Supporting Information For

"Extending the Chevrel-type superatoms to nitrogen family"

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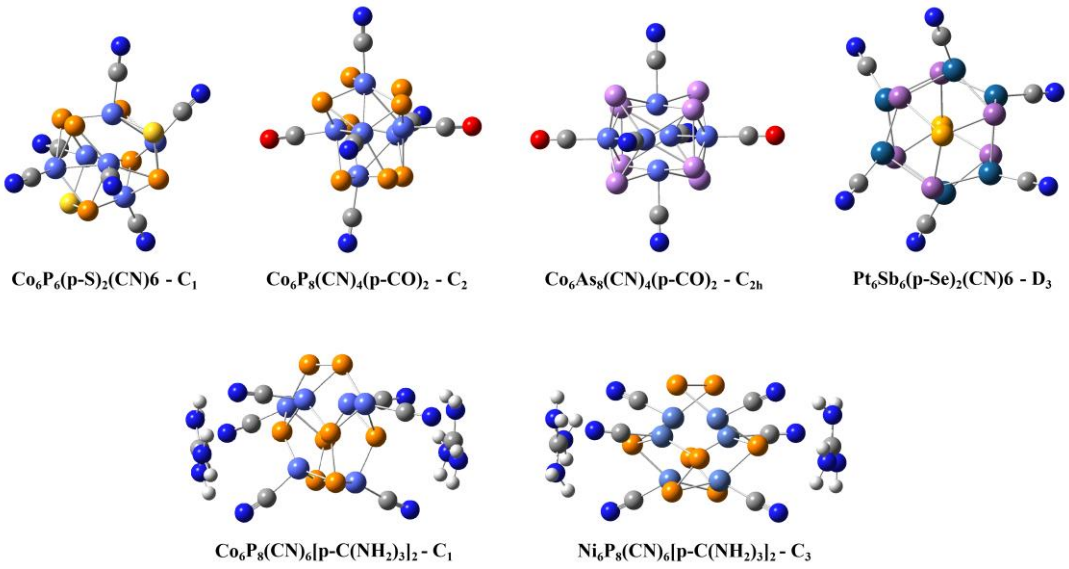

Fig. S1. Optimized stable structures of the neutral substitutions with low symmetry.

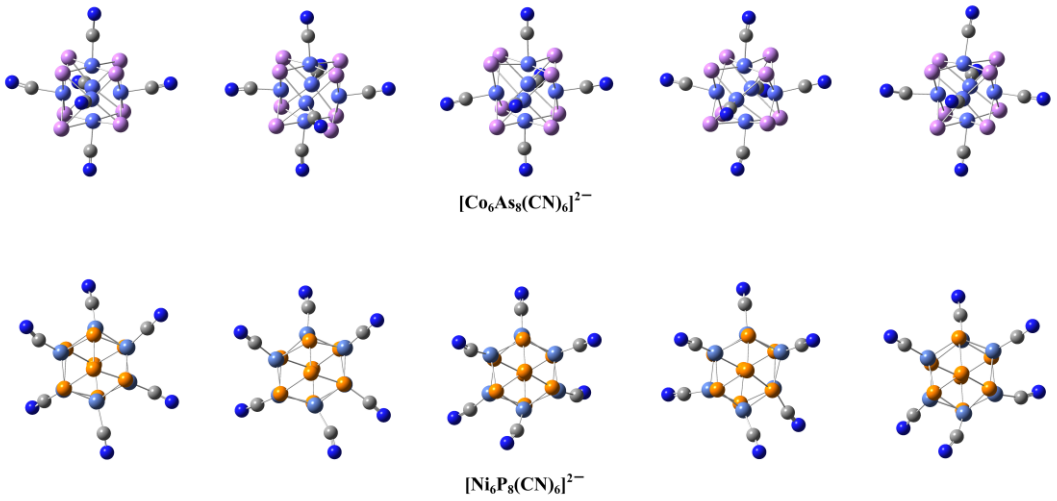

Fig. S2. The structures are snapshots at steps with smallest energies (the upper peaks at Fig. 3) in the last 2 ps, which correspond the most deformed geometries close the end of the MD simulations.

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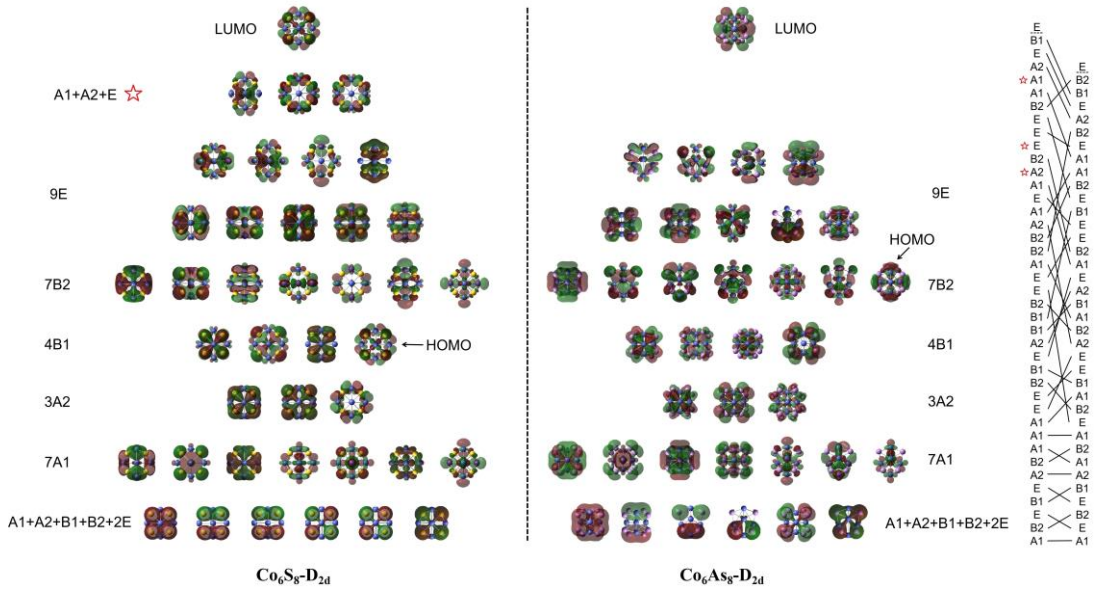

Fig. S3. Valence molecular orbitals of Co_6S_8 and Co_6As_8 cores with D_{2d} symmetry.

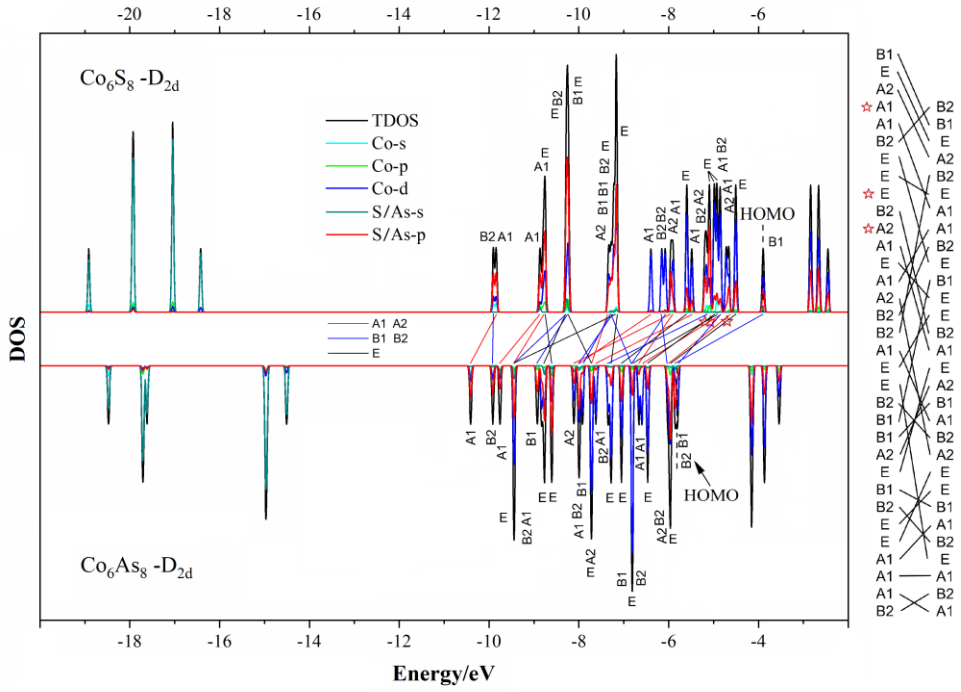

Fig. S4. Total and partial DOS (FWHM= 0.07) of Co_6S_8 and Co_6As_8 cores with D_{2d} symmetry.

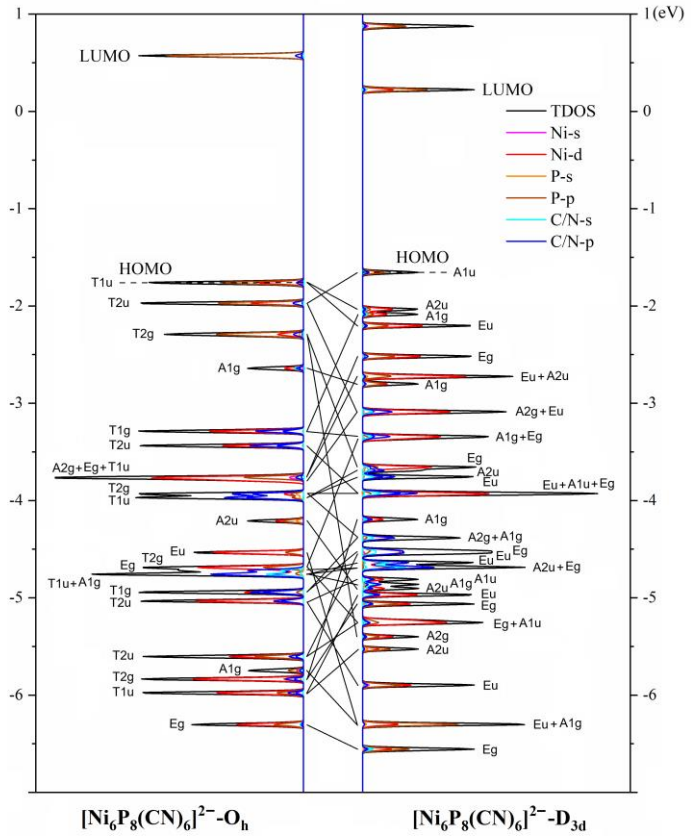

Fig. S5. Total and partial DOS (FWHM= 0.03) of the O_h and D_{3d} structures of $[Ni_6P_8(CN)_6]^{2-}$.

Table S1. Comparison of the B3LYP/Def2-TZVP, PBE0/Def2-TZVP and CCSD/Def2-TZVP results.

	E_b			Gap		
	B3LYP	PBE0	CCSD	B3LYP	PBE0	CCSD
$Co_6S_8^-$-O_h	-41.63	-43.98	-37.63	0.55	0.67	2.65
Co_6S_8-D_{3d}	-36.91	-39.00	-33.43	1.82	2.24	5.34
Co_6P_8-D_{2d}	-34.68	-35.89	-29.19	1.41	1.07	5.29
Co_6As_8-D_{2d}	-30.52	-31.64	-27.66	1.65	1.99	4.09
Rh_6P_8-O_h	-41.92	-45.14	-35.70	1.49	1.80	4.84
Ni_6P_8-D_{3d}	-39.01	-41.20	-33.38	2.15	2.46	4.54
Pt_6Sb_8-D_{3d}	-42.60	-46.36	-44.38	1.42	1.67	5.90
$Co_6S_8(CO)_6$-O_h	-47.64	-51.48	-44.83	3.29	3.80	9.83
$[Co_6As_8(CN)_6]^{2-}$-O_h	-58.81	-61.09	-55.16	1.48	1.81	2.48
$[Ni_6P_8(CN)_6]^{2-}$-D_{3d}	-65.59	-68.30	-59.68	1.88	2.25	2.75

Table S2. Symmetries, bond lengths, binding energy E_b (eV) and HOMO-LUMO gap of $[M_6Q_8(CN)_6]^{0/2-}$ (M=Co, Rh, Ir; Q=P, As, Sb) calculated using B3LYP/Def2-TZVP.

	Symmetry	R_{M-M}	R_{M-Q}	R_{Q-Q}	R_{M-C}	E_b	Gap
$[Co_6P_8(CN)_6]^{2-}$	C_2	2.44~2.85	2.09~2.75	2.22~3.54	1.87~1.90	-63.37	1.94
$Co_6P_8(CN)_6$	C_2	2.60~2.89	2.11~2.35	2.19~3.02	1.84~1.86	-55.67	1.78
$[Co_6As_8(CN)_6]^{2-}$	C_{2h}	2.40/2.52/2.56	2.26~2.48	2.46~3.68	1.88/1.90	-59.99	1.53
$[Co_6As_8(CN)_6]^{2-}$	O_h	2.50	2.34	3.30	1.88	-58.81	1.49
$Co_6As_8(CN)_6$	D_{4h}	2.43/2.59	2.32/2.39	3.17/3.38	1.87/1.88	-51.23	1.46
$[Co_6Sb_8(CN)_6]^{2-}$	C_{2h}	2.49~2.63	2.43~2.64	2.84~3.92	1.88/1.91	-56.52	1.44
$[Rh_6P_8(CN)_6]^{2-}$	C_2	2.71~2.90	2.19~2.86	2.21~3.85	1.99~2.02	-74.42	1.80
$[Rh_6P_8(CN)_6]^{2-}$	O_h	2.68	2.41	3.39	2.02	-70.68	1.67
$Rh_6P_8(CN)_6$	D_{4h}	2.64/2.74	2.39/2.42	3.30/3.42	2.00/2.02	-61.82	1.04
$[Rh_6As_8(CN)_6]^{2-}$	C_2	2.77~2.89	2.30~2.83	2.45~3.99	1.98~2.03	-71.14	1.81
$[Rh_6As_8(CN)_6]^{2-}$	O_h	2.72	2.50	3.52	2.01	-69.38	1.58
$[Rh_6Sb_8(CN)_6]^{2-}$	C_{2h}	2.73/2.82/2.94	2.56~2.77	2.91~3.96	1.99/2.02	-68.11	1.42
$[Rh_6Sb_8(CN)_6]^{2-}$	O_h	2.81	2.65	3.75	2.00	-67.80	1.36
$[Ir_6P_8(CN)_6]^{2-}$	C_2	2.73~2.92	2.21~2.98	2.17~3.89	1.99/2.05	-83.90	1.82
$[Ir_6P_8(CN)_6]^{2-}$	O_h	2.70	2.44	3.44	2.02	-81.93	2.24
$Ir_6P_8(CN)_6$	D_{4h}	2.68/2.76	2.42/2.45	3.36/3.46	2.01/2.03	-73.00	0.94
$[Ir_6As_8(CN)_6]^{2-}$	O_h	2.75	2.53	3.57	2.01	-80.07	2.13
$[Ir_6Sb_8(CN)_6]^{2-}$	O_h	2.83	2.69	3.80	2.01	-77.90	1.86

Table S3. Symmetries, bond lengths, binding energy E_b (eV) and HOMO-LUMO gap of $[M_6Q_8(CN)_6]^{0/2-}$ (M=Ni, Pd, Pt; Q=P, As, Sb) calculated using B3LYP/Def2-TZVP.

	Symmetry	R_{M-M}	R_{M-Q}	R_{Q-Q}	R_{M-C}	E_b	Gap
$[Ni_6P_8(CN)_6]^{2-}$	D_{3d}	2.67	2.22/2.23	2.25/3.30	1.90	-65.59	1.88
$Ni_6P_8(CN)_6$	D_{3d}	2.66	2.24/2.28	2.22/3.11	1.87	-56.86	1.45
$[Ni_6As_8(CN)_6]^{2-}$	D_{3d}	2.76	2.32/2.34	2.49/3.58	1.90	-61.84	1.81
$[Ni_6Sb_8(CN)_6]^{2-}$	D_{2d}	2.71/2.81	2.55/2.56	3.07/3.61	1.85	-59.98	2.35
$[Ni_6Sb_8(CN)_6]^{2-}$	D_3	2.70/2.86	2.53/2.55/2.56	3.03/3.62/3.99	1.85	-59.94	2.41
$[Pd_6P_8(CN)_6]^{2-}$	D_{3d}	2.89	2.38/2.39	2.27/3.40	2.05	-64.14	1.50
$Pd_6P_8(CN)_6$	D_{3d}	2.91	2.37/2.49	2.23/3.23	2.01	-55.74	1.63
$[Pd_6As_8(CN)_6]^{2-}$	D_{3d}	2.98	2.48/2.49	2.49/3.65	2.04	-61.35	1.53
$[Pd_6Sb_8(CN)_6]^{2-}$	D_{3d}	3.14	2.64/2.66	2.86/4.03	2.04	-59.11	1.52
$[Pt_6P_8(CN)_6]^{2-}$	D_3	2.80/3.06	2.34/2.43/2.44	2.30/3.47	2.01	-74.48	1.91
$Pt_6P_8(CN)_6$	D_3	2.84/3.11	2.35/2.40/2.51	2.26/3.33	1.99	-66.28	1.77
$[Pt_6As_8(CN)_6]^{2-}$	D_3	2.84/3.23	2.46/2.52/2.56	2.54/3.76	2.01	-71.48	1.97
$[Pt_6Sb_8(CN)_6]^{2-}$	D_3	3.03/3.45	2.65/2.70	2.91/4.15	2.01	-69.50	1.92