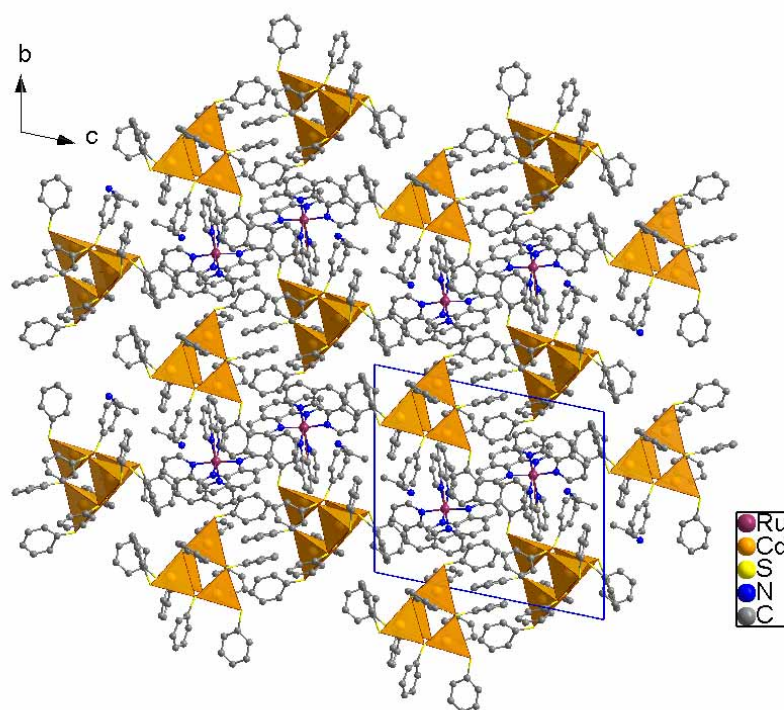


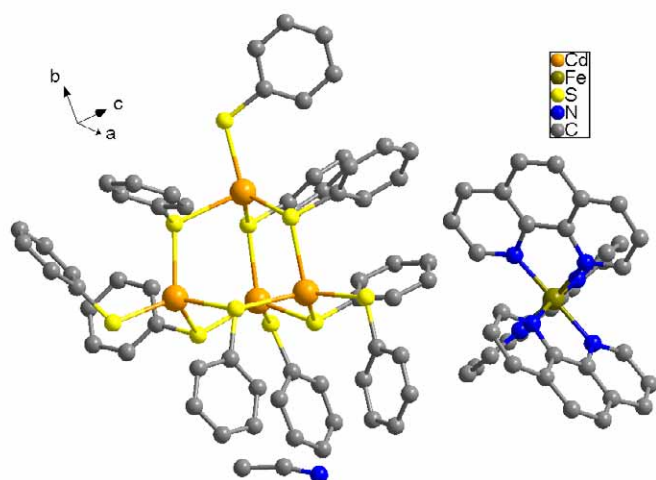
ESI materials for

Anion-Cation Charge-Transfer Properties and Spectral Studies of [M(phen)₃][Cd₄(Sph)₁₀] (M = Ru, Fe, and Ni)

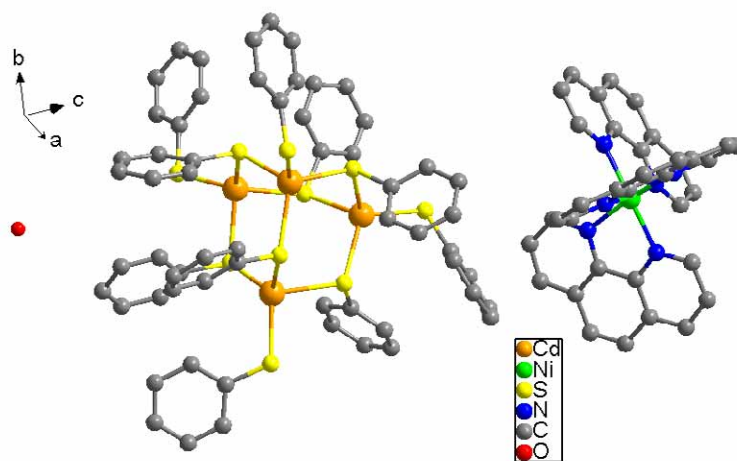
Jian-Bing Jiang, Guo-Qing Bian, Ya-Ping Zhang, Wen Luo, Qin-Yu Zhu,* and Jie Dai*



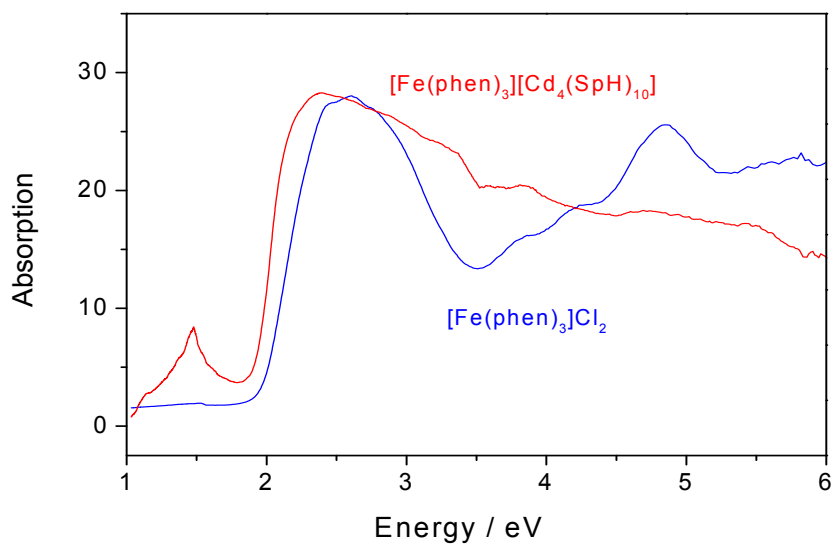
ESI-Fig. 1 Molecular packing of [Ru(phen)₃][Cd₄Sph₁₀] \cdot CH₃CN (**1**), showing the crystal cell.



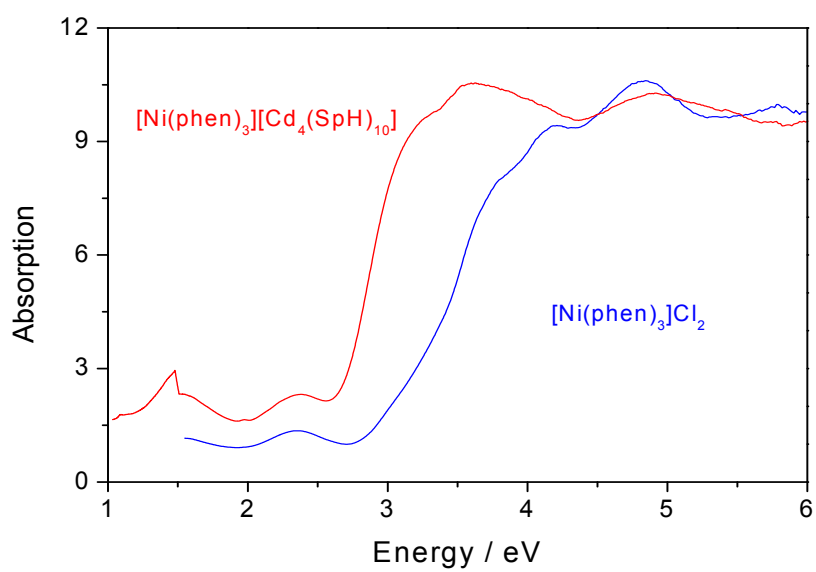
ESI-Fig. 2 Molecular structure of $[\text{Fe}(\text{phen})_3][\text{Cd}_4\text{Sph}_{10}]\cdot\text{CH}_3\text{CN}$ (**2**), hydrogen atoms are omitted for clarity.



ESI-Fig. 3 Molecular structure of $[\text{Ni}(\text{phen})_3][\text{Cd}_4\text{Sph}_{10}]\cdot\text{H}_2\text{O}$ (**3**), hydrogen atoms are omitted for clarity.

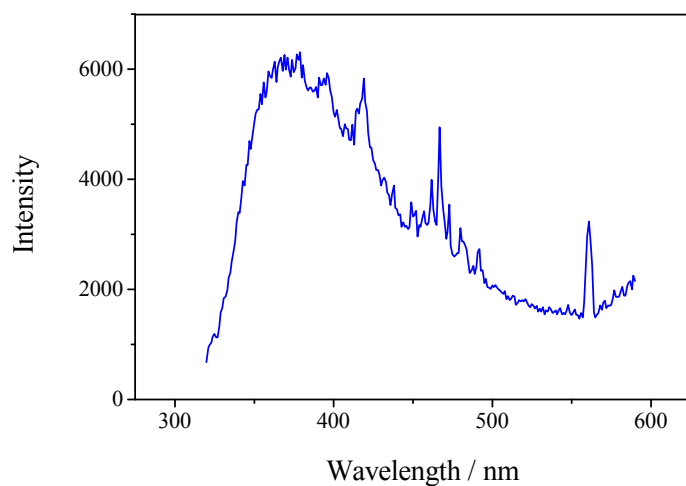


(a)

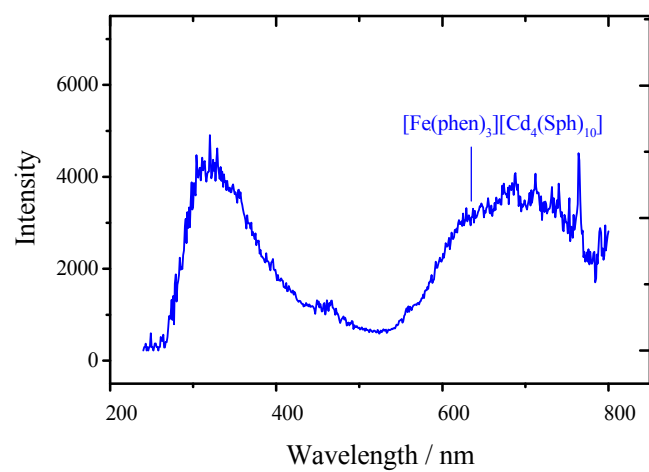


(b)

ESI-Fig. 4 Solid-state electronic spectra of $[\text{M}(\text{phen})_3]\text{Cl}_2$ and $[\text{M}(\text{phen})_3][\text{Cd}_4(\text{SpH})_{10}]$, (a) $\text{M} = \text{Fe}(\text{II})$, (b) $\text{M} = \text{Ni}(\text{II})$.



(a)



(b)

ESI-Fig. 5 Fluorescence emission spectra of $[\text{Me}_4\text{N}]_2[\text{Cd}_4\text{Sph}_{10}]$ (a) and $[\text{Fe}(\text{phen})_3][\text{Cd}_4\text{Sph}_{10}]$ (b) measured in the solid state.

ESI-Table 1 **Calculated results by MP3:**

(1) [Cd ₄ Sph ₁₀] ²⁻	(2) Fe(phen) ₃ Cl ₂	(3) [M(phen) ₃][Cd ₄ (Sph) ₁₀]
Energy:	Energy:	Energy:
HOMO-3: E = -4.327053 eV	HOMO-3: E = -8.728138 eV	HOMO-3: E = -7.05157 eV
HOMO-2: E = -4.253053 eV	HOMO-2: E = -8.509764 eV	HOMO-2: E = -6.85387 eV
HOMO-1: E = -4.165588 eV	HOMO-1: E = -7.331138 eV	HOMO-2: E = -6.634559 eV
HOMO: E = -4.130404 eV	HOMO: E = -6.955764 eV	HOMO: E = -6.594343 eV
LUMO: E = 2.675658 eV	LUMO: E = -1.352436 eV	LUMO: E = -3.675894 eV
LUMO+1: E = 3.733966 eV	LUMO+1: E = -1.201955 eV	LUMO+1: E = -3.599601 eV
LUMO+2: E = 3.783419 eV	LUMO+2: E = -0.8432351 eV	LUMO+2: E = -3.391407 eV
LUMO+3: E = 3.836052 eV	LUMO+3: E = -0.7294009 eV	LUMO+3: E = -3.303386 eV

ESI-Table 2

	A_s	$n_s(\text{acetonitrile})$	F_s	Ex (nm)	φ_s / φ_r
Ru(phen) ₃ Cl ₂	0.793	1.344	-3.68236E7	284	2.10
Ru(phen) ₃ Cd ₄ (sph) ₁₀	0.407	1.344	-3.41877E7	284	
Ru(phen) ₃ Cl ₂	0.490	1.344	-9.64033E7	420	3.62
Ru(phen) ₃ Cd ₄ (sph) ₁₀	0.190	1.344	-6.87687E7	420	