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Perfluoroalkylation of square-planar transition metal complexes: a strategy to assemble them into solid state materials with a π - π stacked lamellar structure

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KEYWORDS. Perfluoroalkylation, Transition Metal Complex, π – π Interaction, Crystal Structure, Fluorine-fluorine Interaction; Semiconductor, Electrochemistry, Redox Potential

ABSTRACT: Formation of π - π stacked lamellar structure is important for high performance organic semiconductor materials. We previously demonstrated that perfluoroalkylation of aromatics and heteroaromatics was one of the strategies to design organic crystalline materials with π - π stacked lamellar structures while improving air-stability as a result of the strong electron withdrawing ability of perfluoroalkyl substituents. Square-planar transition metal complexes with large π -conjugated ligands are also an important category of semiconductor materials. We have perfluoroalkylated square-planar transition metal complexes, leading to the formation of π - π stacked lamellar crystal packing motif in the solid state. Here we report six crystal structures of Pd and Pt complexes with bisperfluorobutylated catechol ligand as one of the two ligands that bonds to the metal centers. This structural design possesses similar molecular topology when compared to perfluoroalkylated aromatics and heteroaromatics we have reported previously, again, demonstrating the steering power of the perfluoroalkyl substituents in engineering organic and organometallic solid state materials.

1. Introduction

Controlling and modulating the structure solid state organic materials is a significant, yet challenging, task faced by material scientists to reach the goal of "materials by design".¹⁻³ From supramolecular chemistry to metal-organic-framework (MOF)⁴ and, most recently, covalent-organic-framework (COF)⁵, researchers engage in activities that could potentially control and modulate the solid state structure of organic- and metal-organic based functional materials.⁵⁻⁷ By manipulating the coordination and covalent bonding within the three-dimensional (3D) structure, researchers have gained the ground to control and modulate the 3D solid state structure of MOF and COF materials.⁷⁻⁹ On the other hand, many solid state functional materials are small charge-neutral molecular-based in which the 3D structure and the functions of these materials primarily relies on non-covalent and non-coordinating weak intermolecular interactions,¹⁰⁻¹² for example, hydrogen bonding^{13, 14} and van der Waals interactions.¹² Because the energy of these weak non-covalent and non-coordinating interactions is estimated less than 10% of the bonding energy of a typical covalent or coordinating bonds, modulating and controlling these weak interactions through molecular design is paramount, yet tremendously challenging.¹⁵

Recent work done by several groups^{8, 13, 14, 16-21} demonstrated the potential of utilizing noncovalent bonding including halogen bonding^{17, 18, 22} for engineering solid state organic materials and controlling organic reactions in the solid state.^{14, 19-21} Recently, we have demonstrated that perfluoroalkylation of aromatics and heteroaromatics is capable of engineering organic semiconductor materials with π - π stacked lamellar structures while improving air-stability.^{15, 23-²⁶ This dual improvement in this type of functional organic materials is mainly due to the strong electron withdrawing ability of perfluoroalkyl substituents²⁶ and multiple C-F---F-C attractive intermolecular interactions between perfluoroalkyl chains^{15, 23, 27-30}. The formation of the π - π}

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stacked lamellar structure is a key to improve the charge mobility for high performance organic semiconductor devices.³¹⁻³⁵ While aromatics with large π -conjugation are one type of candidates for modern organic semiconductor materials,^{31, 32, 36, 37} the planar metal complexes represent another candidate type for such applications.^{35, 38-43}

One thing in common for both aromatic and metal complex based semiconductor materials is that both are charge-neutral molecular materials forming molecular crystals based upon attractive weak non-covalent intermolecular interactions.^{8, 10, 44, 45} Thus based upon our previous results of aromatic perfluoroalkylation assisting in the formation of lamellar π - π stacked solid structure of aromatics and heteromatics,^{15, 23, 27} we hypothesize that planar metal complexes with perfluoroalkylated ligand(s) and similar molecular topology are expected to form lamellar $\pi - \pi$ stacked solid state structures as well. To test our hypothesis, we synthesized square-planar palladium and platinum complexes with bisperfluorobutylated catechol and various substituted 2,2'-bipyridine ligands and a phenanthroline ligand (Chart 1). These compounds possess similar molecular topology compared to our previously reported perfluorobutylated aromatics (Chart 2). Here we report the synthesis and characterization of six new compounds and their crystal structures. All of these six compounds are four-coordinating square-planar complexes that form exclusively lamellar $\pi - \pi$ stacked solid state structures even though some have substituents with very large steric hindrance, for example, the t-butyl group. This result provides a new pathway to engineer solid state metal complex materials not only in the fields of semiconductor materials but also optical materials in which solid state structure determines their function and performance.



Chart 1. Compounds studied



Chart 2. Comparison of molecular topology



Left: metal complex reported in this work; right: aromatic molecule reported previously²³. Both molecules form lamellar π - π stacked solid state structures with very similar inter-planar distances.

2. Results and Discussion

2.1 Synthesis and Characterization

Our strategy for preparing square-planar transition metal complexes involves the use of bidentate chelating aromatic ligands that possess perfluorobutyl substituents. To reach the similar topology of our previously reported compound 7, and generate charge-neutral complexes, we chose 4,5-bisperfluorobutyl catechol dianion as one ligand and 2,2'-bipyridine as the other ligand for the metal complexes. Pd(II) and Pt(II) metal ions were selected to form the corresponding four coordinate square-planar metal complexes.





Scheme 2. Synthesis of Pd^(II) complexes.



Bisperfluoroalkylated catechol was prepared through a four-step reaction pathway starting with a diol-protection step (Scheme 1). Methylation is often used for protecting catechol in organic synthesis as it provides an efficient and inexpensive means for protecting diol functionality in a multistep synthetic process.⁴⁶ To a mixture of catechol and potassium carbonate in degassed DMF solution, methyl iodide was added drop wise at 0 °C controlled by an ice bath. Then, the reaction mixture was stirred at 80 °C for 12 hours to reach completion.⁴⁷ One of the major advantages of using this protection step in the synthetic process is avoiding the formation of Cu complexes resulting from the subsequent perfluoroalkylation reaction.¹⁵ Bromination was carried out using bromine in dichloromethane at 0 °C to yield the dibrominated compound **9** in 85 % yield. The brominated derivative was subjected to iodoperfluorobutane in the presence of copper in dry DMSO and perfluorobutyl ethyl ether (HFE-7200) at 135 °C to afford bisperfluorobutylated compound **10** in 65 % yield. The deprotection step was accomplished by

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treating compound 10 with boron tribromide dissolved in dichloromethane at 0 °C to afford compound 11 as a yellow oil in 67 % yield.

The complexation of 2,2'-bipyridine derivatives and 1,10-phenanthroline with palladium dichloride was carried out under dry N₂ atmosphere in acetonitrile.⁴⁸ The progress of the reactions was monitored by TLC. The final complexation process in the reaction was proceeded by adding compound **11** in methanol dropwise to the CHCl₃/Methanol solution of bpyPd(II)Cl₂ at room temperature followed by addition of triethylamine. Color change of the reaction mixture was observed after about one hour for all the Pd complexes. The platinum complex was prepared using a slightly modified synthetic procedure in which one equivalent of platinum dichloride was added to a solution of 1.2 equivalents of the ligand and stirred for 12 hours at 100 °C. Both reactions proceeded in moderate to good yields. Expanding on this methodology, a library of perfluoralkylated square planar of Pd and Pt complexes was prepared and subjected to single crystal growth with slow evaporation method.

All the compounds were then characterized by ¹H, ¹⁹F NMR spectra, ESI-MS spectra, elemental analysis, and x-ray single crystal structure analysis. Detailed synthetic procedures, characterization methods, and all characterization data are given in the supporting information. ESI-MS spectra of these metal complexes give the molecular mass according to the isotope natural abundance distribution and matches well with simulated MS results with the exact isotope distribution pattern. It is also worth noting that the ¹H NMR spectra of compound **6** show clear ¹⁹⁵Pt-¹H coupling for proton signal at 9.17 ppm with a coupling constant of 29.52 Hz (See supporting information). The chemical shift information of this signal together with the coupling information clearly concludes this signal belongs to the ortho proton on the bipyridine adjacent to the nitrogen atom.

2.2 Crystal Structure Characterizations

Single crystals suitable for x-ray diffraction were obtained using slow evaporation method over the period of a couple weeks to a couple months at room temperature in darkness. Long glass tubes (30 to 60 cm long, ID 4 mm, OD 5mm) with a plastic cap (for example, caps for 5 mm NMR tube) were used for crystal growing. More detailed experimental procedures are given in the supporting information or in our previous publications²⁷. Single crystal XRD data were collected at 100 K using Mo-K α radiation ($\lambda = 0.71073$ Å) on a Bruker CCD APEXII diffractometer. Structures were solved by the Direct Method using SHELXL-97 in conjunction with standard differential Fourier transformation techniques and subsequently refined by fullmatrix least-squares analyses. All hydrogen atoms were placed in their ideal positions and all non-hydrogen atoms were refined anisotropically except for the cases where minor disorder was observed on the terminal fluorine atoms of the perfluoroalkyl chains in compounds **1** and **6**.

The quality of single crystal of compound **3** was not as good as single crystal for other compounds. The reason for poor quality crystal might be very complicate, one thing in common that we observed for this type pefluoroalkylated aromatics, heteroaromatics, and square-planar metal complexes is they intend form long needle crystals if they form the π - π stacked solid state structures. Though the longer dimension of such long needle crystals can be as long as couple center meters, the short dimensions could be less than 100 micrometers. This very thin needle crystal creates a challenging problem for x-ray single crystal diffraction data collection. Furthermore, the crystals were very fragile because they were formed with charge-neutral molecules, and the stability of the crystal structures relay only on weak non-covalent interactions. For compound **3**, we solved the main structure, but there were unsolved, likely, solvent molecules in the crystal packing due the poor diffraction data and possibly disordered.

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Repetitive attempts to grow high quality crystal were yet still unsuccessful. The main frame of the crystal structure of compound **3** should be in correct form though the distance measurement error might be larger than other perfectly-solved structures. Detailed crystal structure refinement data are listed in table **1** and the corresponding cif files are given in the supporting information. Table **1**. Summary of Crystallographic and Refinement Data for Compounds **1-6**

Compound	1	2	3	4
Formula	$\begin{array}{c} C_{24}H_{10}F_{18} \\ N_2O_2Pd \end{array}$	$\begin{array}{c} C_{24}H_8Br_2F_{18}N_2O_2\\Pd \end{array}$	$C_{34}H_{26}F_{18}N_2O_2Pd \\$	$C_{26}H_{14}F_{18}N_2O_4Pd$
formula wt	806.74	964.54	918.95	866.79
temp, K	100	100	100	100
cryst setting	tetragonal	orthorhombic	monoclinic	triclinic
space group	I-42d	F d d d	P21/c	P -1
Hall symbol	I-42bw	-F 2uv 2vw	-P2ybc	-P 1
international tables no.	122	70	14	2
a, Å	29.374	6.3920	6.9281	7.8439
b, Å	29.374	39.810	28.342	10.2745
c, Å	6.3995	45.443	18.780	18.498
a, deg	90	90	90	87.522
β, deg	90	90	96.496	86.574
γ, deg	90	90	90	78.561
Ζ	8	16	4	2
cell vol (Å ³)	5521.5	11563.6	3664.0	1457.8
density (diffrn), g cm ⁻³	1.941	2.216	1.666	1.975
Absorb coeff, mm^{-1}	0.822	3.552	0.633	0.791

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$\begin{array}{c} 40\\ 41\\ 42\\ 43\\ 44\\ 45\\ 46\\ 47\\ 48\\ 49\\ 551\\ 52\\ 53\\ 55\\ 56\\ 57\\ 58\end{array}$
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F(000)	3136	7360	1872	848	
data range (θmin-θmax), deg	1.386-25.422	1.360-26.480	1.307-22.486	2.21-28.78	
index ranges	±35,±35,±7	±8,±53,±61	±7, ±30, ±20	$\pm 10, \pm 13, \pm 24$	
measured reflns	9922	9914	9882	9996	
Independent reflns	2571	3722	4789	6891	
reflns with $I > 2\sigma(I)$	2479	3396	4329	6329	
max/min trans	0.960/0.921	0.837/0.718	0.892/0.931	0.931/0.892	
restraints/para ms	1/194	0/222	0/496	0/460	
GOF	1.113	1.261	1.090	1.229	
$\begin{array}{ll} R & [F2 > \\ 2\sigma(F2)] \end{array}$	0.0565	0.0164	0.0691	0.0744	
wR (F2)	0.1636	0.0636	0.2014	0.2064	

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Table 1. Summary of Crystallographic and Refinement Data for Compounds 1-6 (continued)

Compound	5	6
Formula	$C_{52}H_{22}F_{36}N_4O_5Pd_2$	$C_{24}H_{10}F_{18}N_2O_2Pt$
formula wt	1679.54	895.43
temp, K	100	100
cryst setting	monoclinic	tetragonal
space group	C 2/c	I-4 2d
Hall symbol	-C 2yc	I-4 2bw
international tables no.	15	122
a, Å	39.386	29.345
b, Å	10.8745	29.345
c, Å	12.9106	6.4395
a, deg	90.00	90
β, deg	95.913	90
γ, deg	90.00	90
Ζ	4	8
cell vol (Å ³)	5500.2	5545
density (diffrn), g cm^{-3}	2.028	2.145
Absorb coeff, mm ⁻¹	0.831	5.210
F(000)	3272	3392
data range (θmin–θmax), deg	1.04-25.312	1.388-25.351
index ranges	±47, ±13, ±15	±35,±35,±7
measured reflns	9966	9117
Independent reflns	5012	2553

reflns with $I > 2\sigma(I)$	4570	2374		
max/min trans	0.9365/0.6355	0.949/0.541		
restraints/params	0/481	0/195		
GOF	1.103	1.082		
R [F2 > $2\sigma(F2)$]	0.0262	0.0366		
wR (F2)	0.0744	0.0960		

Overall, all these Pd and Pt metal complexes show four coordinate square-planar molecular structures with some of them having distortions due to different substituents on the bipyridine ring (*via infra*). There is no fifth ligand coordinated to the metal center although a water molecule was involved in the crystal structure of compound **5**. Compound **1** shows a perfect square planar molecular structure for the coordinating center. As we expected from our previous observation on perfluoroalkylated aromatics^{15, 23, 27}, structure **1** display almost perfect lamellar π - π stacked crystal packing motif as shown in Figure **1**. The only imperfection is the angle between two adjacent planes is 0.6 degree, the distance between Pd of one molecule to its adjacent plane is 3.200 Å, and the average distance from one molecule to the plane of the other molecule is 3.199 Å. Its non-perfluoroalkylated analog shows locally π - π stacked lamellar structure with interplanar distance of 3.233 Å, however, its entire solid state packing shows a distorted lamellar packing motif towards T-shape based herringbone packing motif.⁴⁹ This observation is dramatically amplified in its phenanthroline analog which has a T-shape based herringbone packing motif (*via infra*).⁵⁰



Figure 1. Molecular packing and interplanar distances of compound 1. Top left: top view of adjacent two molecules in a π - π stacked molecular column; top right, side view of the same two molecules in the left; bottom, view along *a*-axis of a 2x2x2 crystal packing units.

Compared to our previously reported perfluoroalkylated aromatics (for example, compound 7) with similar molecular topology, compound 1 possesses the smallest interplanar π - π distance partially due to the Pd donor effect.⁵¹ In the same metal complex stack, Pd is not linearly connected with each other, it shows an angle of 141 degree for the Pd-Pd-Pd, indicating the shortest distance is Pd- π interactions, not the Pd–Pd metal-metal bonding. This observation is similar to what was observed in Pd allyic complexes where the Pd d-orbitals overlap with the π orbital of the allyic ligand.^{52, 53}

Addition of large diameter bromine atoms onto the bipyridine ring further reduces the interplanar distance of the π - π stacked column to an average of 3.196 Å, (from the 21 non-

hydrogen atom mean plane of the metal complex core) with shortest distance of 2.978 Å and longest distance of 3.414 Å. Because of bromine atom's high polarizability, it forms halogen bonding with halogen atoms on adjacent molecules.^{17, 18, 54-62} Figure **2** clearly shows Br---Br and Br---F halogen bindings within the crystal packing. The distance of Br---Br is 0.122 Å shorter than the sum of van der Waals radius of two bromine atoms; the distance of Br---F is 0.118 Å shorter than the sum of van der Waals radius of bromine and fluorine. The bond angle of Br---F is 85.12°, indicating this is a Type-II halogen bonding.^{18, 56, 61}

In addition to the short contacts of Br---Br and Br---F halogen bindings^{55, 63-65}, many short contacts between carbons, and carbon to oxygen, showing relatively stronger π - π quadrupole interactions between adjacent molecules compared to other weak intermolecular interactions observed in the crystal structure. Further, Pd---C short contacts are also observed, perhaps due to Pd--- π interaction that is similar to the Pd---allylic interactions.⁵³ The strong π - π quadrupole interactions and Pd--- π interaction were further demonstrated by a crystal structure of a t-butyl substituent analog, compound **3** (Figure **3**). Two bulky t-butyl groups possess very large steric hindrance that is against the two Pd complex cores packing together through π - π quadrupole interactions and Pd--- π interaction. However, these intermolecular interactions are strong enough to slightly bend the entire metal complex core to reach to an equilibrium between attractive π - π quadrupole interactions and Pd--- π interactions as well as repulsive interactions caused by steric hindrance of the t-butyl groups. The molecular packing motif clearly shows the bulky t-butyl groups and perfluorobutyl groups are away from each other similar to solution phase separation between flourocarbon and hydrocarbon solvents.⁶⁶⁻⁶⁸



Figure 2. Crystal packing of compound 2. Left, side view of a crystal packing column; right: halogen bonding involving bromine and fluorine in compound 2. The short contact distances and angles involving Br and F atoms are listed here, other short contact distances are given in the supporting information.



Figure 3. Crystal packing of compound 3. Left: side view of a π - π stacked column shows slightly bended coordination core. Right: top view of the same π - π stacked column shows

perfluorobutyl and t-butyl groups avoid each other to minimize the steric hindrance to keep the $\pi-\pi$ stacked molecular packing motif.

The bent structure of the coordination core was further observed in -OMe substituted Pd complex (compound 4) and the degree of structure bending was further amplified by this strong electron donating substituent. Additionally, the electron-donating -OMe group and electronwithdrawing $-n-C_4F_9$ group located at the opposite ends of the molecule, establishing a perfect "Push-and-Pull" electronic effect (or D-A effect) in compound 4. This effect creates a larger uneven electron density distribution across the molecular surface, resulting in stronger quadrupole-quadrupole interaction between two adjacent molecules compared to similar molecules without a strong Push-and-Pull effect (i.e. compound 1). This interaction tends to pull two adjacent molecules close to each other which results in a smaller interplanar distance. On the other hand, the steric hindrance of a -OMe group resists two adjacent molecules getting closer. It is apparent that the quadrupole-quadrupole interaction is strong enough to overcome the energy needed for bending the molecule and reaching the optimized position while only slightly changing the interplanar distance, but maintained overall lamellar structure. The significant bending in the same π stack results in the molecules pairing up to reach a more stable structure. However, it is still a significant challenge to judge if the structure is indeed a thermodynamically stable structure from the crystal engineering view point. High level quantum mechanical energy calculation is needed to further explain this observation.



Figure 4. Crystal packing of compound 4. Left: side view of a π - π stacked column shows bended coordination core. Right: top view of the same π - π stacked column shows perfluorobutyl and -OMe groups avoid each other to minimize the steric hindrance to keep the π - π stacked molecular packing motif.

When we change the bipydrine ligand in compound 1 to phenanthroline ligand, the overall molecular packing motif of a new compound 5 still maintains lamellar π - π stacked structure without significant change though slight changes in antiparallel stacking is observed when compared to compound 1 (see SI, Figure S-1). The interplanar distance for the structure of compound 5 is 3.244 Å, slightly longer than that of compound 1.

One common observation for these five Pd complexes is that the interplanar distances are smaller than, or at least comparable with, that of perfluoroalkylated aromatics with similar molecular topology and size.²³ The large steric hindrance caused by the t-butyl groups or –OMe groups does not significantly change the overall interplanar distances though bending of the molecular core structures were observed. For all these perfluoroutylated Pd complexes, we

observed multiple short C-F---F-C contacts in the crystal structures which are similar to previously reported perfluoalkylated aromatics.^{15, 23, 27} Though we did not observe direct Pd-Pd short contact in these five complexes, we did observe the short contact between Pd and carbon and/or oxygen in the complex core where the π orbitals are located. This observation is consistent with recently reported metal- π interactions.^{69, 70} This metal- π interaction, perhaps, plays an important role in bring the two square-planar metal complexes closer when compared to its counterpart of the perfluoalkylated aromatics.

In a Pt(II) complex (compound 6) having same ligands compared to compound 1, we clearly observed Pt---Pt short contact though the interplanar distance is slightly longer (3.220 Å for compound 6 vs. 3.199 Å for compound 1) than that of compound 1, mainly caused by a larger radius of platinum compared to that of palladium. The molecular packing motif of compound 6 is almost identical to compound 1 (Figure 5). The Pt---Pt short contact falls in a zig-zag mode within a π - π stacked column as shown in Figure 5.



Figure 5. Molecular packing and interplanar distances of compound 6. Left, side view of a π - π stacked column; right, top view of the same column.

Solid state structures of charge-neutral molecular materials are determined by the relative strength of each different type of weak non-covalent intermolecular interactions involved. Any disturbance of these weak non-covalent intermolecular interactions could potentially change the solid state structure though molecular structure remains unchanged. We discussed earlier that the anhydrous form of compound **1** forms perfect lamellar 1-D column structure insulated by perfluoroalkyl substituents. Viewing the crystal packing structure along the *c*-axis, we observed that each metal complex column core (cycled with semitransparent red ovals) is surrounded by perfluoroalkyl groups and closely π - π stacked columns, we expect that this type of materials could potentially be one-dimensional semiconductor materials along *c*-axis of the single crystal though significant challenges on growing and handling large size fragile organic single crystal remains.



Figure 6. Crystal packing of compound 1 view along *c*-axis of 2x2x2 unit cells. Red ovals highlight the column stacks in the crystal.

2.3 Physicochemistry properties characterization

The fundamental physiochemical properties of these Pd and Pt complexes were characterized by cyclic voltammetry and UV-visible absorption spectroscopy. All the compounds exhibit reversible single electron transfer reduction and oxidation (Figure 7) in 1,2-difluorobenzene (DFB) solution with 0.1 M TBAPF₆ as supporting electrolyte on Pt working electrode. The first oxidation for compounds 1-4 occurs at very similar potentials around 0.4 V with compound 2 slightly higher and compound 4 slightly lower due to the electronic effect of the substituents on bipyridine ligand. The first oxidation potential of phenanthroline containing compound 5 is almost identical to compound 1. The first reduction potentials of compounds 1-4 show strong

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dependence on the electronic effect of the substituents on bipyridine ligand where electron withdrawing Br substituents shift its first reduction potential to the positive direction for 232 mV compared to compound **1**. In contrast, electron donating –OMe groups shift its first reduction potential to the negative direction for 156 mV compared to compound **1**. These observations on redox potential shift upon substitution of bipyridine ligand suggest the first reduction of these compounds occurs mainly on bipyridine ligands and the first oxidation occurs on bisperfluorobutylated catechol ligand.



Figure 7. Cyclic voltammogram of compounds 1-6 in 1,2-difluorobenzene (DFB) with 0.1 M TBAPF₆ as supporting electrolyte. Potential sweep rate 100 mV/s.



Figure 8. Solid state UV-visible absorption spectra of compounds 1 through 6 (pure sample).

The absorption spectra of these compounds in the solid state were measured on a Carry-5000 UV-visible-Near-IR spectrometer with the Praying MantisTM Diffuse Reflection Accessory between 200 nm to 800 nm (Figure 8). The compounds show a broad and featureless absorption band at long wavelength. We calculated the optical bandgap according to the onsite bandgap calculation procedure which is commonly accepted in the materials chemistry community.⁷¹⁻⁷⁵ The value of the onsite optical bandgap is in line with the bandgap value estimated from solution redox potential with compounds **3** and **6** slightly large difference between those two bandgap values. The long wavelength absorption peaks of these compounds are likely caused by metal to ligands charge transfer (MLCT).^{76, 77} However, pinpointing the exact transit of these absorption peaks would require further TD-DFT calculation which gives the detailed contribution of transit mode. Further investigation in OFET assembly and testing is underway; we hope that the idea presented in this report will shed some light on engineering new organic semiconductor materials.

Table 2. Measured interplanar distances, electrochemical properties, and optical bandgaps ofcompounds 1 through 6.

Cmpd	Packing mode	$\mathbf{d}_{\pi\text{-}\pi}/\mathbf{\mathring{A}}$	$\lambda_{max}/nm/eV^b$	ε/(L mol ⁻¹ cm ⁻¹) ^c	E _{1/2} ^{red} / V	E _{1/2} °x/ V	E _{gap} ^{EC} / eV	E _{gap} ^{opt} / eV ^d
1	π–π	3.199	502/2.47	3.3×10^3	-1.693	0.455	2.148	2.150
2	π–π	3.196	516/2.48	3.8×10^3	-1.461	0.479	1.940	1.954
3	π–π	3.319 (3.275) ^a	456/2.72	3.6×10^3	-1.813	0.422	2.235	2.048
4	π—π	3.315 (3.182) ^a	515/2.49	3.4×10^3	-1.849	0.381	2.230	2.302
5	π–π	3.244 (3.214) ^a	466/2.66	6.7×10^3	-1.720	0.460	2.180	2.169
6	π–π	3.220	498/2.49	3.6×10^3	-1.667	0.547	2.214	1.972

a, shortest distance between Pd atom to the average plane of the adjacent molecule; b, solution maximum absorption in nm and in eV units; c, molar absorption coefficiency of the maximum absorption peak (long wavelength one) in solution; d, optical bandgap measured from the solid state absorption spectra.

3. Conclusion

In summary, with six examples of Pd and Pt complexes containing bisperfluorobutylated catechol ligand we demonstrate that four coordinating square-planar metal complexes with perfluoroalklated ligand could form lamellar π - π stacked structures similar to what we observed in perfluoroalkylated aromatic compounds. Compared to those previously reported perfluoroalkylated aromatic compounds, our current results further support that molecular topology and relative strength of the weak non-covalent intermolecular interactions are key to the solid state structures in charge-neutral molecular materials. The crystal structures together with the electrochemical and optical results show that we can tune the electronic properties of the

materials through modification of substituents on the ligands without worry about the disruption of overall lamellar π - π stacked packing motif in square-planar transition metal complexes.

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures, NMR and mass spectra, additional structure information, cif and checkcif files, additional references. This material is available free of charge via the Internet at http://pubs.acs.org.

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interests.

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Perfluoroalkylation of square-planar transition metal complexes: a strategy to assemble them into solid state materials with a π - π stacked lamellar structure

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Synopsis: Similarity in molecular topology and intermolecular interactions between perfluoroalkylated square-planar metal complexes and heteroaromatics is key to the formation of π - π stacked lamellar crystal packing motifs for perfluoroalkylated metal complexes. This result extends the steering power of perfluoroalkyl substituents into engineering crystalline materials with charge-neutral metal complexes.

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