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SUPPORTING INFORMATION

Multiple phase and dielectric transitions on a novel multisensitive $[TPrA][M(dca)_3]$ (M: Fe^{2+}, Co^{2+} and Ni^{2+}) hybrid inorganic-organic perovskite family

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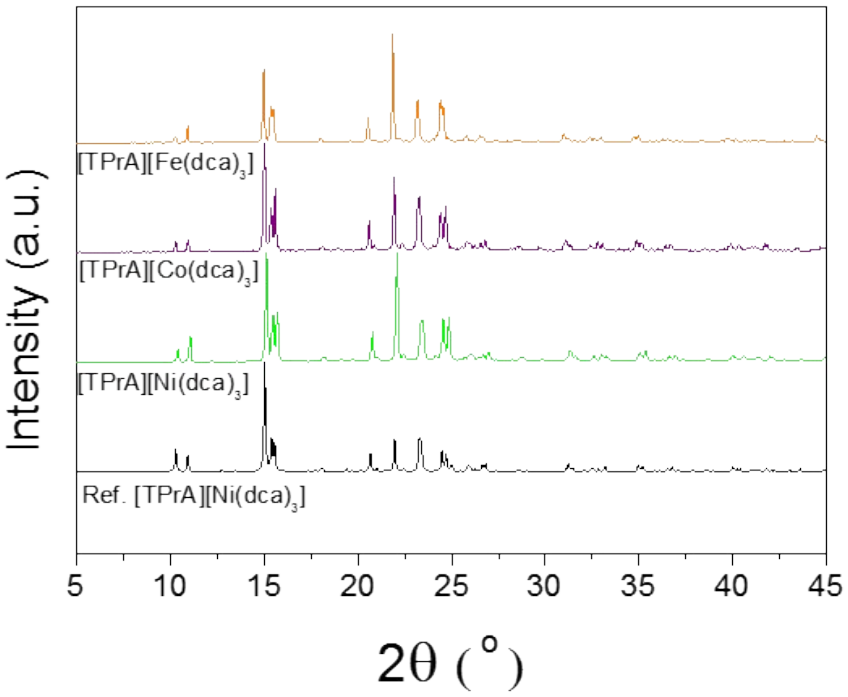

Fig. S1. Room temperature PXRD patterns for the obtained $[TPrA][M(dca)_3]$ (M: Fe^{2+}, Co^{2+} and Ni^{2+}) compounds and the simulated pattern based on the single crystal structures at room temperature.

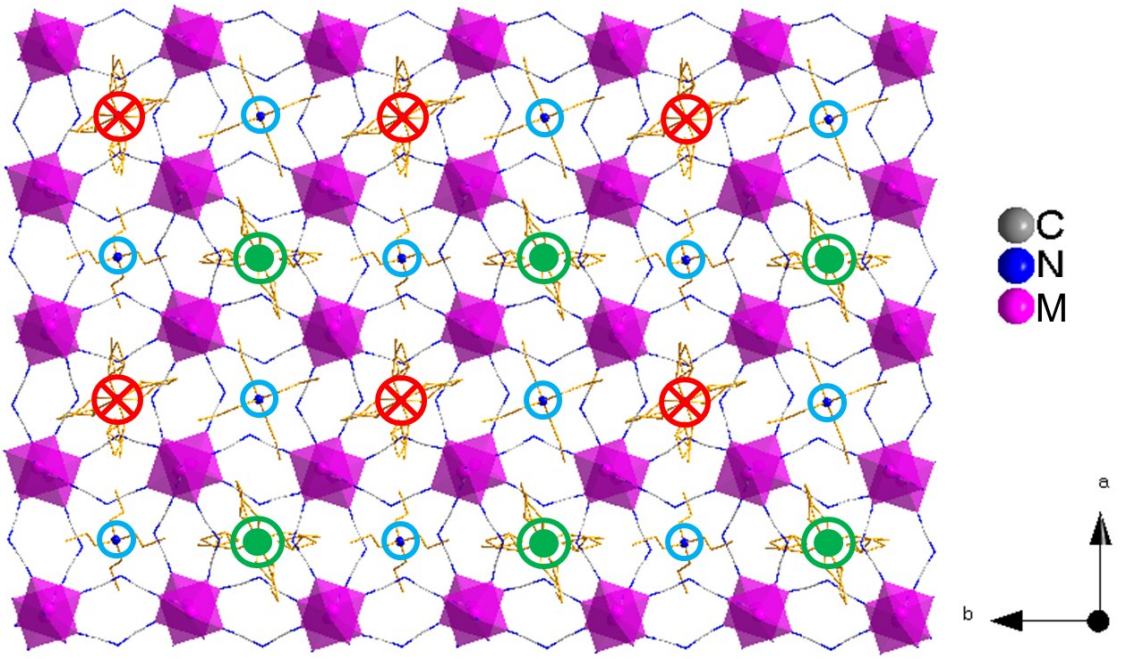

Fig. S2. Cooperative displacement of the TPrA cations in the crystal structure of *polymorph I*. Half of the TPrA cations (represented by green circles and red crosses) show a cooperatively off-center shift along the *c*-axis, following an antiferrodistorsive up down/up-down pattern: The green circles indicates the off-center shift towards the up face of the pseudo-cubooctahedral cavity (out of the page) and the red crosses represent the off-center shift towards its down face (into the page). The blue small circles represent the half of the TPrA cations that remains centered in the middle of the pseudo-cubooctahedral cavities.

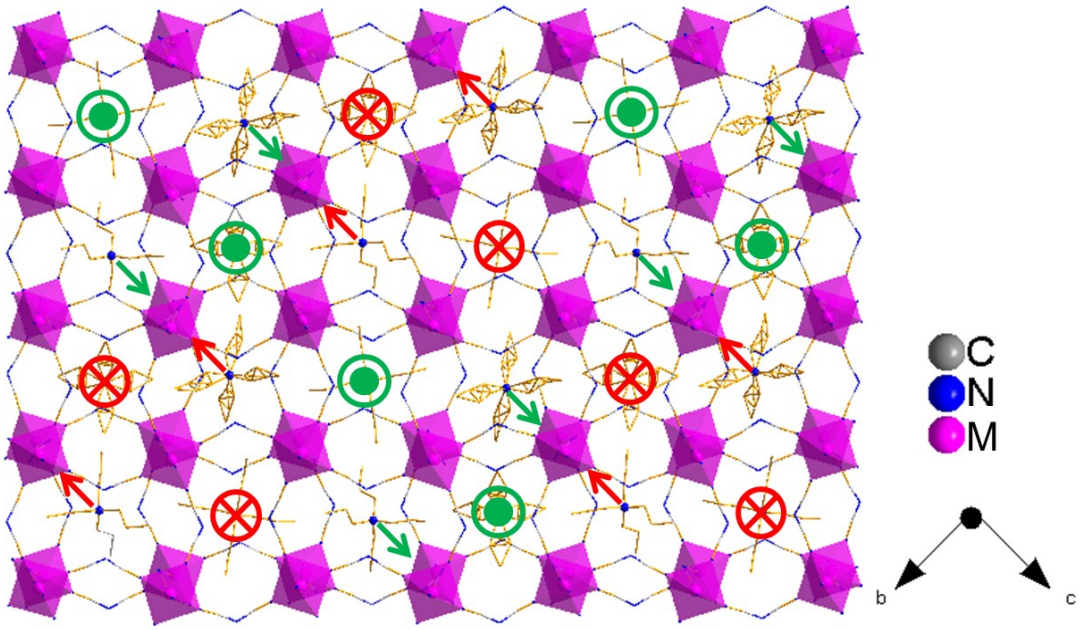

Fig. S3. Cooperative displacement of the TPrA cations in the crystal structure of *polymorph Ia*. Half of the TPrA cations (represented by green circles and red crosses) show a cooperative off-center shift along the *a*-axis towards one side of these cavities. These displaced TPrA cations are antiferrodistorsively arranged along the *b*-axis, displaying an up-down-up-down pattern: The green circles indicates the off-center shift towards the up face of the pseudo-cubooctahedral cavity (out of the page) and the red crosses represent the off-center shift towards its down face (into the page). The other half of the TPrA cations (represented by green and red arrows) show a cooperative off-center shift along the *c*-axis towards one edge of these cavities, following an antiferrodistorsive pattern.

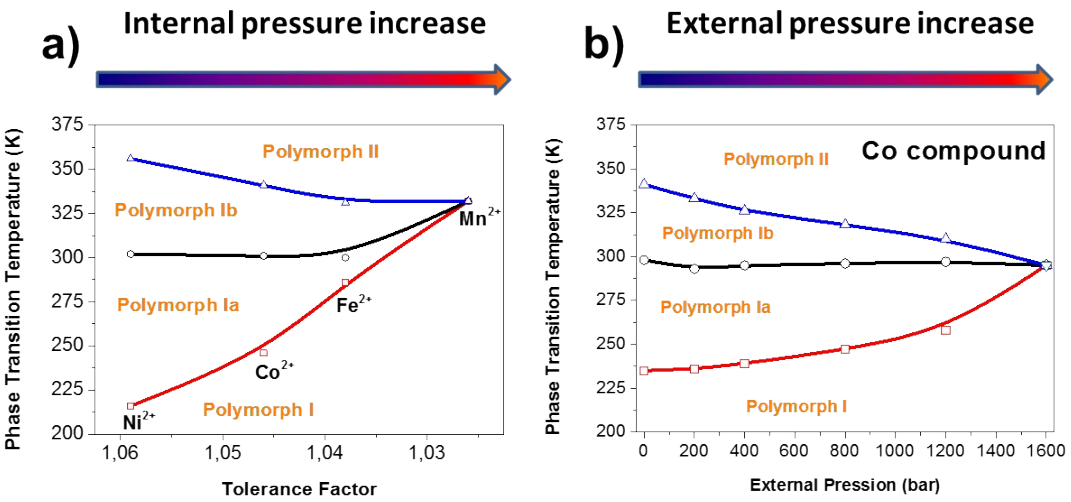

Fig. S4. (a) Tolerance factor and internal pressure effect on the phase transition temperature for different transition metal substitution in [TPrA][M(dca)$_3$] (M: Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}). (b) External pressure effect on the phase transition temperature for the different polymorphs of [TPrA][Co(dca)$_3$]. Similar results are obtained for the other Fe and Ni compounds.

Table SI. Enthalpy and entropy obtained for the different structural transitions by DSC on heating and cooling for the Fe, Co and Ni compounds.

		ΔH (heating) J mol^{-1}	ΔH (cooling) J mol^{-1}	ΔS (heating) J K mol^{-1}	ΔS (cooling) J K mol^{-1}	N (average)
Fe	T1	2096	2307	7.3	8.3	2.6
	T2	1266	1253	4.2	4.3	1.7
	T3	2343	2673	7.1	8.1	2.5
Co	T1	1786	1940	7.3	8.4	2.6
	T2	1341	1356	4.5	4.6	1.7
	T3	2116	2580	6.2	7.6	2.3
Ni	T1	362	387	1.7	2.2	1.2
	T2	1182	1203	3.9	4.1	1.6
	T3	2005	2140	5.6	6.0	2.0

Table SII. Crystallographic data obtained from single crystal X-ray diffraction for the three polymorphs of the [TPrA][Fe(dca)$_3$] compound. The *polymorph Ia* data are not available because the refinement of this structure is excessively complicated due to the proximity of the transition temperatures T1 and T2. We have to note that the Fe compound exhibit the same crystal structure at 100 K and 200 K, so we only will show the 200 K data.

	1Fe	**1bFe**	**2Fe**
Formula	$C_{18}H_{28}N_{10}Fe$	$C_{18}H_{28}N_{10}Fe$	$C_{18}H_{28}N_{10}Fe$
Formula weight	440.33	440.33	440.33
Temperature (K)	200(2)	323(2)	368(2)
Crystal system	Tetragonal	Orthorhombic	Tetragonal
Space group	*P*-42(1)*c*	*Ibam*	*I4/mcm*
Superlattice	2ax2ax2a	≈√2ax≈√2ax2a	≈√2ax≈√2ax2a
***a* (Å)**	16.1494(6)	11.5219(4)	11.4980(2)
***b* (Å)**		11.5355(4)	
***c* (Å)**	17.2252(5)	17.3841(5)	17.4980(3)
Unit cell volume (Å^3)	4492.4(3)	2310.54(13)	2313.31(7)
Z	8	4	4
V/Z (Å^3)	561.5(5)	577.63(5)	578.32(9)
Nº. of reflections measured	39586	16957	17874
Nº. of independent reflections	4558	1319	713
R_{int}	0.0605	0.0308	0.0269
Final R_1 values ($I > 2\sigma(I)$)	0.0480	0.0445	0.0423
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1315	0.1271	0.1310
Final R_1 values (all data)	0.0549	0.0605	0.0514
Final $wR(F^2)$ values (all data)	0.1370	0.1425	0.1436
Goodness of fit on F^2	1.142	1.036	1.122
Flack parameter	0.58(3)		
CSD-number	431141	431140	431139

Table SIII. Crystallographic data obtained from single crystal X-ray diffraction for the four polymorphs of the [TPrA][Co(dca)$_3$] compound. We have to note that this compound exhibit the same crystal structure at 100 K and 200 K, so we only will show the 200 K data.

	1Co	1aCo	1bCo	2Co
Formula	$C_{18}H_{28}N_{10}Co$	$C_{18}H_{28}N_{10}Co$	$C_{18}H_{28}N_{10}Co$	$C_{18}H_{28}N_{10}Co$
Formula weight	443.41	443.41	443.41	443.41
Temperature (K)	200(2)	300(2)	323(2)	368(2)
Crystal system	Tetragonal	Orthorhombic	Orthorhombic	Tetragonal
Space group	*P-42(1)c*	*Pnna*	*Ibam*	*I4/mcm*
Superlattice	2ax2ax2a	2a≈2√2ax≈2√2a	≈√2ax≈√2ax2a	≈√2ax≈√2ax2a
***a* (Å)**	16.1258(4)	17.2246(6)	11.4145(2)	11.4551(2)
***b* (Å)**		23.0205(9)	11.5693(2)	
***c* (Å)**	17.1229(4)	22.8310(8)	17.3062(3)	17.4294(3)
Unit cell volume (Å^3)	4452.66(19)	9052.9(6)	2285.42(7)	2287.07(7)
Z	8	16	4	4
V/Z (Å^3)	556.58(27)	565.8(1)	571.35(6)	571.76(9)
Nº. of reflections measured	9646	90479	12962	790
Nº. of independent reflections	4953	7731	1316	790
R_{int}	0.0134	0.1592	0.0211	0.0000
Final R_1 values ($I > 2\sigma(I)$)	0.0507	0.0747	0.0402	0.0493
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1389	0.2068	0.1145	0.1433
Final R_1 values (all data)	0.0529	0.1370	0.0491	0.0587
Final $wR(F^2)$ values (all data)	0.1409	0.2717	0.1251	0.1559
Goodness of fit on F^2	1.198	1.036	1.115	1.127
Flack parameter	0.53(3)			
CSD-number	431145	431144	431143	431142

Table SIV. Crystallographic data obtained from single crystal X-ray diffraction for the four polymorphs of the [TPrA][Ni(dca)$_3$] compound. This material exhibit the same crystal structure at 100 K and 180 K, so we only will show the 180 K data.

	1Ni	1aNi	1bNi	2Ni
Formula	$C_{18}H_{28}N_{10}Ni$	$C_{18}H_{28}N_{10}Ni$	$C_{18}H_{28}N_{10}Ni$	$C_{18}H_{28}N_{10}Ni$
Formula weight	443.17	443.17	443.17	443.17
Temperature (K)	180(2)	300(2)	323(2)	368(2)
Crystal system	Tetragonal	Orthorhombic	Orthorhombic	Tetragonal
Space group	*P-42(1)c*	*Pnna*	*Ibam*	*I4/mcm*
Superlattice	2ax2ax2a	2a≈2√2ax≈2√2a	≈√2ax≈√2ax2a	≈√2ax≈√2ax2a
***a* (Å)**	16.0830(4)	17.1299(5)	11.3524(3)	11.390(5)
***b* (Å)**		22.9364(6)	11.5038(3)	
***c* (Å)**	17.0185(4)	22.6975(6)	17.1916(4)	17.301(5)
Unit cell volume (Å^3)	4402.05(19)	8917.8(4)	2245.15(10)	2244.5(15)
Z	8	16	4	4
V/Z (Å^3)	550.25(64)	557.3(6)	561.28(77)	561.12(87)
Nº. of reflections measured	75393	84174	24633	27474
Nº. of independent reflections	4868	7354	1292	699
R_{int}	0.0412	0.1158	0.0491	0.0480
Final R_1 values ($I > 2\sigma(I)$)	0.0720	0.0671	0.0382	0.0364
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1724	0.1814	0.1019	0.1036
Final R_1 values (all data)	0.0740	0.1075	0.0470	0.0440
Final $wR(F^2)$ values (all data)	0.1757	0.2257	0.1140	0.1157
Goodness of fit on F^2	1.262	1.042	1.091	1.162
Flack parameter	0.45(4)			
CSD-number	431138	431137	431136	431135

Table SV. Summary of selected bond length and angles for the *polymorph I* of [TPrA][M(dca)$_3$] (M: Fe^{2+}, Co^{2+} and Ni^{2+}) compounds.

Distance (Å)	Fe 200 K	Co 200K	Ni 200 K	Angle (°)	Fe 200 K	Co 200K	Ni 200 K
M-N1	2.161(5)	2.119(4)	2.099(5)	**M-N1-C1**	175.4(5)	176.6(5)	175.1(7)
M-N2	2.188(3)	2.106(3)	2.051(5)	**M-N2-C2**	169.9(4)	160.5(4)	162.0(7)
M-N3	2.167(3)	2.153(3)	2.075(5)	**M-N3-C3**	173.1(3)	170.6(4)	165.0(5)
M-N4	2.185(3)	2.145(3)	2.096(5)	**M-N4-C4**	161.1(4)	163.3(4)	173.3(5)
M-N5	2.154(3)	2.130(3)	2.109(5)	**M-N5-C5**	162.7(3)	172.7(4)	171.8(6)
M-N6	2.138(4)	2.116(3)	2.092(5)	**M-N6-C6**	159.6(4)	164.6(3)	165.2(5)
M-M (*c*-axis)	8.640(3)	8.582(8)	8.525(1)	**Tilting**	**Fe 200 K**	**Co 200K**	**Ni 200 K**
M-M (*ab*-plane)	8.151(4)-8.183(5)	8.126(2)-8.156(1)	8.091(1)-8.118(1)	***c*-axis**	4.6(1)-12.6(1)	5.4(1)-13.0(1)	6.2(2)-12.8(2)
				***ab*-plane**	26.0(4)-32.3(1)	25.4(1)-31.2(7)	24.6(1)-30.2(1)

Table SVI. Summary of selected bond length and angles for the *polymorph Ia* of [TPrA][M(dca)$_3$] (M: Fe^{2+}, Co^{2+} and Ni^{2+}) compounds.

Distance (Å)	Co 300K	Ni 300 K	Angle (°)	Co 300K	Ni 300 K
M1-N1	2.136 (5)	2.090(5)	**M1-N1-C***	171.6(8)	169.9(5)
M1-N2	2.098 (5)	2.086(5)	**M1-N2-C***	161.5(7)	174.6(6)
M1-N3	2.133 (7)	2.090(5)	**M1-N3-C***	166.9(6)	175.9(5)
M1-N4	2.122 (5)	2.081(5)	**M1-N4-C***	168.7(5)	173.3(5)
M1-N5	2.123 (5)	2.087(5)	**M1-N5-C***	175.8(5)	170.0(5)
M1-N6	2.121 (5)	2.082(5)	**M1-N6-C***	170.7(5)	172.7(4)
M2-N7	2.128 (7)	2.057(5)	**M2-N7-C***	168.0(8)	162.1(6)
M2-N8	2.110 (5)	2.104(5)	**M2-N8-C***	173.7(7)	170.9(7)
M2-N9	2.124 (5)	2.085(5)	**M2-N9-C***	171.3(5)	169.0(4)
M2-N10	2.126 (5)	2.094(5)	**M2-N10-C***	169.8(5)	176.0(5)
M2-N11	2.110 (5)	2.080(5)	**M2-N11-C***	173.1(5)	171.4(4)
M2-N12	2.133 (5)	2.095(5)	**M2-N12-C***	175.6(5)	167.5(5)
M1-M1 (*a*-axis)	8.529(1)-8.707(1)	8.478(4)-8.659(9)	**Tilting**	**Co 300K**	**Ni 300 K**
M2-M2 (*a*-axis)	8.619(1)-8.619(1)	8.570(1)-8.570(1)	***a*-axis**	2.5(1) - 10.5(2)	2.8(1)-10.5(1)
M1-M2 (*bc*-plane)	8.094(1)-8.154(1)	8.058(1)-8.112(1)	***bc*-plane**	26.1(1)-31.0(2)	25.2(1)-30.1(1)

C*: carbon bonded to the respective dicyanamide N-terminal atom.

Table SVII. Summary of selected bond length and angles for the *polymorph Ib* of [TPrA][M(dca)$_3$] (M: Fe^{2+}, Co^{2+} and Ni^{2+}) compounds.

Distance (Å)	Fe 323 K	Co 323 K	Ni 323 K	Angle (°)	Fe 323 K	Co 323 K	Ni 323 K
M-N1	2.158(3)	2.127(2)	2.082(3)	**M-N1-C1**	172.2(3)	173.4(3)	174.2(3)
M-N2	2.158(3)	2.120(2)	2.078(2)	**M-N2-C2**	172.0(3)	172.5(3)	173.2(3)
M-N4	2.149(5)	2.125(3)	2.082(3)	**M-N4-C3i**	150(2)	150 (2)-157 (3)	151(2)-158(2)
M-M (*c*-axis)	8.692(1)	8.653(1)	8.595(8)	**Tilting**	**Fe 323 K**	**Co 323 K**	**Ni 323 K**
M-M (*ab*-*plane*)	8.152(0)	8.126(2)	8.081(1)	***c*-axis**	0.0(1)	0.00(9)	0.00(9)
				***ab*-plane**	28.86(9)-28.97(9)	27.93(8)-28.48(6)	27.13(8)-27.62(8)

C3i: carbon bonded to the respective dicyanamide N-terminal atom, where i = A, B.

Table SVIII. Summary of selected bond length and angles for the *polymorph II* of [TPrA][M(dca)$_3$] (M: Fe^{2+}, Co^{2+} and Ni^{2+}) compounds.

Distance (Å)	Fe 368 K	Co 368 K	Ni 368 K	Angle (°)	Fe 368 K	Co 368 K	Ni 368 K
M-N1	2.164(3)	2.131(3)	2.104(5)	**M-N1-C1i**	160.7(7)-174.9(7)	160.6(7)-174.7(6)	160.7(7)-175.4(6)
M-N2	2.170(5)	2.149(5)	2.083(4)	**M-N2-C2**	156(4)	156.1(8)	157(6)
M-M (*c*-axis)	8.749(0)	8.714(7)	8.650(2)	**Tilting**	**Fe 368 K**	**Co 368 K**	**Ni 368 K**
M-M (*ab*-plane)	8.130(3)	8.100(0)	8.054(3)	***c*-axis**	0.0(1)	0.0(1)	0.0(1)
				***ab*-plane**	29.56(9)	29.19(9)	28.42(9)

C1i: carbon bonded to the respective dicyanamide N-terminal atom, where i = A, B.

Table SIX. The ionic radii for the B-site transition metal cations were obtained from the Shannon ionic radii tables [R. D. Shannon, *Acta Cryst. A*, 1976, **32**, 751]. The effective radii for the TPrA cations ($r_{A(eff)} = r_{A(mass)} + r_{A(ion)}$) and the cylinder parameters of the dca anions ($h_{X(eff)}$ *and* $r_{X(eff)} = r_{X(mass)} + r_{X(ion)}$) were calculated by using experimental room temperature crystallographic data. Differences between the TPrA and dca ligands were observed as a function of the crystallographic structure due to their large flexibility. Thus, an average value was calculated with and estimated error of 3%.

Calculated cationic radii and anionic cylinder parameters					Tolerance Factor $\alpha = (r_{A(eff)} + r_{X(eff)}) / \sqrt{2}(r_B + 0.5\, h_{X(eff)})$	
TPrA	$r_{A(mass)}$ (pm)	$r_{A(ion)}$ (pm)	$r_{A(eff)}$ (pm)		Mn	1.02(6)
	388	15	403		Fe	1.03(8)
dca	$r_{X(mass)}$ (pm)	$r_{X(ion)}$ (pm)	$r_{X(eff)}$ (pm)	$h_{X(eff)}$ (pm)	Co	1.04(6)
	103	146	249	732	Ni	1.05(9)