Supporting Information

A supramolecular perspective of coordination effects on fluorine interactions

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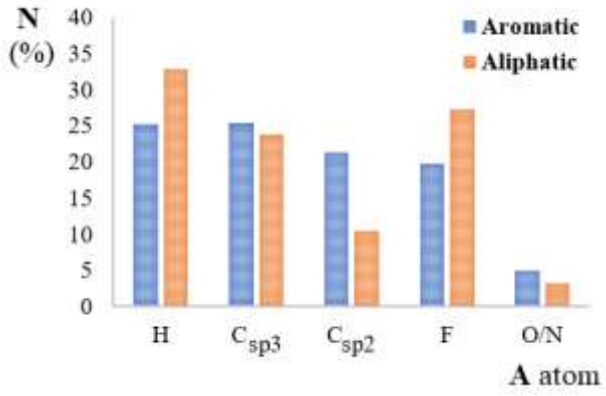


Figure S1. The distribution of the relative abundance of atoms at position A in two the most frequent groups of contacts.

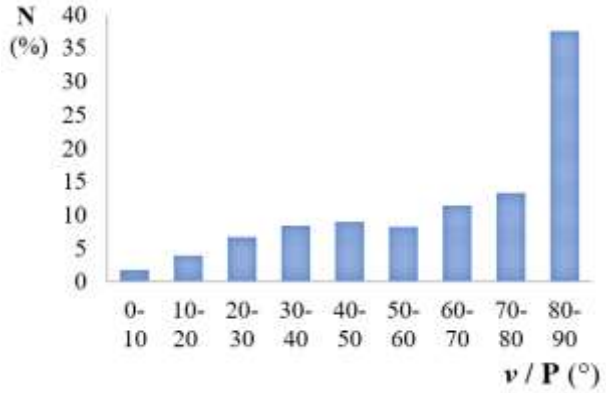


Figure S2. The distribution of parameter v/P, corresponding to the angle between the vector B–A (Scheme 1) and the aromatic C_6-ring is used to describe F/F interactions among aromatic contacts.

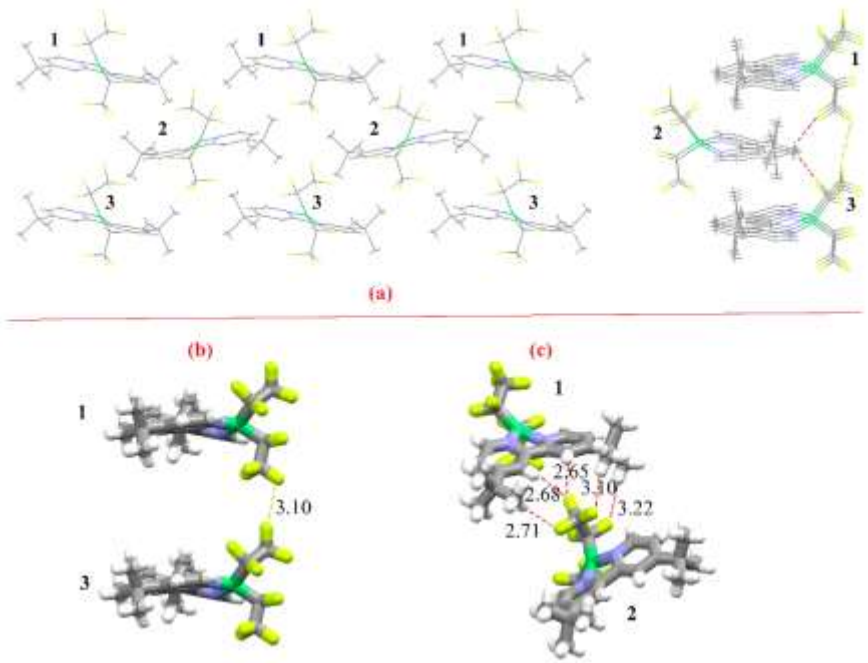


Figure S3. Crystal structure with refcode BEBZAL (a),[19] and Ni(II) complex dimers with F/F interaction (b) and C-H/F interaction (c), used as initial structures for modelling the influence of coordination on the interactions of the F atoms bonded to the aliphatic groups. Numerals 1, 2, and 3 denote the row in which molecules are arranged in the crystal structure. The green dashed lines denote F/F interactions and the red dashed lines denote C-H/F interactions. The numbers next to the dashed lines are the distances between interacting atoms in Å.

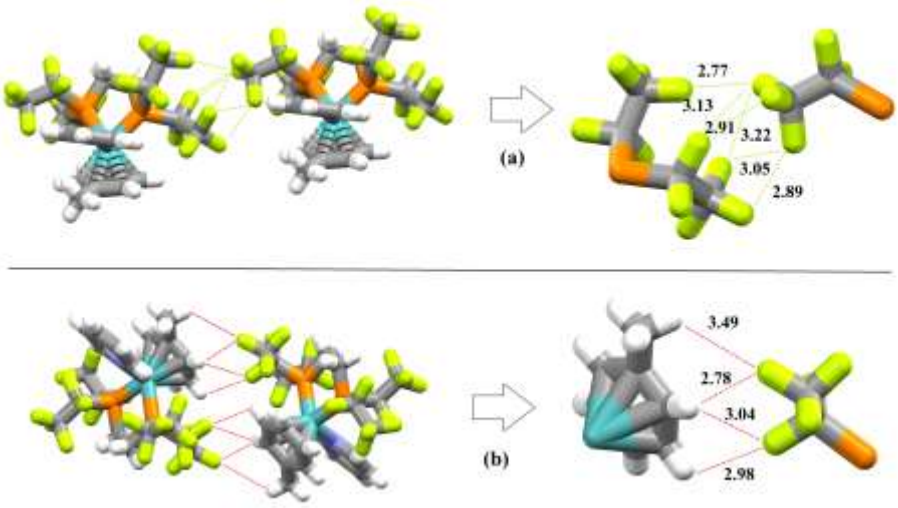
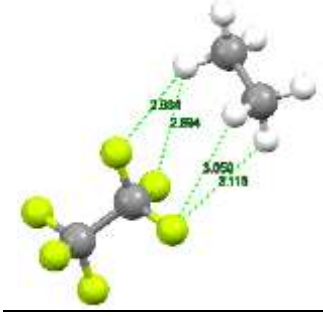


Figure S4. The dimer structures of Mo(0) complexes with F/F interaction (a) and C-H/F interaction (b), extracted from the crystal structure with refcode VESLOU,[20] and used as initial structures for modelling the influence of coordination on the interactions of the F atoms bonded to the aliphatic groups.

Table S1. The values of F/F interaction energies in dimer model system of two hexafluoroethane molecules calculated at CCSD (T)/CBS and APDF/dgauss-dzvp level of theory.

Model system for F/F interactions	Level of theory	Interaction energy (in kcal/mol)		
		Corrected	Uncorrected	Mean
	CCSD(T)/aug-cc-pVDZ	–0.73	–3.35	–2.03
	MP2/aug-cc-pVDZ	–0.52	–2.64	–1.58
	MP2/aug-cc-pVTZ	–0.82	–1.83	–1.33
	MP2/aug-cc-pVQZ	–0.90	–1.37	–1.14
	MP2/CBS	–0.95	–1.10	–1.03
	CCSD(T)/CBS	–1.16	–1.81	**–1.49**
	APDF/ dgauss-dzvp	**–1.53**	–	–

Table S2. The values of C−H/F interaction energies in the dimer model system of hexafluoroethane and ethane molecules calculated at CCSD (T)/CBS and APDF/dgauss-dzvp level of theory.

Model system for C−H/F interactions	Level of theory	Interaction energy (in kcal/mol)		
		Corrected	Uncorrected	Mean
	CCSD(T)/aug-cc-pVDZ	–0.82	–2.51	–1.67
	MP2/aug-cc-pVDZ	–0.72	–2.29	–1.51
	MP2/aug-cc-pVTZ	–0.94	–1.64	–1.29
	MP2/aug-cc-pVQZ	–0.99	–1.34	–1.17
	MP2/CBS	–1.02	–1.17	–1.09
	CCSD(T)/CBS	–1.12	–1.39	**–1.25**
	APDF/ dgauss-dzvp	**–1.30**	–	–

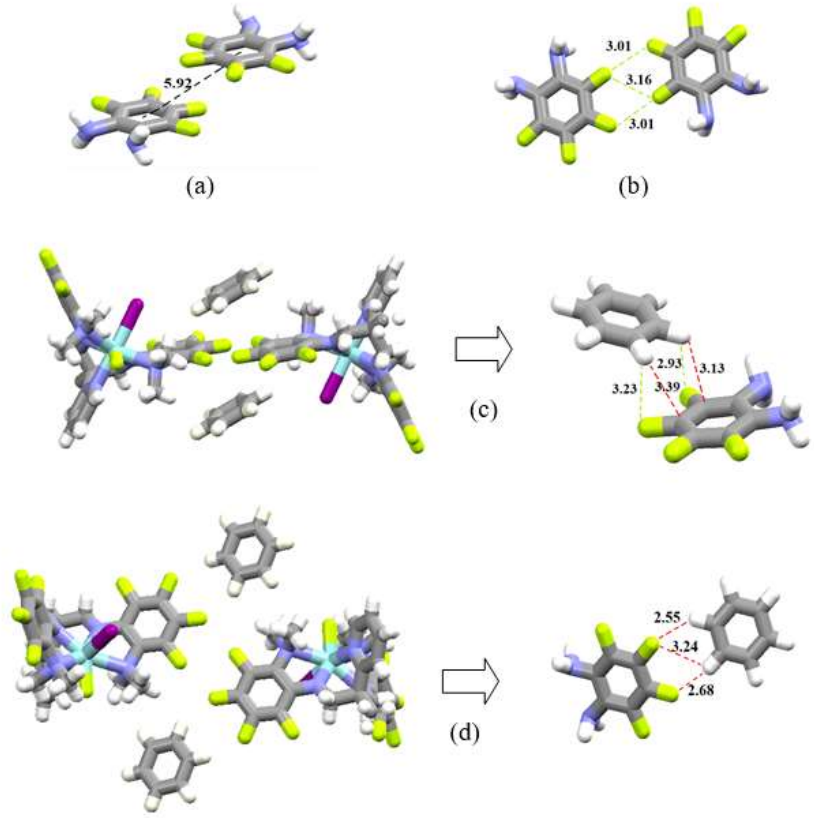


Figure S5. Model systems for assessing the strength of F/F interactions with parallel orientation at large distance (a) and planar orientation of the aromatic rings (b), as well as model systems with C–H/π (c) and C–H/F interactions (d) between the benzene molecule and the fluorinated C_6-aromatic ring. Model systems are extracted from the crystal structure with refcode MINMAZ[22] or obtained by reduction of their structures, and used for the evaluation of the coordination influence on interactions of the fluorine atom bound to the aromatic group.

Table S3. Total interaction energy (ΔE_{APFD}), Hartree–Fock energy (ΔE_{HF}) and dispersion energy (ΔE_{disp}, $\Delta E_{disp}=\Delta E_{APFD} - \Delta E_{HF}$) calculated at the model system from Figure 7. Energies are expressed in kcal/mol.

Model system	ΔE_{APFD}	ΔE_{HF}	ΔE_{disp*}
Figure 7a	–3.51	0.40	–3.91
Figure 7b	–3.32	0.82	–4.14
Figure 7c	–3.12	0.79	–3.91
Figure 7d	–2.02	0.00	–2.02
Figure 7e	–1.10	0.70	–1.80
Figure 7f	–0.70	0.83	–1.53

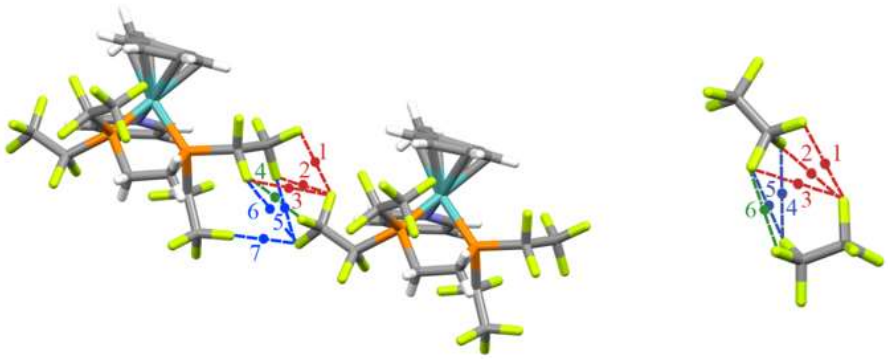


Figure S6. Molecular graphs obtained from the QTAIM analyses of the model systems (shown in Figure 5a and 5c) for assessment of the strength of the F/F interactions. The dashed lines correspond to noncovalent interactions, while the circles correspond to (3,–1) bond critical points (BCP). The structures of model systems are extracted from the crystal structure with the refcode VESLOU[20] or obtained by reduction of their structures.

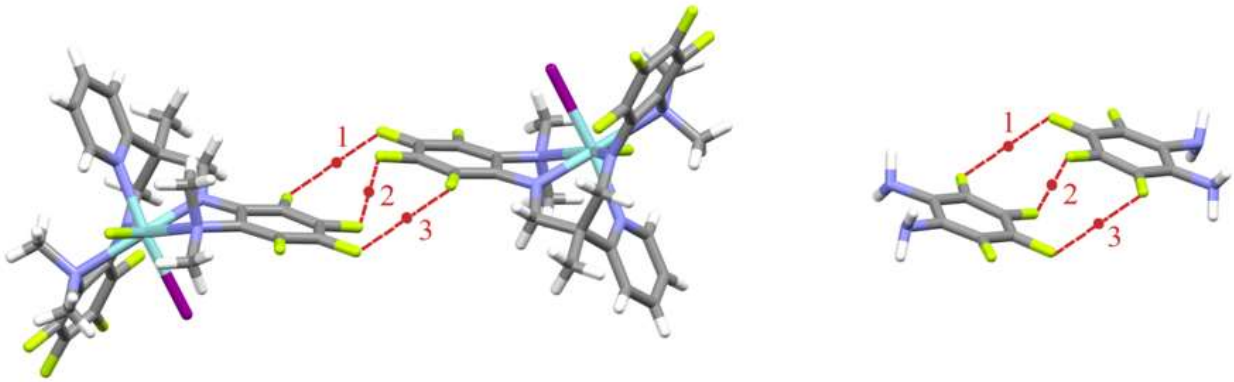


Figure S7. Molecular graphs obtained from the QTAIM analyses of the model systems (presented in Figure 7a and 7c) for assessment of the strength of the F/F interactions. The dashed lines correspond to noncovalent interactions, while the circles correspond to (3,–1) bond critical points (BCP). The structures of model systems are extracted from the crystal structure with the *refcode* MINMAZ[22] or obtained by reduction of their structures.

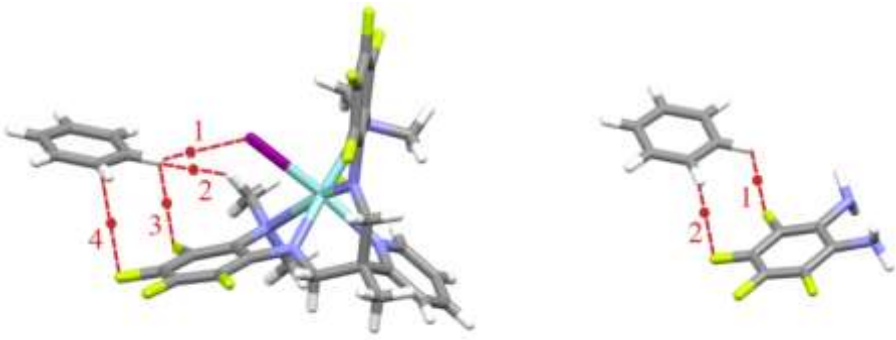


Figure S8. Molecular graphs obtained from the QTAIM analyses of the model systems (presented in Figure 7g and 7h) for assessment of the strength of the C–H/F interactions. The dashed lines correspond to noncovalent interactions, while the circles correspond to (3,–1) bond critical points (BCP). The structures of model systems are extracted from the crystal structure with the *refcode* MINMAZ[22] or obtained by reduction of their structures.

Table S4. Values of some geometrical (in Å) and topological parameters (in au) at the (3, –1) CBP, obtained from the QTAIM analyses, for the investigated F/F interactions between uncoordinated species, in model system presented in Figure 5c.

r_{ij}	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$V(r)$	$G(r)$
2.910	0.005551	0.025840	0.001139	–0.004181	0.005322
3.130	0.003727	0.017174	0.000727	–0.002839	0.003566
3.163	0.003742	0.016886	0.000680	–0.002862	0.003542
3.218	0.004753	0.019838	0.000698	–0.003564	0.004262
3.051	0.006096	0.027360	0.001136	–0.004568	0.005704
2.894	0.003185	0.013855	0.000533	–0.002399	0.002930

Table S5. Values of some geometrical (in Å) and topological parameters (in au) at the (3, –1) BCP, obtained from the QTAIM analyses, for the investigated F/F interactions between coordinated species, in model system presented in Figure 5a.

r_{ij}	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$V(r)$	$G(r)$
2.910	0.006153	0.027632	0.001145	–0.004617	0.005763
3.130	0.004794	0.020035	0.000704	–0.003602	0.004305
3.163	0.003780	0.017144	0.000682	–0.002922	0.003604
3.218	0.005700	0.026057	0.001111	–0.004293	0.005404
3.051	0.003212	0.014050	0.000544	–0.002424	0.002968
2.894	0.003785	0.017434	0.000726	–0.002906	0.003632
2.769	0.006414	0.036102	0.001943	–0.005139	0.007082

Table S6. Values of some geometrical (in Å) and topological parameters (in au) at the (3, –1) CBP, obtained from the QTAIM analyses, for the investigated F/F interactions between uncoordinated species, in model system presented in Figure 7c.

r_{ij}	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$V(r)$	$G(r)$
3.576	0.001325	0.006775	0.000364	–0.000965	0.001330
2.763	0.009029	0.045395	0.002171	–0.007006	0.009177
3.576	0.001325	0.006775	0.000364	–0.000965	0.001330

Table S7. Values of some geometrical (in Å) and topological parameters (in au) at the (3, –1) BCP, obtained from the QTAIM analyses, for the investigated F/F interactions between coordinated species, in model system presented in Figure 7a.

r_{ij}	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$V(r)$	$G(r)$
3.576	0.001332	0.006817	0.000367	–0.000971	0.001337
2.763	0.009011	0.045379	0.002178	–0.006989	0.009167
3.576	0.001332	0.006818	0.000367	–0.000971	0.001338

Table S8. Values of some geometrical (in Å) and topological parameters (in au) at the (3, –1) CBP, obtained from the QTAIM analyses, for the investigated C-H/F interactions between uncoordinated species, in model system presented in Figure 7h.

r_{ij}	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$V(r)$	$G(r)$
2.933	0.003841	0.015608	0.000857	–0.002188	0.003045
3.233	0.002587	0.009583	0.000507	–0.001382	0.001891

Table S9. Values of some geometrical (in Å) and topological parameters (in au) at the (3, –1) CBP, obtained from the QTAIM analyses, for the investigated C-H/F interactions between coordinated species, in model system presented in Figure 7g.

r_{ij}	$\rho(r)$	$\nabla^2\rho(r)$	$H(r)$	$V(r)$	$G(r)$
3.584	0.003007	0.009572	0.000664	–0.001065	0.001729
2.448	0.003204	0.013811	0.001046	–0.001361	0.002407
2.933	0.003531	0.014450	0.000805	–0.002002	0.002807
3.233	0.002484	0.009138	0.000489	–0.001307	0.001796

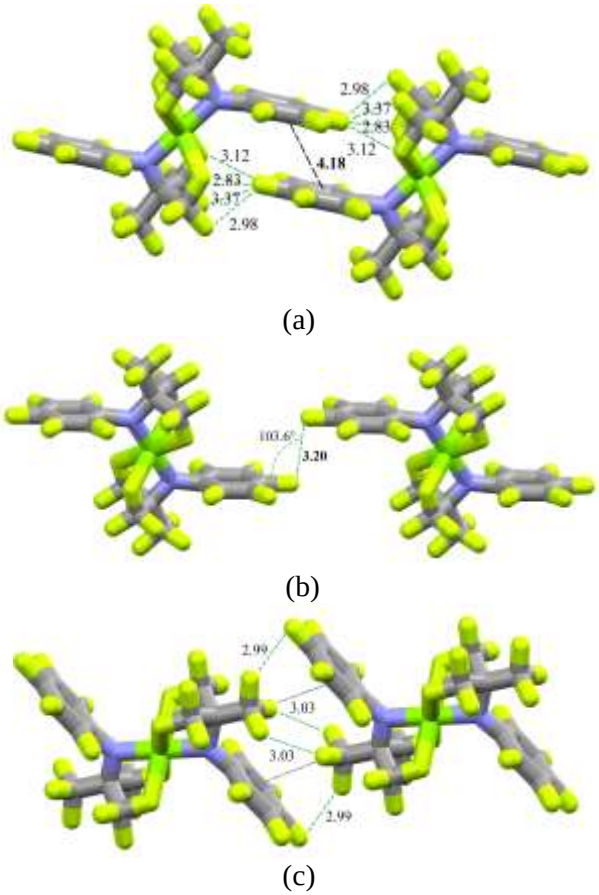
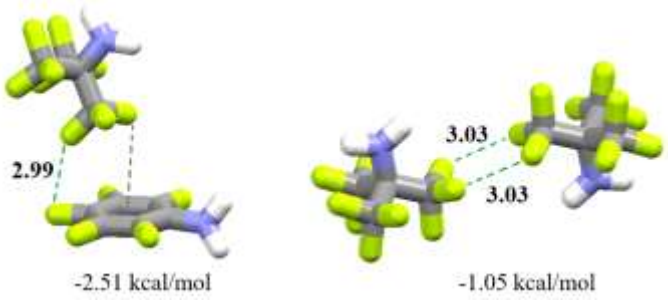


Figure S9. The dimer structures of Mg(II) complexes with coupled F/F and stacking interactions (a), with coupled F/F and parallel interactions at large offsets (b) and with coupled F/F and F/π interactions (c), extracted from the crystal structure with refcode JODMIA,[25] used as initial structures for modelling the influence of coordination on the interactions of the F atoms. The black dashed lines denote stacking interactions and the grey dashed lines denote F/π interactions.



(a) (b)

Figure S10. Model systems for assessing the strength of the coupled F/F and F/π interactions between the aliphatic and aromatic species (a) and of double F/F interaction between two aliphatic species (b), obtained from the crystal structure with refcode JODMIA,[25] and used to estimate the contributions of these interactions in dimer structures from Figure 9g.

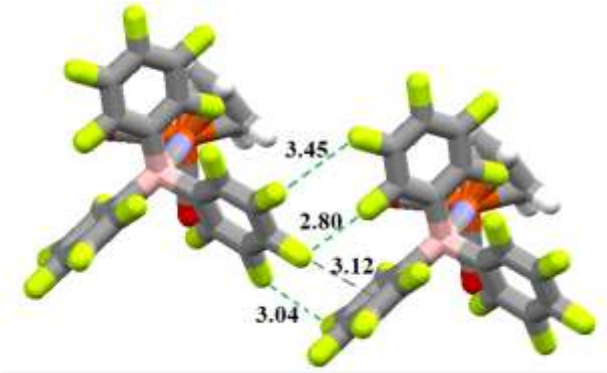
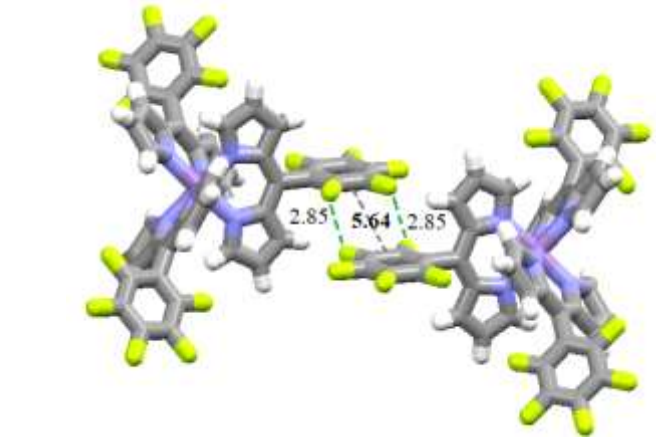
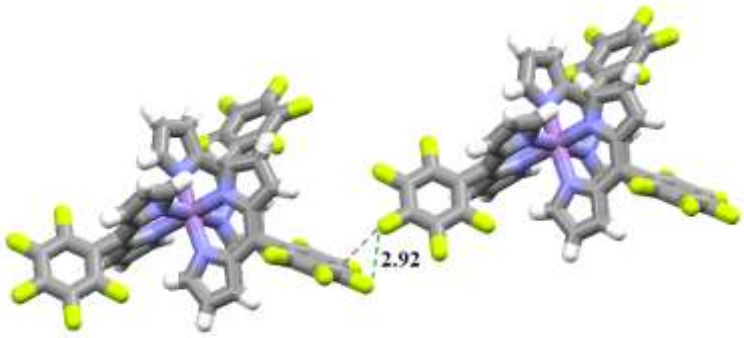


Figure S11. The dimer structure of Fe(II) complexes with simultaneous T-shape orientation of the aromatic rings (with coupled F/F and F/π interactions) and orientation of the aromatic rings that forms a pair of F/F interactions, extracted from the crystal structure with refcode TAGKUI,[26] used for the evaluation of the coordination effects on interactions of the F atom bound to the aromatic group.



(a)



(b)

Figure S12. The dimer structures of Mn(III) complexes with coupled PILO and a pair of F/F interactions (a) and with coupled F/π and F/F interactions (b), extracted from the crystal structure with refcode IZEVUF,[27] used for the evaluation of the coordination influence on interactions of the F atom bound to the aromatic group.