $Ni(SO_4)\cdot 6H_2O$, $Ni(acac)_2(H_2O)_2$ and $K_2[Ni(CN)_4]$ were used as Ni(II) standards. A series of Ni-contained EMAC compounds, $Ni_3(dpa)_4Cl_2$, $MnNiMn(dpa)_4Cl_2$, $NiPdNi(dpa)_4Cl_2$ and $Mo_2NiMo_2(tpda)_4(NCS)_2$ were chosen for comparison. All spectra were measured in X-ray total electron yield mode in an ultrahigh-vacuum chamber. The energy scan was performed using a high-energy spherical grating monochromator in "FLY" scan mode with an energy resolution of 0.01 eV. Five scans for each standard and 25 scans for each EMAC compound were measured and averaged, Each spectrum was recorded for 40 seconds. Energy calibration was carried out according to Ni oxide (870.3 and 853.2 eV for L_2 and L_3 absorption edge).

The HS compounds $NiSO_4\cdot 6H_2O$, $Ni(acac)_2(H_2O)_2$ and the LS compound $K_2[Ni(CN)_4]$ have been measured as standards for comparison. The L_3 ($2p_{3/2}$) absorption peaks for $NiSO_4\cdot 6H_2O$ and $Ni(acac)_2(H_2O)_2$ are located at 852.898 eV and 853.516 eV respectively, while the L_3 peak of $K_2[Ni(CN)_4]$ is shifted ~ 2.5 eV to a higher energy of 855.322 eV. The L_2 ($2p_{1/2}$) peaks of the two HS compounds are broadened in comparison to the shaper L_2 peak, of $K_2[Ni(CN)_4]$.

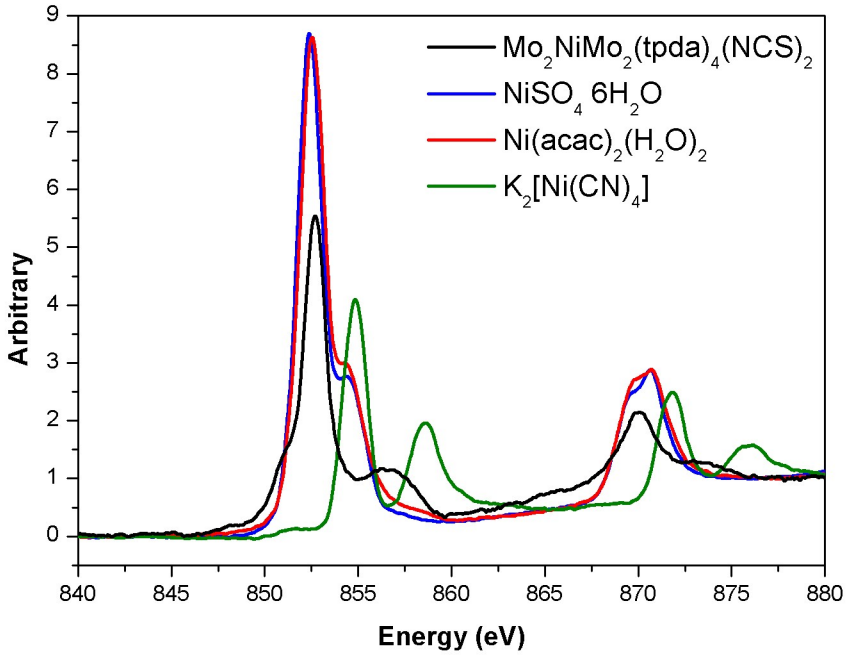

Fig. S2 X-ray absorption $L_{2,3}$-edge of Ni(II) standards and $Mo_2NiMo_2(tpda)_4(NCS)_2$ (**1**).

Table. S1 The integration area of $L_{2,3}$ absorption peak and branch ration of Ni-complexes.

	L_3	L_2	Branch ratio	Spin state
	Area	Area	$L_3/(L_3+L_2)$	
$K_2[Ni(CN)_4]$	11.115	5.763	0.659	LS
$NiSO_4 \cdot 6H_2O$	19.404	6.436	0.751	HS
$Ni(acac)_{2(}H_2O)_2$	20.579	7.433	0.735	HS
$MnNiMn(dpa)_4Cl_2$	9.753	4.979	0.662	LS
$NiPdNi(dpa)_4Cl_2$	13.585	4.658	0.745	HS
$Ni_3(dpa)_4Cl_2$	11.180	4.446	0.715	LS,HS
$Mo_2NiMo_2(tpda)_4(NCS)_2$	10.516	3.800	0.735	HS

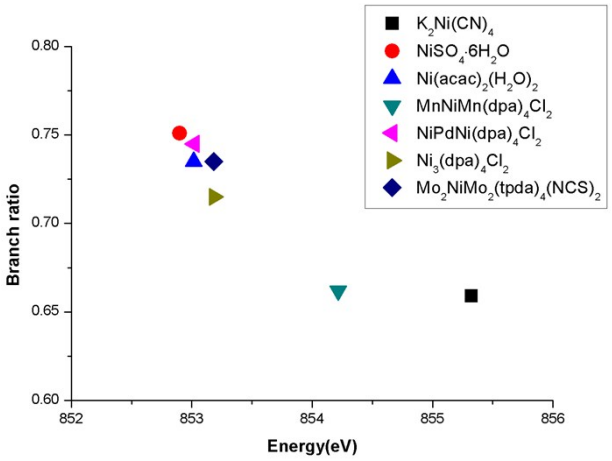

Fig. S3 The correlation diagram of L_3 absorption centroids vs. branch ratio of $[L_3/(L_2+L_3)]$.