Prediction of High Bond-Order Metal-Metal Multiple-Bonds in Heterobimetallic 3d−4f/5f Complexes [TM-M{N(*o*-[$NCH_2P(CH_3)_2$]C_6H_4)$_3$}] (TM = Cr, Mn, Fe; M = U, Np, Pu, and Nd)

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Table S1. The relative energy (kcal/mol) of different spin state and the selected calculated geometrical parameters (bond distances in Å and bond angles in degree) of CrUL at the PBE/def2-TZVPP level.

	Doublet	Quartet	Sextet
ΔE_{DFT}	0.0	22.9	31.9
ΔE_{CASSCF}	0.0	15.7	31.5
ΔE_{CASPT}	0.0	30.0	58.8
U-Cr	1.968	2.076	2.444
U-N_{sp}	2.573	2.520	2.604
U-N_{eq} (avg.)	2.275	2.293	2.289
Cr-P (avg.)	2.397	2.404	2.345
N-U-Cr	178.0	168.6	143.9
N_{eq}-U-N_{eq} (avg.)	107.3	108.8	106.0
P-Cr-P (avg.)	120.0	119.9	119.6
N-U-Cr (avg.)	111.1	109.0	109.8
P-Cr-U (avg.)	89.9	88.8	85.9
N_{eq}-C-P	112.3	111.8	110.8

Table S2. The relative energy (kcal/mol) of different spin state and the selected calculated geometrical parameters (bond distances in Å and bond angles in degree) of MnUL at the PBE/def2-TZVPP level.

	singlet	Triplet	Quintet
ΔE_{DFT}	0.0	23.9	52.4
ΔE_{CASSCF}	0.0	22.1	44.2
ΔE_{CASPT}	0.0	37.7	NA*
U-Mn	1.918	2.008	2.213
U-N_{sp}	2.557	2.515	2.526
U-N_{eq} (avg.)	2.264	2.285	2.296
Mn-P (avg.)	2.345	2.349	2.332
N-U-Mn	179.9	173.0	163.2
N_{eq}-U-N_{eq} (avg.)	108.4	109.3	109.0
P-Mn-P(avg.)	119.8	120.0	119.5
N-U-Mn (avg.)	110.5	108.9	108.3
P-Mn-U (avg.)	92.4	90.6	86.6
N_{eq}-C-P	113.1	111.9	111.3

*NA denote not considered

Table S3. The relative energy (kcal/mol) of different spin state and the selected calculated geometrical parameters (bond distances in Å and bond angles in degree) of FeUL at the PBE/def2-TZVPP level.

	Doublet	Quartet	Sextet
ΔE_{DFT}	0.0	31.0	52.5
ΔE_{CASSCF}	0.0	24.4	128.0
ΔE_{CASPT}	0.0	43.8	NA*
U-Fe	1.984	2.154	2.594
U-N_{sp}	2.494	2.525	2.611
U-N_{eq} (avg.)	2.273	2.280	2.240
Fe-P (avg.)	2.308	2.289	2.311
N-U-Fe	179.9	164.2	179.8
N_{eq}-U-N_{eq} (avg.)	110.4	109.3	108.4
P-Fe-P (avg.)	119.8	119.7	113.5
N-U-Fe (avg.)	108.5	108.1	110.5
P-Fe-U (avg.)	92.5	88.3	75.0
N_{eq}-C-P	112.6	111.7	111.4

*NA denote not considered

Table S4. The relative energy (kcal/mol) of two isomers with different spin states for TMNdL and NdTML, and for TMUL and UTML at the PBE/def2-TZVPP level.

TM	Multiplicity	TMNdL	NdTML	TMUL	UTML
Cr	Doublet	13.32	1.93	0.00	66.41
	Quartet	8.57		23.31	
	Sextet	7.66	0.00	32.36	68.57
Mn	Singlet	0.00	13.99	0.00	92.82
	Triplet	10.47	15.72	24.07	86.59
	Quintet	16.12	21.18	53.93	
Fe	Doublet	0.00	0.91	0.00	76.74
	Quartet	7.18	27.86	30.94	85.63
	Sextet	12.78	24.88	55.29	

Table S5. The relative energy (kcal/mol) of different spin states for TMAnL (An = U, Np, Pu) at the PBE, CASSCF and CASPT2 levels.

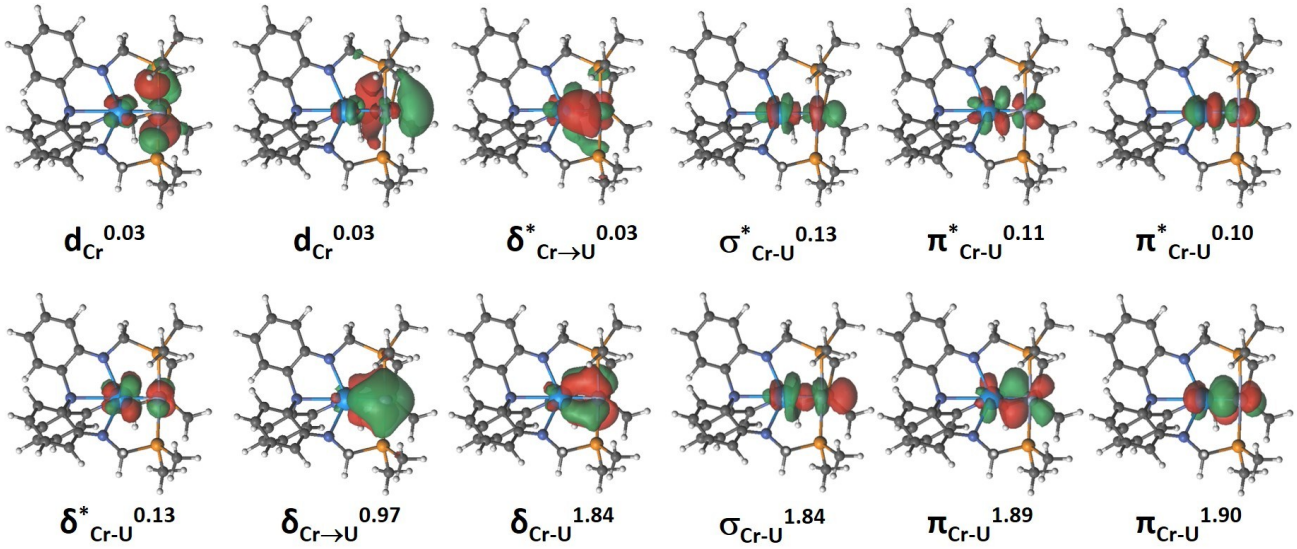
	CrUL			CrNpL				CrPuL			
2S+1	2	4	6	1	3	5	7	2	4	6	8
PBE	0.0	22.9	31.9	0.0	7.6	29.8	35.1	0.0	14.7	27.4	29.6
CASSCF	0.0	15.7	31.5	0.0	44.6	25.4	26.7	0.0	11.8	23.2	30.5
CASPT2	0.0	30.0	58.8	0.0	80.6	46.4	58.4	0.0	66.3	85.1	93.6
	MnUL			MnNpL				MnPuL			
2S+1	1	3	5	2	4	6	8	1	3	5	7
PBE	0.0	23.9	52.4	0.0	20.4	41.8	44.4	16.1	0.0	15.7	26.1
CASSCF	0.0	22.1	44.2	0.0	10.6	21.9	3.9	34.7	0.0	10.3	12.6
CASPT2	0.0	37.7	78.9	0.0	39.7	71.1	64.1	35.0	0.0	27.2	27.9
	FeUL			FeNpL				FePuL			
2S+1	2	4	6	1	3	5	7	2	4	6	8
PBE	0.0	31.0	52.5	9.1	0.0	17.3	36.8	19.9	0.0	10.9	19.3
CASSCF	0.0	24.4	128.0	21.7	0.0	11.6	24.2	32.0	0.0	12.0	17.8
CASPT2	0.0	43.8	134.4	NA	0.0	18.9	46.6	NA	0.0	20.2	10.4

Table S6. Molecular orbitals (MO), energy levels (ε_i, eV), occupation numbers (Occ.) and major percent compositions (%) on metal AOs of the highest occupied and lowest unoccupied valence molecular orbitals of doublet TMUL complex.

CrUL											
MO	ε_i	Type	Occ.	U					Cr		
				6p	5f	7s	6d	**Total**	3d	4p	**Total**
96	-4.203	π	2	1.17	7.47		1.52	**10.16**	22.59		**22.59**
97	-4.087	π	2	1.67	16.17			**17.84**	25.93		**25.93**
98	-3.927	σ	2	1.36	26.55	1.31	3.93	**33.15**	36.04	6.79	**42.83**
99	-3.881	δ	2		16.51		3.33	**19.84**	45.52		**45.52**
100[&]	-3.401	$3d_\delta$	1		19.65		7.72	**27.37**	30.35	6.67	**37.02**
101	-2.249	f_ϕ	0		80.67	10.78		**91.45**			**0**
102	-2.052	f_ϕ	0		81.28			**81.28**			**0**
103	-1.663	f_π	0		51.50		11.71	**63.21**	5.43		**5.43**
104	-1.601	f_π	0		56.34		9.27	**65.61**	6.01		**6.01**
105	-1.556	f_δ	0		58.33		2.22	**60.55**	7.90		**7.9**
106	-1.405	f_δ	0		58.33		2.22	**60.55**	7.90		**7.9**
MnUL											

MO	ε_i	Type	Occ.	U					Mn		
				6p	5f	7s	6d	**Total**	3d	4p	**Total**
93	-5.20	π	2	1.02	14.36		3.75	**19.13**	35.01		**35.01**
94	-5.20	π	2	1.03	13.93		4.33	**19.29**	34.92		**34.92**
96	-4.41	σ	2	1.84	19.41		1.21	**22.46**	19.95	2.98	**22.93**
99	-3.86	δ	2		17.70		5.44	**23.14**	41.69	3.79	**45.48**
100[&]	-3.85	δ	2		17.66		4.74	**22.40**	41.29		**41.29**
101	-2.27	f_ϕ	0		81.51	12.29	1.71	**95.51**			**0.00**
102	-2.05	f_ϕ	0		78.68			**78.68**			**0.00**
103	-1.72	f_π	0		56.12		12.34	**68.46**	6.72		**6.72**
104	-1.72	f_π	0		56.89	12.2		**69.09**	6.04		**6.04**
105	-1.51	f_δ	0		65.26			**65.26**	9.51		**9.51**
106	-1.51	f_δ	0		64.93			**64.93**	8.80		**8.8**
FeUL											
MO	ε_i	Type	Occ.	U					Fe		
				6p	5f	7s	6d	**Total**	3d	4p	**Total**
93	-5.396	π	2	1.53	11.79		3.44	**16.76**	39.98		**39.98**
94	-5.392	π	2	1.53	10.05		4.13	**15.71**	39.93		**39.93**
95	-4.961	σ	2	3.02	22.86		4.13	**30.01**	41.85	4.5	**46.35**
99	-4.162	δ	2		12.36		2.09	**14.45**	41.79	4.93	**46.72**
100	-4.16	δ	2		12.37		2.08	**14.45**	41.70	5.00	**46.70**
101[&]	-2.376	f_ϕ	1		79.87	11.92	2.11	**93.90**		1.08	**1.08**
102	-2.043	f_π	0		67.52		10.64	**78.16**	5.47		**5.47**
103	-2.042	f_π	0		66.28		10.59	**76.87**	5.49		**5.49**
104	-1.882	f_δ	0		74.83			**74.83**	12.36		**12.36**
105	-1.879	f_δ	0		75.70			**75.70**	12.25		**12.25**
106	-1.54	f_ϕ	0		73.90			**73.90**			**0.00**

[&] Highest occupied molecular orbital (HOMO).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$d_{Cr}^{0.03}$
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$\pi^*_{Cr\text{-}U}{}^{0.10}$
$\delta^*_{Cr\text{-}U}{}^{0.13}$
$\delta_{Cr\rightarrow U}{}^{0.97}$
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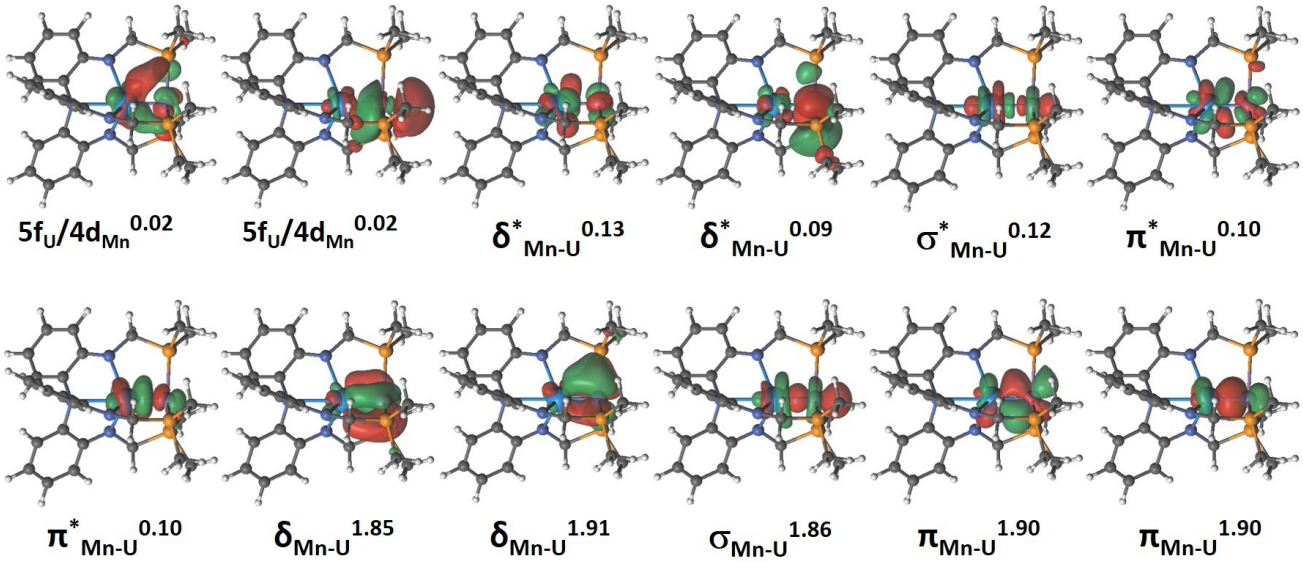
(a)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$\sigma^*_{Mn\text{-}U}{}^{0.12}$
$\pi^*_{Mn\text{-}U}{}^{0.10}$
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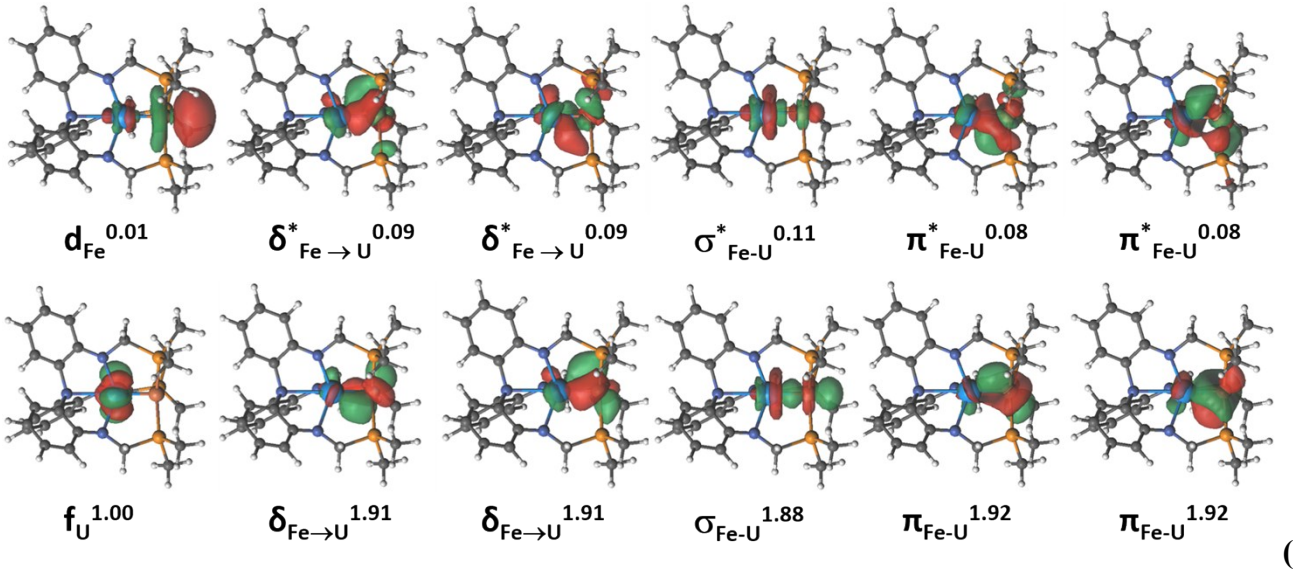
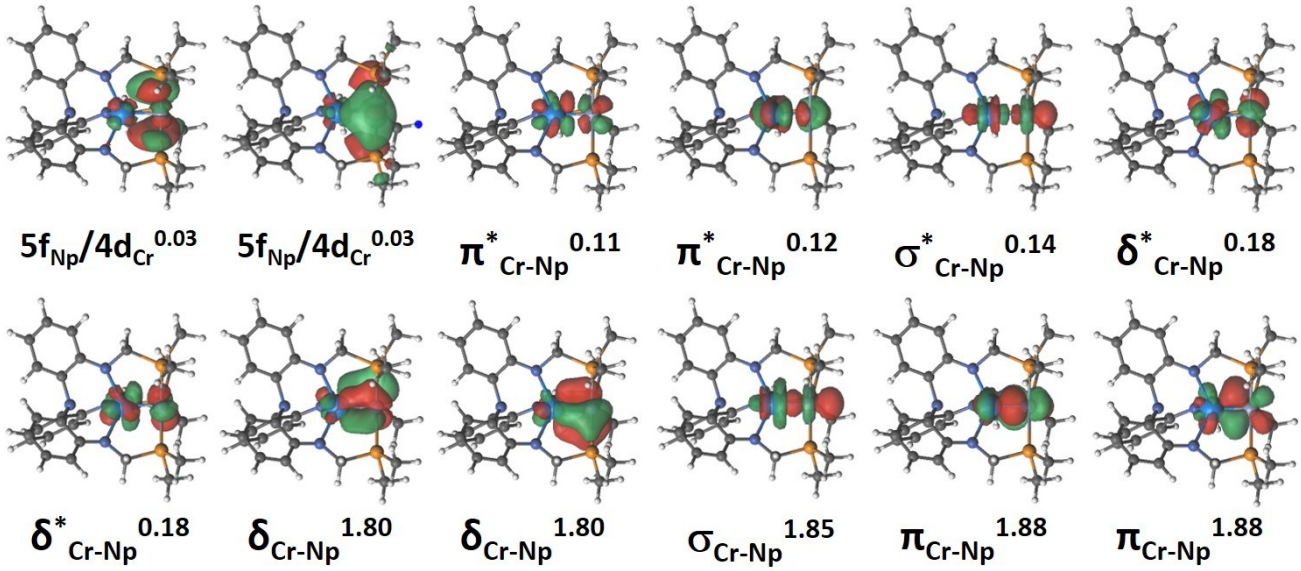
(b)



(

c)

Figure S1. Natural orbitals and occupation numbers of TMUL from CASSCF calculations with an active space of (9e,12o), (10e,12o) and (11e,12o) for the ^{2}A CrUL (a), ^{1}A MnUL (b) and ^{2}A FeUL (c), respectively.



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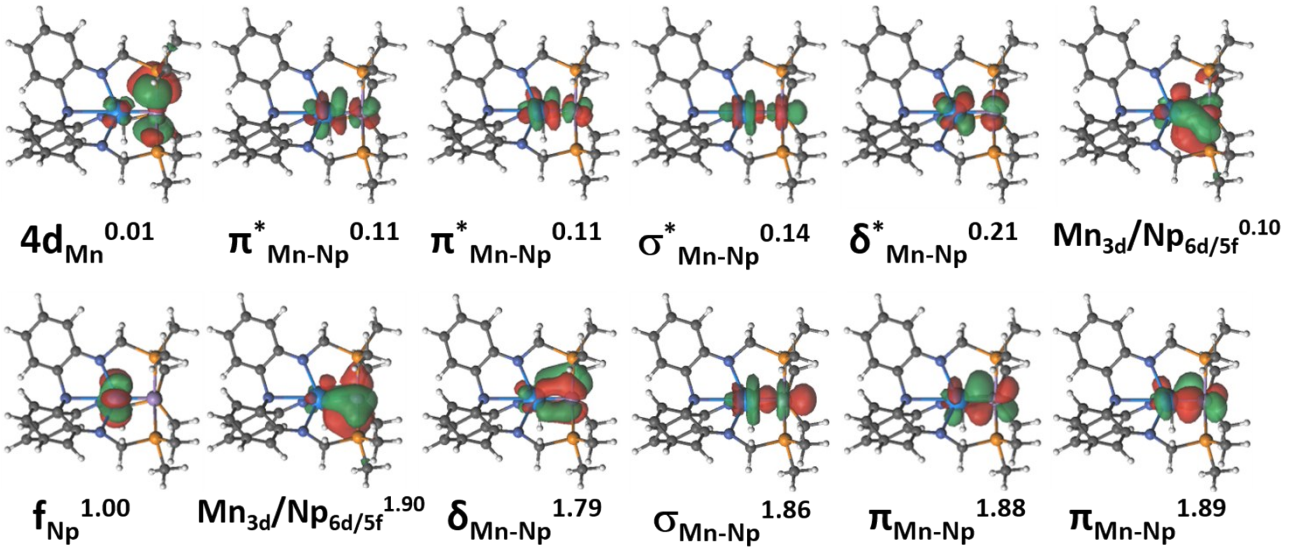

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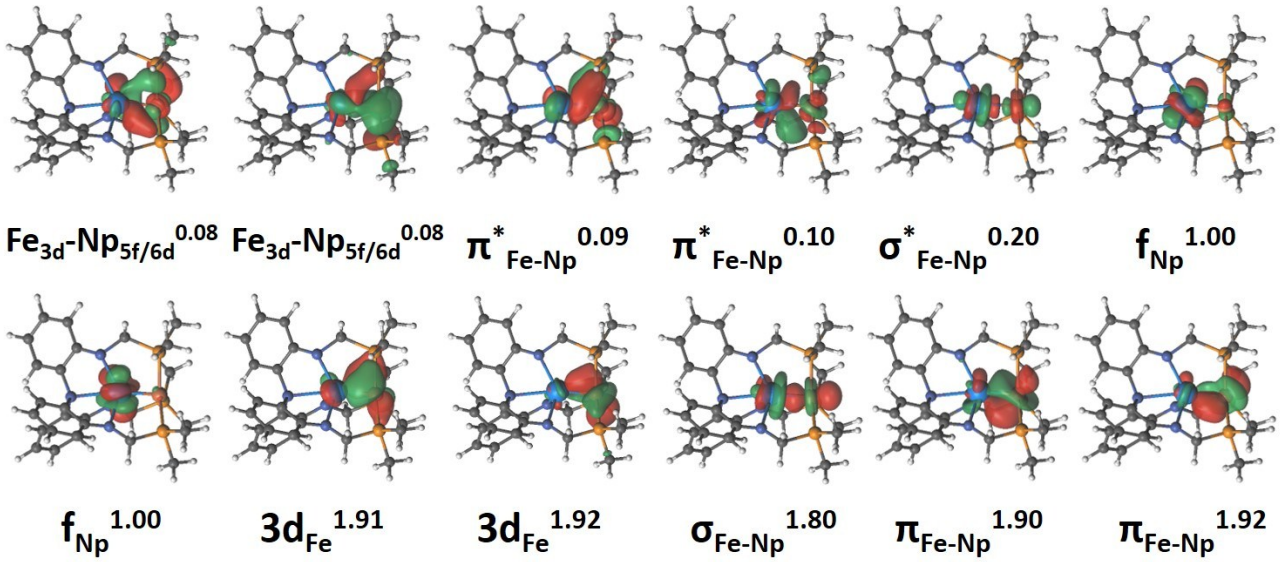
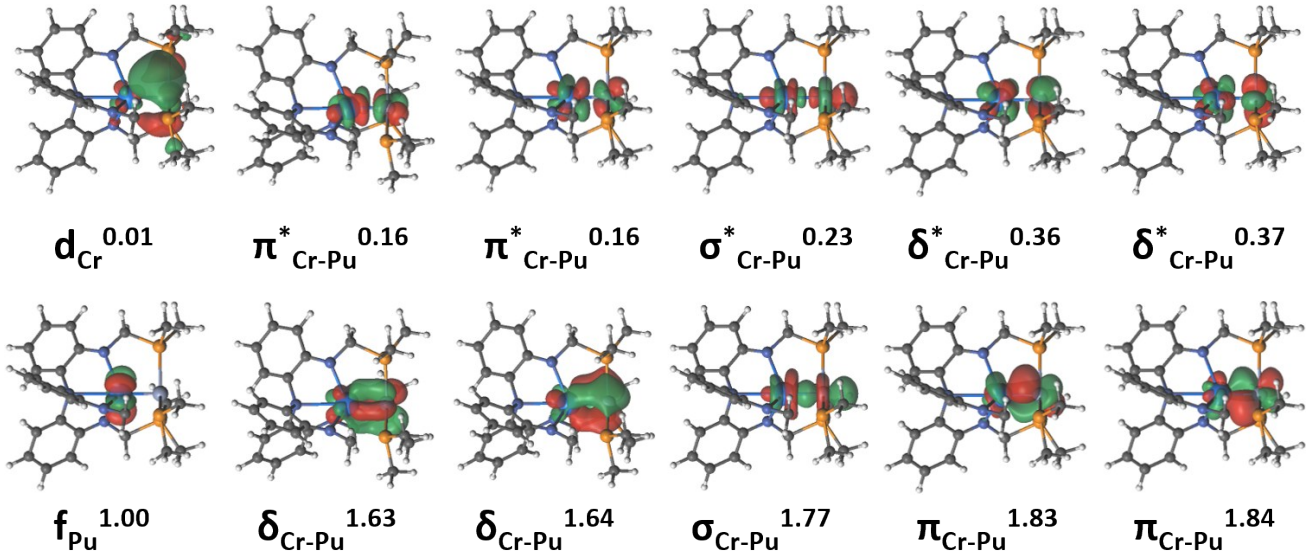


(f)

Figure S2. Natural orbitals and occupation numbers of TMNpL from CASSCF calculations with an active space of (10e,12o), (11e,12o) and (12e,12o) for the ^{1}A CrNpL (d), ^{2}A MnNpL (e) and ^{3}A FeNpL (f), respectively.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$\delta^*_{Cr\text{-}Pu}{}^{0.36}$
$\delta^*_{Cr\text{-}Pu}{}^{0.37}$
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$\delta_{Cr\text{-}Pu}{}^{1.64}$
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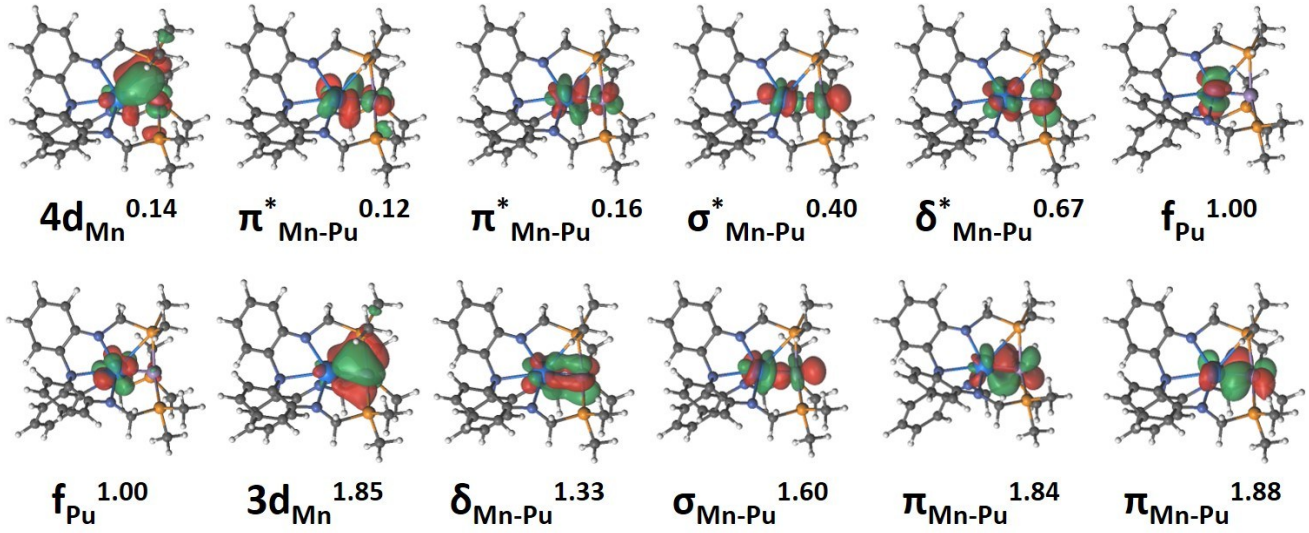
(g)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$f_{Pu}^{1.00}$
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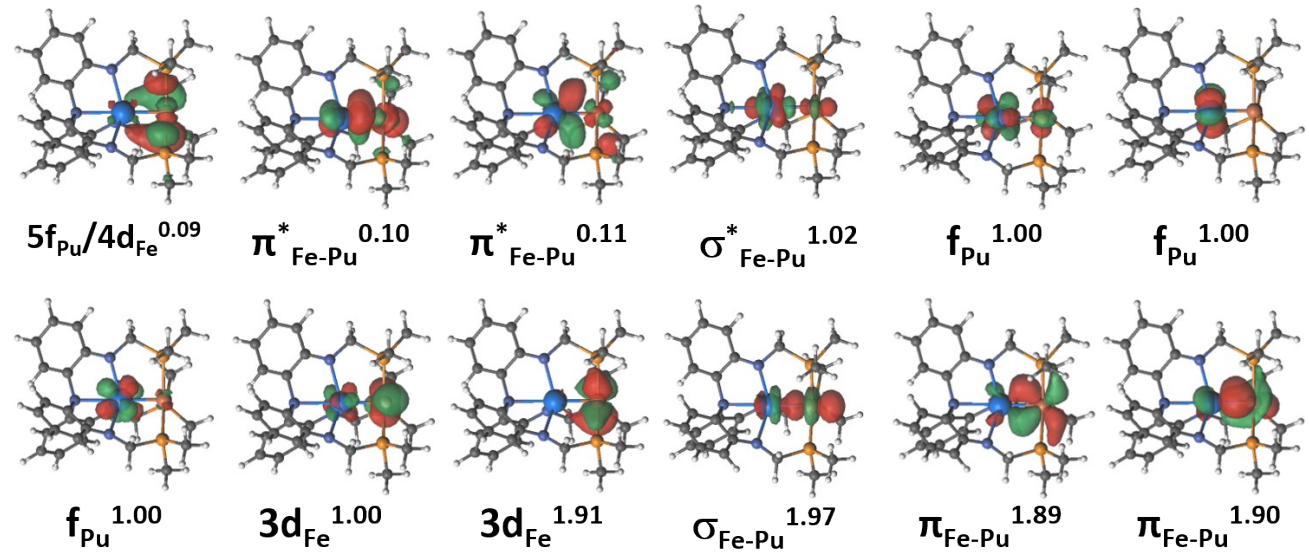
(h)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$f_{Pu}^{1.00}$
$f_{Pu}^{1.00}$
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$3d_{Fe}^{1.91}$
$\sigma_{Fe\text{-}Pu}{}^{1.97}$
$\pi_{Fe\text{-}Pu}{}^{1.89}$
$\pi_{Fe\text{-}Pu}{}^{1.90}$

(i)

Figure S3. Natural orbitals and occupation numbers of TMPuL from CASSCF calculations with an active space of (11e,12o), (12e,12o) and (13e,12o) for the ^{2}A CrPuL (g), ^{3}A MnPuL (h) and ^{6}A FePuL (i), respectively.

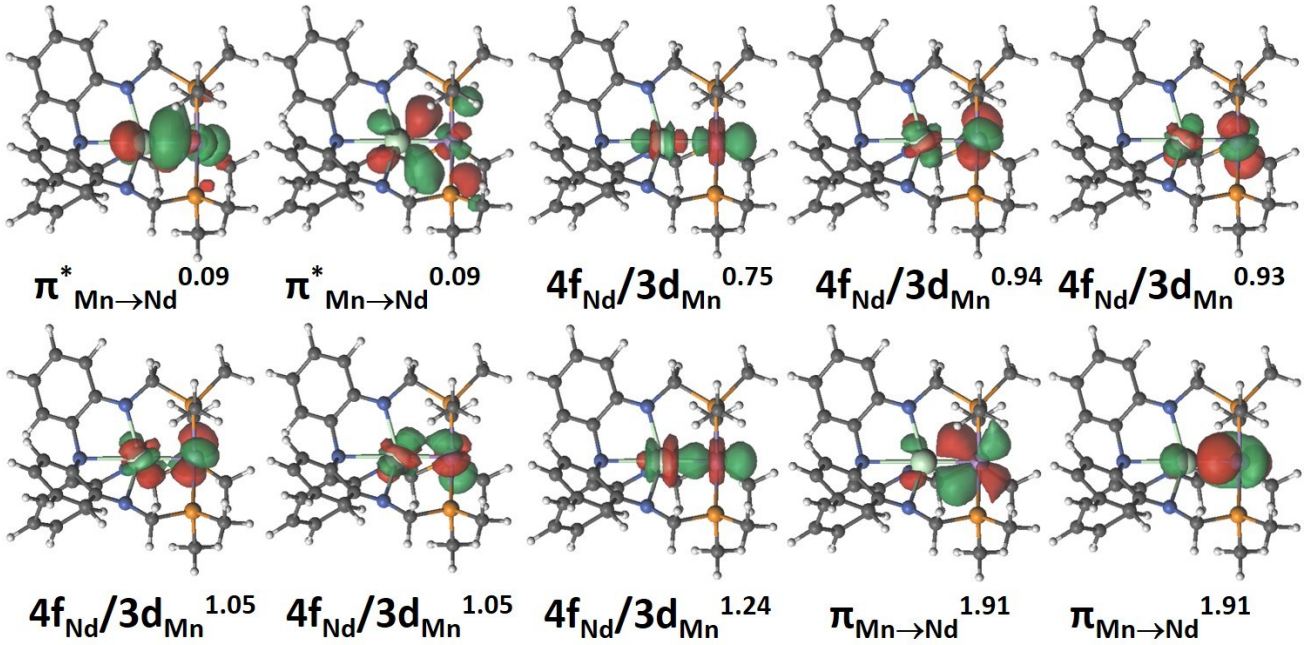

Figure S4. Natural orbitals and occupation numbers of anti-ferromagnetic coupling for singlet MnNdL from CASSCF (10,12)/VTZP/VDZP calculations. Two MOs with less than 0.1 |e| occupancies are not shown.