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## PAPER

# Supramolecular assemblies of dimolybdenum transoids built by Mo<sub>2</sub>-enhanced perfluorophenyl-perfluorophenyl synthons†

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Two supramolecular assemblies were developed by the dimmolybdenum paddlewheel complex *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1) (ancillary ligand DAniF = N,N'-di-(p-anisyl)formamidinate) through intermolecular offset face to face C<sub>6</sub>F<sub>5</sub>  $\cdots$  C<sub>6</sub>F<sub>5</sub> interactions. The two networks are different because of the presence and absence of tetrahydrofuran (THF) axial coordination to the Mo<sub>2</sub> units, but feature commonly short interplanar distances between the two paired perfluorophenyl groups, that is, 3.30 Å and 3.23 Å, respectively, which are similar to the shortest intermolecular C $\cdots$  F contacts between two atoms in *meta* and *ortho* positions. Consistently, as indicated by the Mulliken population analysis, the dipole moments for the *meta* and *ortho* C–F bonds are considerably enlarged because the pentafluorobenzoate groups are bonded to the dimetal unit. In comparison, X-ray structural and theoretical analyses were also made for the parent molecule pentafluorobenzoic acid. The resultant data show that charge distribution on the perfluorophenyl group has a major influence on the C<sub>6</sub>F<sub>5</sub> $\cdots$  C<sub>6</sub>F<sub>5</sub> binding mode. Therefore, it is evidenced that the dimetal unit plays a role in further polarizing the highly polarized C–F bonds and the intermolecular perfluorophenyl interactions are dominated by the C $\cdots$  F dipole–dipole interaction, rather than aromatic-aromatic  $\pi$ - $\pi$  stacking.

### Introduction

Face to face phenyl-perfluorophenyl stacking is a fairly strong (3.7–4.7 kcal mol<sup>-1</sup>) non-covalent interaction which encompasses three attractive forces, quadrupole–quadrupole,  $\pi$ - $\pi$  and C–  $F \cdots H - C^{1,2}$  This concomitant binding interaction has been widely exploited in numerous studies.3-5 Perfluorophenyl-perfluorophenyl interaction, on the other hand, has been much less observed until recently. An increasing number of examples have shown the offset face to face stacking between two C6F5 rings with short interplanar distances.<sup>6</sup> It was unexpected that in the cases where hydrophenyl and perfluorophenyl groups coexist, the  $C_6F_5 \cdots C_6F_5$  stacking, rather than C<sub>6</sub>H<sub>5</sub>···C<sub>6</sub>H<sub>5</sub>, was crystallographically defined.<sup>7,8</sup> However, the nature of this type of interaction is not yet well understood. Owing to the presence of the most electronegative atoms (F) on a C<sub>6</sub> ring periphery, the quadrupole and dipole properties for the C<sub>6</sub>F<sub>5</sub> group are significantly altered. In addition, electronic delocalization creates a deficiency of the  $\pi$  electron cloud on the fluorinated phenyl ring, which impedes efficient  $\pi$ - $\pi$  stacking. However, in the literature including recent works,

the differences between perfluorophenyl–perfluorophenyl and the well defined aromatic–aromatic interactions were insufficiently acknowledged.<sup>7,9,10</sup> It is also noteworthy that  $C_6F_5\cdots C_6F_5$  interaction occurs frequently in perfluorinated coordination and organometallic crystalline solids,<sup>8-11</sup> which prompts further explanation.

In order to gain additional insights into perfluorophenylperfluorophenyl interactions, specifically in the metal-containing solids, a novel quadruply bonded dimolybdenum compound with two transoid  $C_6F_5$  pendants was prepared. Compound **1** (Fig. 1) is a mixed-ligand complex, namely *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>, on which the auxiliary ligands DAniF (*N*,*N*'-di-*p*-anisylformamidinate) are used to block the unnecessary coordination sites. Given the transoid geometry of the Mo<sub>2</sub> complex, the intermolecular  $C_6F_5 \cdots C_6F_5$  binding interaction was expected to generate infinite extension of the supramolecular motifs along a single direction.

As is well known, the metal-metal bond distance is a probe of electron density on the dimetal center which is tunable by electron donation from the axial ligand. In this work, we found that the electronic property of the metal center has a critical impact on the binding mode of the perfluorophenyl synthons. Self-assembling of the *trans* Mo<sub>2</sub> building blocks produced two distinct networks, which is attributed to the difference in axial coordination. Scheme 1 depicts the observed two different  $C_6F_5 \cdots C_6F_5$  binding patterns for the two supramolecular structures, along with that for pentafluorobenzoic acid. Pattern **A** is for the network derived from the THF solvated complex, while pattern **B** is for the one

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Fig. 1 Molecular structures of *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (THF)<sub>2ax</sub> (A) and *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (B). For the THF solvated molecule, Mo(1)–Mo(1A): 2.1176(6) Å, Mo(1)–O(1): 2.119(3) Å, Mo(1)–O(2): 2.117(3) Å, Mo(1)–O(THF): 2.615 Å and C(1)–C(7): 1.494(5) Å. For the non-solvated molecule, Mo(1)–Mo(1A): 2.0895(4), Mo(1)–O(1): 2.126(2) Å, Mo(1)–O(2A): 2.113(2) Å and C(1)–C(7): 1.492(3) Å.

without axial THF molecules. Importantly, for both **A** and **B**, the interplanar distances, 3.30 Å and 3.23 Å, respectively, are similar to the shortest intermolecular  $C \cdots F$  distances. This implies that the  $C \cdots F$  contacts occuring at the *meta* and *ortho* atoms may be responsible for the perfluorophenyl–perfluorophenyl interaction

(Scheme 1, A and B). In the crystal structure, the molecules of pentafluorobenzoic acid are also packed via C6F5...C6F5 interaction with interplanar distance 3.20 Å.<sup>12</sup> In this case, the  $C_6F_5$  groups are paired by interactions of the *ortho* F atom with the center of the benzene ring (3.19 Å), and  $C \cdots F$  contacts between the *meta* F atom and C atom of the carboxylate group (3.20 Å) (Scheme 1, C). Therefore, these perfluorophenyl-perfluorophenyl interactions occur commonly in offset face to face mode but with different binding sites. Furthermore, from the geometries of the three structural motifs, these  $C_6F_5 \cdots C_6F_5$  interactions are unlikely classified as conventional aromatic-aromatic  $\pi$ - $\pi$ stacking. Mulliken population analyses at the density functional theory (DFT) level reveal that in the complex system, the Mo<sub>2</sub> unit plays a role in further polarizing the highly polarized C-F bonds and the  $C_6F_5 \cdots C_6F_5$  interactions are dominated by intermolecular C ··· F dipole-dipole interactions.

#### **Results and discussion**

Dimolybdenum complex trans-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1) was prepared by starting with trans mixed-ligand complex precursor, or trans-Mo<sub>2</sub>(DAniF)<sub>2</sub>( $O_2CCH_3$ )<sub>2</sub>. Ligand replacement between carboxylates is a kinetically unfavorable reaction, which may yield a ligand scribbling mixture. However, this transformation can be readily achieved by addition of sodium methoxide to the reaction system. Reaction of sodium methoxide (in methanol) with the precursor removes the acetates and generates the methoxide-methanol coordinated intermediate. This material is very active toward pentafluorobenzoic acid, thus producing the target molecule in good yield without geometry alternation. A similar procedure has been utilized for substitution of the acetate in Mo<sub>2</sub>(DAniF)<sub>3</sub>(OAc),<sup>13</sup> from which the methoxide-methanol intermediate Mo<sub>2</sub>(DAniF)<sub>3</sub>(OCH<sub>3</sub>)(OHCH<sub>3</sub>) has been structurally characterized.<sup>14</sup> This preparative method can be described by the equations as follows.

trans-Mo<sub>2</sub>(DAniF)<sub>2</sub>(OAc)<sub>2</sub> + 2NaOCH<sub>3</sub>(CH<sub>3</sub>OH) 
$$\xrightarrow{\text{THF}}_{\text{rt}}$$
  
trans-Mo<sub>2</sub>(DAniF)<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub> + 2NaOAc

*trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>OH)<sub>2</sub> + 2HO<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>  $\xrightarrow{\text{THF}}$ *trans*-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> + 4CH<sub>3</sub>OH

When compound 1 crystallized in tetrahydrofuran, two THF molecules occupied the axial sites of the  $Mo_2$  unit, while crystallization in  $CH_2Cl_2$ /hexane produced a non-solvated molecule.





**Fig. 2** Single crystal structures of the dimolybdenum supramolecular aggregate **I** showing: the perfluorophenyl–perfluorophenyl interaction (inset); the view along the Mo–Mo bond vector (top) and the projection on the perfluorophenyl planes (bottom). The anisyl groups in the top diagram have been removed for clarity.

The crystallographic data are presented in Table 1 and the crystal structures are shown in Fig. 1 with selected structural parameters. It is worthy to note that complexation of THF lengthens the Mo–Mo bond from 2.0895 (4) to 2.1175(7) Å due to the extra electron density added to the antibonding orbitals of the Mo<sub>2</sub> unit. The increased metal–metal bond distance implies that the solvated Mo<sub>2</sub> unit is less electron-withdrawing from the ligands. Furthermore, for both molecules, the C–C bond that connects the C<sub>6</sub>F<sub>5</sub> group and dimolybdenum chelating ring, *ca.* 1.49 Å in length, is slightly but significantly shorter than a normal C–C single bond, *e.g.*, 1.54 Å. This result suggests that electronic charge transfer may take place between the perfluorophenyl group and the dimetal unit.

In the THF-containing crystal lattice, denoted as I, the Mo<sub>2</sub> molecules are packed in layers perpendicular to the Mo–Mo bond vector (Fig. 2); between the layers are the solvated THF molecules. In I, the methine H atoms on the DAniF ligands are bonded to the neighboring molecules through C–F···H–C interactions with short F···H contacts (*ca.* 2.66 Å).<sup>15</sup> As shown in Fig. 2 (inset), the perfluorophenyl–perfluorophenyl interaction occurs in an offset face to face stacking mode with the interplanar distance  $D_{perp} = 3.30$  Å, center to center distance  $D_{cent} = 3.53$  Å and relatively small  $\theta$  (21.2°), an angle defined by the  $D_{perp}$  and  $D_{cent}$  vectors. Projection onto the C<sub>6</sub>F<sub>5</sub> ring planes (Fig. 2, bottom) shows that for each

Table 1Crystallographic data for  $1 \cdot CH_2Cl_2$  and  $1 \cdot 2THF$ 

Complex	$1 \cdot CH_2Cl_2$	1.2THF	
Empirical formula	$C_{45}H_{32}F_{10}Mo_2N_4O_8Cl_2$	$C_{52}H_{46}F_{10}Mo_2N_4O_{10}$	
fw	1209.53	1268.81	
Crystal system	Monoclinic	Triclinic	
Space group	C2/c (No. 15)	<i>P</i> ī (No. 2)	
T/K	293(2)	293(2)	
a/Å	22.421(3)	9.226(2)	
b/Å	12.265(2)	11.920(2)	
c/Å	17.654(2)	12.857(2)	
$\alpha$ (°)	90	76.551(2)	
$\beta$ (°)	106.386(1)	82.545(2)	
$\gamma$ (°)	90	72.299(2)	
$V/Å^3$	4657.3(1)	1307.3(3)	
Ζ	4	1	
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.725	1.612	
$\mu/\text{mm}^{-1}$	0.751	0.577	
Final $R_1(I > 2s(I))$	0.0289	0.0394	
$WR_2$ (all data)	0.0810	0.0921	
$\overrightarrow{\text{GOF on } F^2} \qquad 1.055$		1.018	

perfluorophenyl pair, one  $C_6F_5$  ring is placed on the other *via* two  $C \cdots F$  contacts. The  $C \cdots F$  contacts occur at the *ortho* C and *meta* F atoms with a distance equal to the interplanar separation (3.30 Å).



Fig. 3 Single crystal structures of the dimolybdenum supramolecular aggregate II showing: the perfluorophenyl-perfluorophenyl interaction (inset and top); the projection on *100* direction (bottom). The anisyl groups have been removed for clarity.

The  $\pi$ - $\pi$  stacking in displaced or offset mode between two parallel hydrophenyl groups has been predicted at various levels of theory to give an interplanar distance of 3.4–3.6 Å,<sup>16</sup> which agrees well with the experimental observation in many crystal structures. The short planar separation (3.30 Å) and near center to center stacking ( $\theta = 21.2^{\circ}$ ) would impose a considerable quadrupole– quadrupole repulsion between the two stacked C<sub>6</sub>F<sub>5</sub> groups. Thus, it is believed that the network (**I**) is retained by a strong attractive C<sub>6</sub>F<sub>5</sub> ··· C<sub>6</sub>F<sub>5</sub> interaction, which may not share the same physical origin with aromatic  $\pi$ - $\pi$  stacking.

In the absence of a donor solvent, intermolecular interactions associated with the perfluorophenyl groups generated a distinct supramolecular array (II). One commonality among the two supramolecular aggregates is that the perfluorophenyl rings are paired and arranged in parallel to one another. The architecture of II also has a layered structure but the complex building blocks lie in two orientations within each layer and thus, the molecular chains are developed in two directions (Fig. 3, top). The formation of the different lattice structure can be likely attributable to the observed intermolecular Mo $\cdots$ F interaction of 3.49 Å. Although

metal  $\cdots$  F (ArF) weak coordination has been documented,<sup>17</sup> this is the first example that shows the Mo  $\cdots$  F (ArF) interaction.

In II, the interplanar separation for the  $C_6F_5$  pair is observed to be as short as 3.23 Å, but the two aromatic rings slide away from each other as indicated by the large center to center distance  $(D_{\text{cent}} = 4.78 \text{ Å})$  and  $\theta$  angle  $(47.8^{\circ})$  (Fig. 3, inset). The C  $\cdots$  F interactions occur once again between the ortho and meta atoms with a distance (3.30–3.32 Å) similar to the  $D_{\text{nern}}$  in I (3.30 Å), although the perfluorophenyl-perfluorophenyl motifs for the two structures differ in stacking pattern. This observation reflects that the C  $\cdots$  F contact, rather than  $\pi$ - $\pi$  stacking, is likely the physical origin for the  $C_6F_5\cdots C_6F_5$  binding interactions occurring in the supramolecular assemblies I and II. As shown by the projection onto the 100 direction (Fig. 3, bottom), in II, intermolecular interactions include  $F \cdots F$  contact of 2.85 Å (< van der waals radii 2.94 Å), which should be considered as an attractive interaction.<sup>18</sup> On this basis, we conclude that the supramolecular architecture II is sustained by cooperative intermolecular interactions including Mo...F, C...F and F...F with exclusion of aromatic  $\pi$ - $\pi$ stacking interaction.

Table 2	Calculated charge distributions over a C <sub>6</sub> F <sub>5</sub> group in pentafluo-
robenzoi	c acid and the dimolybdenum models of <b>1</b>

C <sub>6</sub> F <sub>5</sub> -CO <sub>2</sub> H	C(1) <sup><i>a</i></sup> 0.080	C(2), C(6) 0.137	C(3), C(5) 0.113	C(4) 0.152
		F(1), F(5) -0.144	F(2), F(4) -0.151	F(3) -0.142
C <sub>6</sub> F <sub>5</sub> -Mo <sub>2</sub> -THF <sup>b</sup>	C(1) -0.086	C(2), C(6) 0.176	C(3), C(5) 0.122	C(4) 0.156
		F(1), F(5) -0.166	F(2), F(4) -0.175	F(3) -0.166
C <sub>6</sub> F <sub>5</sub> -Mo <sub>2</sub> <sup>c</sup>	C(1) -0.082	C(2), C(6) 0.185	C(3), C(5) 0.125	C(4) 0.160
		F(1), F(5) -0.161	F(2), F(4) -0.171	F(3) -0.163

<sup>*a*</sup> For the two calculation models, the atoms on a  $C_6F_5$  group are labeled as shown in Fig. 1.  ${}^{b}C_{6}F_{5}$ -Mo<sub>2</sub>-THF = trans- $Mo_2(NHCHNH)_2(O_2CC_6F_5)_2(THF)_{2ax}$ . <sup>c</sup> C<sub>6</sub>F<sub>5</sub>-Mo<sub>2</sub> trans-Mo<sub>2</sub>- $(NHCHNH)_2(O_2CC_6F_5)_2$ .

In order to understand the nature of the perfluorophenylperfluorophenyl interaction that occurs between the dimetal complex motifs, we have performed theoretical work at DFT level to calculate the charge distribution over a perfluorophenyl ring. The computation models employed are trans-Mo<sub>2</sub>(NHCHNH)<sub>2</sub>(O<sub>2</sub>CC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(THF)<sub>2ax</sub> and trans-Mo<sub>2</sub>(NHCH- $NH_{2}(O_{2}CC_{6}F_{5})_{2}$  as the representatives of compound 1 with and without axial THF, respectively. Pentafluorobenzoic acid was also computed for comparison. The calculated Mulliken charges on the atoms of the  $C_6F_5$  moieties, presented in Table 2, are compatible with the published data for perfluorobenzene  $(C_6F_6)$ .<sup>19</sup> It is noted that there are some significant differences in charge distribution between the molecule  $C_6F_6$  and the substituted  $C_6F_5$  groups. The three models have anisotropic charge distributions over the aromatic ring and only the para atoms with charges similar to those of hexafluorobenzene, e.g., +0.15 for the C and -0.15 for the F atoms<sup>23</sup> (See Table 2). Clearly, the C–F bonds in the Mo<sub>2</sub> complexes are further polarized by the [Mo<sub>2</sub>] unit in comparsion with those in  $C_6F_6$  and  $HO_2CC_6F_5$ .

The enlarged dipole moments for the C-F bonds imply that the metal centers in metal coordination and organometallic aggregations would facilitate the  $C_6F_5 \cdots C_6F_5$  dipole-dipole interaction. It is also interesting to note that in the parent acid, the para C atom, or C(4), is the most positive atom (Table 2); in contrast, for both of the two complex models, the ortho carbon atoms, or C(2) and C(6), are more positively charged. The most negatively charged fluorine atoms are those of the *meta* positions, or F(2)and F(4). This result is in good agreement with the experimental observation that in both I and II, the  $C_6F_5 \cdots C_6F_5$  interactions are established via  $C \cdots F$  contacts between the ortho and meta atoms.

By examination of the published X-ray structural data for pentafluorobenzoic acid,<sup>12</sup> it is found that the  $C_6F_5CO_2H$ molecules are also packed in pairs and the two perfluorophenyl rings are parallel with an interplanar distance  $(D_{\text{perp}})$  of 3.20 Å, which is considerably smaller than 3.4-3.6 Å for displaced face to face  $\pi$ - $\pi$  stacking. The center to center distance ( $D_{cent}$ )

is 4.16 Å and  $\theta = 40.6^{\circ}$ , indicating that the aromatic rings have largely slid away from the normal position. From these structural parameters, aromatic–aromatic  $\pi$ – $\pi$  interaction cannot account for the  $C_6F_5 \cdots C_6F_5$  interaction in pentafluorobenzoic acid. However, it can be understood by "point to point" binding interaction within the pair of pentafluorobenzoate. The binding sites are determined by selection of two attractive points with a distance close to the  $D_{\text{nerp}}$  (3.20 Å). It is found there are two types of binding sites which are completely different from those for the complex architectures I and II. As shown by Scheme 1C, each  $C_6F_5$  group has an *ortho* F atom located on the other  $C_6F_5$  ring with a distance of 3.20 Å from the center; the  $C \cdots F$  contacts of 3.19 Å are established between the meta F atom and the C atom on the carboxylate group. The Mulliken population analysis for the pentafluorobenzoate group gives an acceptable explanation for this  $C_6F_5 \cdots C_6F_5$  stacking pattern. As mentioned above, the C-F bonds in pentafluorobenzoic acid are less polarized relative to those in the complexes and on the other hand, the ring center has a large positive potential. Thus, one of the F atoms connects the other  $C_6F_5$  group by dipole interaction with the ring center. According to the calculation, the C atom of the carboxylate group has a Mulliken charge of +0.205, larger than those for the C atoms on the aromatic ring. Consistently, the shortest  $C \cdots F$  distance is found between this carbon atom and the most negative meta F atom (-0.151).

It is significant that calculations based on the two dimolybdenum models reveal that the electron density and the charge distribution over a  $C_6F_5$  group are quite sensitive to the electronic property of the substituent. As mentioned above, there is a subtle difference in structure parameters between the Mo<sub>2</sub> units for the molecules with and without axial THF, which is a reflection that the electron-withdrawing capability for the dimolybdenum unit is altered by the coordination environment. Consistently, theoretical work indicates that the perfluorophenyl group bonded to the Mo<sub>2</sub> unit with coordinated THF molecules bears more electron density than that attached to the axial free dimetal unit. As shown in Table 2, the carbon atoms on the  $C_6F_5$  are less positive but the fluorine atoms are slightly more negative in comparison with the corresponding atoms in the second model compound. In light of this point, the better centroid to centroid stacking in I can be attributed to the reduced quadrupole-quadrupole repulsion between the  $C_6F_5$  groups. The calculation shows that the  $Mo_2$ unit has a major influence on ortho atoms that are closer to the dimetal center (Table 2), implying the electrostatic nature for the  $Mo_2 \cdots C_6 F_5$  interaction. On the other hand, the shortened C–C single bond (1.492–1.494 Å) signals the electronic delocalization *via*  $\delta$ -p  $\pi$  orbital interaction. Therefore, further polarization of the highly polarized C-F bonds is likely due to the two concomitant effects.

Interestingly, the  $C \cdots F$  contacts found in I and II are nearly perpendicular to the associated C-F bond vector. As is known, the fluorine atom on a perfluorous moiety has an anisotropic electron density distribution, that is, negative electrostatic potential for the side region but positive for the bond axial position.<sup>20</sup> The covalent C-F bond has significant electrostatic character,<sup>21</sup> which is significantly enhanced in the perfluorinated metal complex as discussed. Further polarization of the C-F bonds should lead to a relatively strong intermolecular  $C^{\delta_+} \cdots F^{\delta_-}$  dipoledipole interaction. The normality of  $C \cdots F$  contact to the C<sub>6</sub>F<sub>5</sub> rings is indicative of the electrostatic donor-acceptor nature for the perfluorophenyl-perfluorophenyl interaction. Based on these experimental and theoretical results, it is believed that in our case, the perfluorophenyl-perfluorophenyl interaction is essentially electrostatic and the aromatic  $\pi$ - $\pi$  stacking makes negligible contribution in holding the supramolecular motifs in the networks.

#### Conclusion

In summary, we have studied the first perfluorinated dimolybdenum complex in terms of its functionality as supramolecular synthons through X-ray structural analyses and DFT calculations. The present work demonstrates that the perfluorophenyl group as the pendant to a metal unit offers versatile non-covalent interactions at varying bindng sites, of which the C  $\cdots$  F dipole to dipole interactions and F  $\cdots$  F contacts dominate over aromatic  $\pi$ - $\pi$  stacking. Through Mulliken population analysis, it is realized for the first time that the metal center in perfluorous coordination or organometallic compounds has the capability of further polarizing the highly polarized C-F bonds and consequently strengthening the intermolecular C $\cdots$ F dipole interaction. Therefore, metal complexes functionalized with perfluorophenyl groups can be valuable supramolecular synthons of crystal engineering.

#### **Experimental**

#### Materials and methods

All reactions and manipulations were performed under a  $N_2$  atmosphere, using either drybox or standard Schlenk-line techniques. Solvents were purified under  $N_2$  using a Vacuum Atmospheres Company (VAC) solvent purification system or distilled over appropriate drying agents under  $N_2$ . The starting material *trans*-Mo<sub>2</sub>(*cis*-DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> was prepared as reported.<sup>22</sup>

#### Structure determination

Single-crystal X-ray data for  $1.2C_4H_8O$  and  $1.CH_2Cl_2$  were collected at 293(2) K on a Bruker SMART 1000 CCD area detector system. During the course of data collection, no crystal decay was observed. Data reduction and integration were performed with the software package SAINT,<sup>23</sup> while absorption corrections were applied by using the program SADABS.<sup>24</sup> Positions of non-hydrogen atoms were found by using the direct methods program in the Bruker SHELXTL software package.<sup>25</sup> Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of remaining non-hydrogen atoms. Hydrogen atoms were placed in calculated positions in the final structure refinement. Crystal data and structural refinement information are in Table 1. CCDC numbers 825961 [ $1.2C_4H_8O$ ], 825962 [ $1.CH_2Cl_2$ ] contain the supplementary crystallographic data for this paper†.

#### **Density function calculation**

The density functional theory (DFT/B3LYP) calculation was performed using the Gaussian 09 package with the 6-311+G(3df,3pd)basis sets for O, C, F, and H atoms, and the SDD pseudopotential and basis set for the Mo atom. Geometries were fully relaxed during optimization, and the optimized geometry was confirmed by vibrational analysis.

#### Synthesis of trans-Mo<sub>2</sub>(DAniF)<sub>2</sub>(OOCC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(1)

To an orange-red solution of trans-Mo<sub>2</sub>(DAniF)<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub> (0.410 g, 0.500 mmol) in 15 mL of THF, was added 2.0 mL of a NaOCH<sub>3</sub> solution (0.5 M in methanol). After stirring for about 2 h, a colorless microcrystalline material, presumably sodium acetate, was removed by filtration. To the filtrate was added an excess of pentafluorobenzoic acid (0.276 g, 1.300 mmol). After stirring at room temperature for an additional one hour, the solvent was removed under vacuum, and the residue was washed with ethanol  $(2 \times 15 \text{ mL})$ , and then dried under vacuum, yielding compound 1 of 0.478 g (85%). Diffusion of ethanol into the CH<sub>2</sub>Cl<sub>2</sub> solution of the product produced block-shaped yellow crystals of 1·CH<sub>2</sub>Cl<sub>2</sub> or II. Yield: 0.014 g (65%). <sup>1</sup>H NMR(CDCl<sub>3</sub>, ppm): 8.51 (s, 2H, -NCHN-), 6.83 (d, 8H, aromatic), 6.80 (d, 8H, aromatic), 3.74 (s, 12H, -OCH<sub>3</sub>). UV-vis,  $\lambda_{max}$  ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>): 441 nm (5.0 × 10<sup>3</sup>). Anal. Calcd. for  $C_{44}H_{30}N_4O_8F_{10}Mo_2$  (1): C, 46.99; H, 2.69; N, 4.98. Found: C, 46.68; H, 2.46; N, 5.07.

#### Synthesis of 1.2THF

Compound 1 of 0.281 g was dissolved in 8 mL THF and the solution was layered with hexanes. Slow diffusion yielded red needle-shaped crystals of I quantitatively. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 8.50 (s, 2H, –NCHN–), 6.83 (d, 8H, aromatic), 6.80 (d, 8H, aromatic), 3.75 (m, 8H, THF), 3.74 (s, 12H, –OCH<sub>3</sub>), 1.85 (m, 8H, THF). UV-vis,  $\lambda_{max}$  ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>): 442 nm (1.1 × 10<sup>4</sup>).

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