Synthesis and Crystal Structure of Lead(II) Thenoyltrifluoroacetonate Complexes with Substituted 2,2′-Bipyridines: Interplay of Intermolecular Interactions in Crystals

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Three substituted 2,2′-bipyridine adducts of lead(II) thenoyltrifluoroacetonate, [Pb(4,4′-dm-2,2′-bpy)(ttfa)$_2$]$_2$, **1**, [Pb(5,5′-dm-2,2′-bpy)(ttfa)$_2$]$_2$, **2**, and [Pb(4,4′-dmo-2,2′-bpy)(ttfa)$_2$]$_2$, **3**, (4,4′-dm-2,2′-bpy, 5,5′-dm-2,2′-bpy, 4,4′-dmo-2,2′-bpy and ttfa are the abbreviations for 4,4′-dimethyl-, 5,5′-dimethyl-, and 4,4′-dimethoxy-2,2′-bipyridine, and thenoyltrifluoroacetonate, respectively) have been synthesized, characterized by elemental and thermal analysis, IR and ^{1}H- and ^{13}C-NMR spectroscopy, and studied by X-ray crystallography. The supramolecular features in these complexes are guided/controlled by weak directional intermolecular interactions.

Key words: Lead(II), Thenoyltrifluoroacetonate, Intermolecular Interactions

Introduction

The metal coordination chemistry of β-diketone ligands has been investigated for more than 100 years [1], and it has been well demonstrated that these versatile ligands give rise to a diverse range of interesting complexation behavior [2]. There is a growing amount of literature which especially deals with the possible applications of these complexes as components of molecular devices or as precursors in the formation of new materials. Examples such as phosphors for high-efficiency electroluminescent devices for light-emitting diodes, contrast agents for medical magnetic resonance imaging, NMR shift reagents, transport carriers of alkali metal ions across biological membranes, luminescent probes for proteins and amino acids, light-emitting sensors in fluoroimmunoassays, tags for time-resolved luminescent microscopy, nanoparticles, magnetically addressable liquid crystals, specific redox reagents for chemical transformations or molecule-based information, acid catalysts for sophisticated organic transformations or for the cleavage of phosphodiester bridges in RNA, fully justify the efforts made to control the metallic sites and to selectively introduce specific metal ions into organized assemblies [3 – 15]. More recently, there has also been increasing interest in the metallosupramolecular structural aspects of such systems [16, 17]. Row and coworkers have been involved in the investigation and evaluation of the interactions offered by fluorine substituents in different chemical environments and have demonstrated that fluorine provides new types of directional interactions to build different crystal structures in a number of organic compounds [18]. Recently in an effort to explore weak interactions in complexes, the metal(II) complexes with β-diketonate and neutral diimine chelating ligands have been synthesized, and the crystal structures were determined by X-ray diffraction [19]. We report here the preparation and crystal structure of three adducts of lead(II) thenoyltrifluoroacetonate with substituted 2,2′-bipyridines.

Results and Discussion

Synthesis and spectroscopic studies

Reactions between lead(II) acetate and thenoyltrifluoroacetone (ttfa) with 4,4′-dimethyl-, 5,5′-dimethyl- and 4,4′-dimethoxy-2,2′-bipyridines yielded crystalline materials formulated as [Pb(4,4′-dm-2,2′-bpy)-(ttfa)$_2$]$_2$, **1**, [Pb(5,5′-dm-2,2′-bpy)(ttfa)$_2$]$_2$, **2** and [Pb-(4,4′-dmo-2,2′-bpy)(ttfa)$_2$]$_2$, **3**, respectively. The IR spectra display the characteristic absorption bands for substituted 2,2′-bipyridines and ttfa anions. The relatively weak absorption bands at around 3070, 3043

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Table 1. Crystal data and structure refinement for **1**–**3**.

	1	**2**	**3**
Identification code	$[Pb_2(4,4'\text{-dm-}2,2'\text{-bpy})_2(\text{ttfa})_4]$	$[Pb_2(5,5'\text{-dm-}2,2'\text{-bpy})_2(\text{ttfa})_4]$	$[Pb_2(4,4'\text{-dmo-}2,2'\text{-bpy})_2(\text{ttfa})_4]$
Empirical formula	$C_{56}H_{40}F_{12}N_4O_8Pb_2S_4$	$C_{56}H_{40}F_{12}N_4O_8Pb_2S_4$	$C_{56}H_{40}F_{12}N_4O_{12}Pb_2S_4$
Formula weight	1667.54	1667.54	1731.54
Crystal size, mm^3	$0.68 \times 0.12 \times 0.07$	$0.34 \times 0.30 \times 0.06$	$0.35 \times 0.13 \times 0.11$
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	11.5464(9)	11.6083(2)	10.7147(2)
b, Å	12.0043(5)	11.7463(2)	11.8801(2)
c, Å	12.0895(5)	12.6029(2)	12.1042(2)
α, deg	115.820(2)	107.979(1)	98.513(1)
β, deg	101.363(3)	112.338(1)	96.709(1)
γ, deg	94.210(3)	100.396(1)	103.053(1)
Volume, Å^3	1454.56(14)	1422.66(4)	1466.25(4)
Z	1	1	1
D_{calcd}, g cm^{-3}	1.90	1.95	1.96
$\mu(\text{Mo}K_\alpha)$, mm^{-1}	6.0	6.2	6.0
F(000), e	804	804	836
θ range, deg	1.83–35.00	1.94–32.50	1.72–32.50
Index ranges	$-18 \le h \le 17$, $-19 \le k \le 19$ $-19 \le l \le 19$	$-17 \le h \le 16$, $-17 \le k \le 17$ $-19 \le l \le 19$	$-16 \le h \le 16$, $-17 \le k \le 17$ $-18 \le l \le 18$
Reflections coll. / indep.	45181 / 12641	47871 / 10182	49263 / 10477
R_{int}	0.0453	0.0354	0.0363
Completeness to θ, %	98.7	98.8	98.9
Data / restr. / ref. param.	12641 / 282 / 464	10182 / 0 / 398	10477 / 196 / 442
Goodness-of-fit on F^2	1.033	1.062	1.053
$R1/wR2$ [$I \ge 2\sigma(I)$]	0.0337 / 0.0764	0.0278 / 0.0639	0.0259 / 0.0576
$R1/wR2$ (all data)	0.0452 / 0.0861	0.0352 / 0.0674	0.0330 / 0.0602
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	3.71 / −1.50	2.87 / −1.65	2.12 / −1.26

and 3056 cm^{-1} are due to the C–H modes involving the aromatic ring hydrogen atoms. The C–H modes involving the aliphatic hydrogen atoms occured at 2985, 2979 and 2930 cm^{-1}. The absorption bands with variable intensity in the frequency range 1400–1580 cm^{-1} correspond to aromatic ring vibrations of the substituted 2,2′-bipyridines and the ttfa anions. The absorption bands with variable intensity in the frequency range 1100–1350 cm^{-1} correspond to C–F vibrations of the ttfa anions [20]. The ^{1}H-NMR spectra of DMSO solutions of compounds **1**–**3** display three different protons of py groups of the substituted 2,2′-bipyridines at δ = 7.13–8.51 ppm. Three distinct peaks at 6–8 ppm can be assigned to the protons of the thiophene ring. The methine proton, =CH-, is seen as a singlet in the region near 6 ppm for all complexes. The compounds also show signals at 2.48 for **1**, 2.49 for **2** and 3.89 for **3** ppm assigned to protons of $-CH_3$ groups. The ^{13}C-NMR spectra of DMSO solutions of the compounds **1**–**3** have six distinct signals assigned to the aromatic carbons of the py groups. Another eight distinct signals at 85–180 ppm are assigned to carbon atoms of the ttfa anions, and further signals at 21.15, 18.51 and 55.92 ppm to carbons of methyl and methoxy groups.

Thermal studies

To study the stability of the compounds, thermogravimetric analyses (TGA) of these complexes were performed on polycrystalline samples under a nitrogen atmosphere. The TGA curves showed neither weight loss nor structural changes up to about 200 °C demonstrating that the frameworks of **1**–**3** were retained up to these temperatures. The thermal decomposition of **1**–**3** occurs in two steps. The first step in the temperature range 200–300 °C corresponds to the exothermic decomposition of the ttfa anions (in **1**: calcd. 53.2 %, found 51.5 %, in **2**: calcd. 53.24 %, found 54.5 % and in **3**: calcd. 51.2 %, found 53.5 %). The solid residue formed at around 300 °C is suggested to be Pb(bpy)O. The weight loss of 20–25 % from 300 to 600 °C is equivalent to the loss of the coordinated substituted 2,2′-bipyridine molecules (calcd. 22.1 % for **1** and **2**, and 25.4 % for **3**) with exothermic effects. The solid residue formed at the end of the decomposition at around 600 °C is suggested to be PbO. The compounds

Table 2. Selected bond lengths (Å) and angles (deg) for **1**–**3** with estimated standard deviations in parentheses.

1	
Pb1–O4	2.355(2)
Pb1–O2	2.476(2)
Pb1–O3	2.556(2)
Pb1–O1	2.604(2)
Pb1–N2	2.626(3)
Pb1–N1	2.646(3)
Pb1–O1$^{\mathrm{i}}$	3.004(2)
Pb1$\cdots$O3$^{\mathrm{i}}$	3.193(2)
Pb1$\cdots$Pb1$^{\mathrm{i}}$	3.639(3)
O2–Pb1–O3	131.84(7)
O4–Pb1–O1	81.44(8)
O2–Pb1–O1	70.59(7)
O3–Pb1–O1	68.58(7)
O3–Pb1–N2	77.72(7)
O1–Pb1–N2	145.32(7)
O1–Pb1–N1	148.46(7)
Symm. operation: $^{\mathrm{i}}\ 1-x, 1-y, 1-z$	

2	
Pb1–O2	2.362(2)
Pb1–O1	2.427(2)
Pb1–O3	2.582(2)
Pb1–O4	2.617(2)
Pb1–N2	2.626(2)
Pb1–N1	2.664(2)
Pb1–O3$^{\mathrm{i}}$	2.877(2)
Pb1$\cdots$S2$^{\mathrm{i}}$	3.756(2)
Pb1$\cdots$O1$^{\mathrm{i}}$	3.951(2)
Pb1$\cdots$Pb1$^{\mathrm{i}}$	4.035(2)
O2–Pb1–O3	80.83(7)
O1–Pb1–O4	130.00(7)
O1–Pb1–N2	115.60(8)
O3–Pb1–N2	149.84(7)
O3–Pb1–N1	140.73(7)
O4–Pb1–N1	149.06(7)
Symm. operation: $^{\mathrm{i}}\ -x, 1-y, 2-z$	

3	
Pb1–O3	2.357(2)
Pb1–O1	2.479(2)
Pb1–O4	2.511(2)
Pb1–N1	2.579(2)
Pb1–N2	2.592(2)
Pb1–O2	2.703(2)
Pb1–O2$^{\mathrm{i}}$	3.045(2)
Pb1$\cdots$O4$^{\mathrm{i}}$	3.552(2)
Pb1$\cdots$Pb1$^{\mathrm{i}}$	3.667(1)
Pb1$\cdots$S2$^{\mathrm{i}}$	3.940(1)
O3–Pb1–O4	72.67(6)
O1–Pb1–N1	80.89(6)
O3–Pb1–N2	82.03(6)
O4–Pb1–N2	77.67(6)
N1–Pb1–O2	149.57(6)
N2–Pb1–O2	144.31(6)
Symm. operation: $^{\mathrm{i}}\ 1-x, 1-y, 1-z$	

may therefore be potential precursors for lead oxide materials.

Crystal structures of ***1****,* ***2*** *and* ***3***

According to single-crystal X-ray diffraction structure analyses, **1**–**3** form dimers and crystallize in the triclinic space group $P\bar{1}$ (Table 1). Selected bond lengths and angles are listed in Table 2. Each asymmetric unit contains one Pb(II) ion, one 4,4′-dm-2,2′-bpy ligand in **1**, one 5,5′-dm-2,2′-bpy ligand in **2**, one 4,4′-dmo-2,2′-bpy ligand in **3**, and two thenoyltrifluoroacetonate anions (Figs. 1a–3a). The coordination number of Pb(II) in these complexes is seven (two bpy nitrogen atoms and five oxygen atoms of three bridging ttfa anions in **1** (Fig. 1b), two bridging and one chelating ttfa anions in **2** (Fig. 2b) and two bridging and one chelating ttfa anions in **3** (Fig. 3b)). The arrangements of the donor atoms in **1**–**3** suggest the existence of a stereochemically active lone pair (SALP) on the open side of the coordination polyhedron of the Pb atoms [21]. This is supported by the observed shortening of the Pb–O bonds opposite to the putative lone pair (in **1**: 2.355(2) Å compared with the Pb–O bond with a length of 3.004(2) Å adjacent to the lone pair; in **2**: 2.362(2) Å *vs.* 2.877(2) Å; in **3**: 2.357(2) Å *vs.* 3.045(2) Å) [22]. Hence, the geometry of the nearest coordination environment of every lead atom is likely caused by the geometrical constraints of the coordinated neutral ligands and the ttfa anions and by the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal atom. Such an environment leaves space for bonding of atoms of the ttfa anions of an adja-

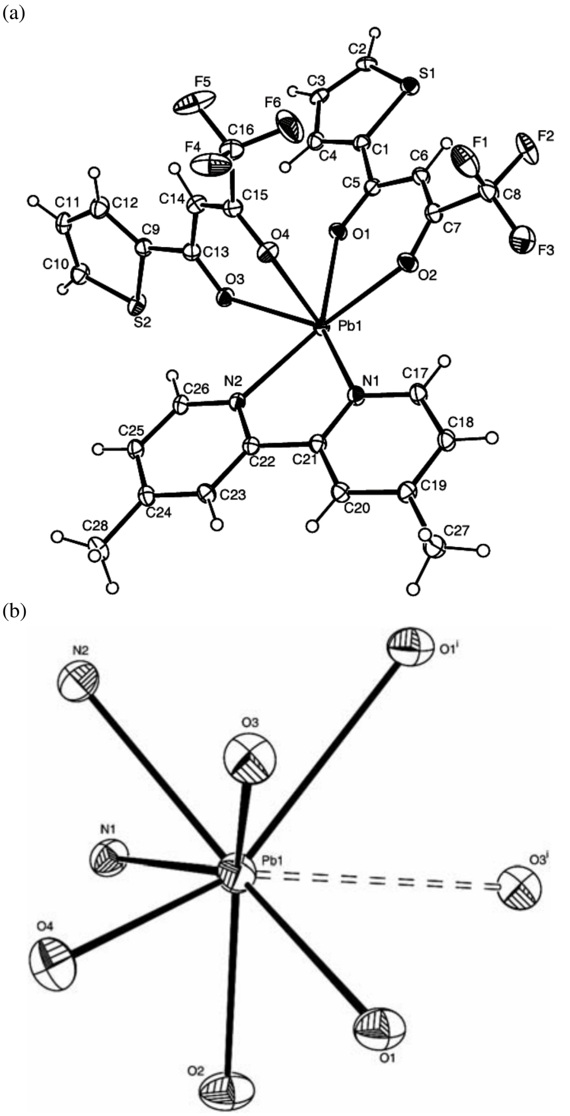

Fig. 1. (a) ORTEP view of the asymmetric unit of **1**. Displacement ellipsoids are shown at the 30 % probability level; (b) representation of the hole in the coordination sphere of the lead atom in **1**.

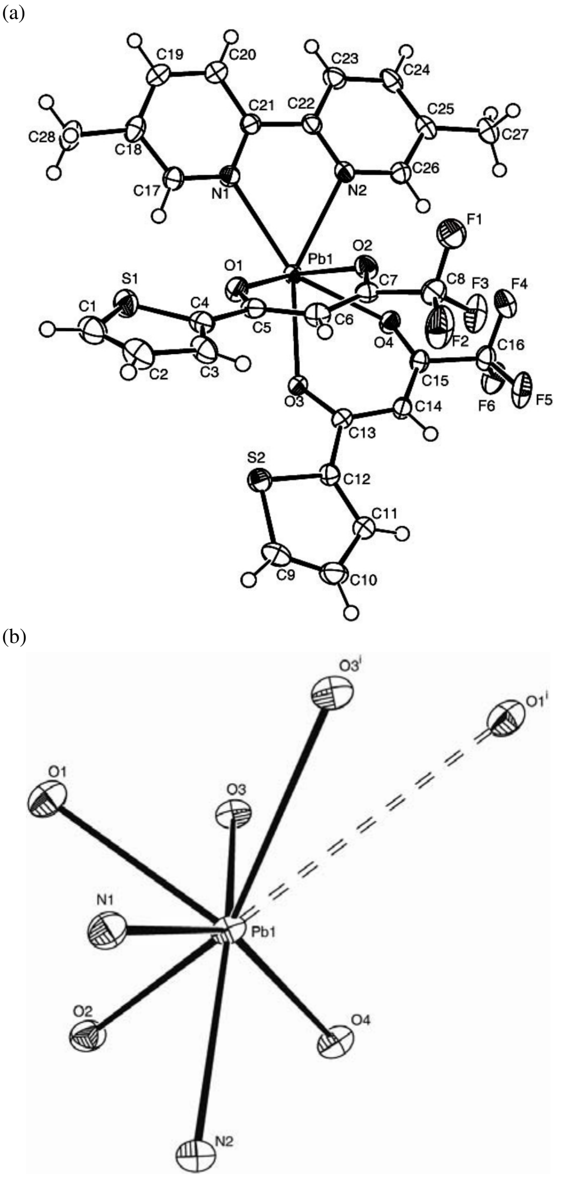

Fig. 2. (a) ORTEP view of the asymmetric unit of **2**. Displacement ellipsoids are shown at the 30 % probability level; (b) representation of the hole in the coordination sphere of the lead atom in **2**.

cent molecule [23]. In **1**: Pb1$\cdots$O3$^{\mathrm{i}}$ = 3.193(2) Å, Pb1$\cdots$S$^{\mathrm{i}}$ = 4.020(2), in **2**: Pb1$\cdots$O1$^{\mathrm{i}}$ = 3.951(2) Å and Pb1$\cdots$S2$^{\mathrm{i}}$ = 3.756(2) Å, in **3**: Pb1$\cdots$O4$^{\mathrm{i}}$ = 3.552(2) Å and Pb1$\cdots$S2$^{\mathrm{i}}$ = 3.940(1) Å.

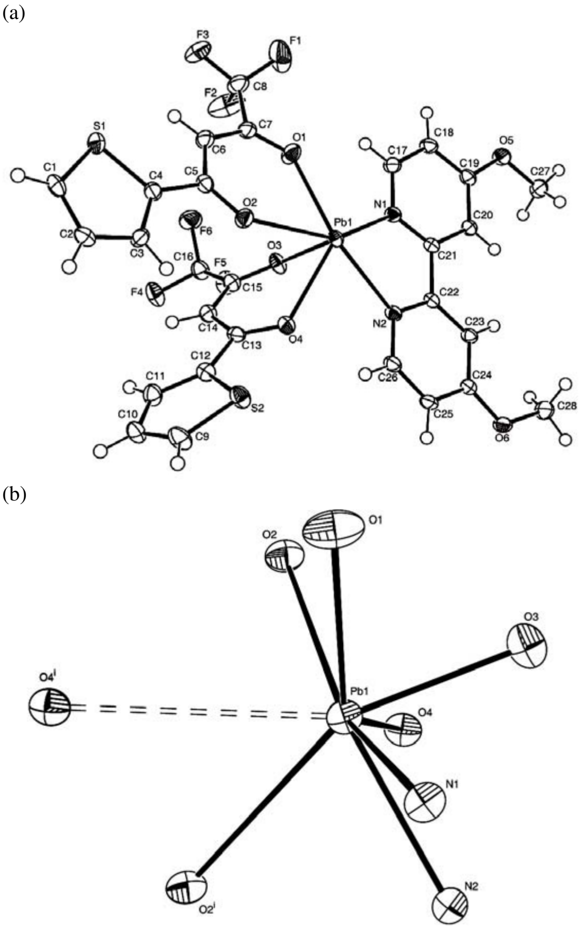

Fig. 3. (a) ORTEP view of the asymmetric unit of **3**. Displacement ellipsoids are shown at the 30 % probability level; (b) representation of the hole in the coordination sphere of the lead atom in **3**.

Intermolecular, intramolecular and π-π stacking interactions are observed in **1**–**3**, and seem to be responsible for the packing of the complexes. An inspection of the data of **1**, **2** and **3** for weak directional intermolecular interactions by the programs PLATON and MERCURY, which were used for calculating the supramolecular interactions, has shown that there are O$\cdots$H–C and C–H$\cdots$F interactions [24, 25] (Table 3). Fig. 4 shows the packing of the molecules of **1** in the crystal highlighting some of the weak intermolecular interactions. The H$\cdots$O and H$\cdots$F separations range from 2.4780 to 2.6980 Å, which is indicative of moderate-to-strong hydrogen bonds [26]. The packing of the molecules of **1**–**3** in the solid state exhibits interesting self-assembled structure topologies through different π-π stacking modes with interlayer distances of 3.380 and 3.396 Å in **1**, 3.402 Å in **2**, 3.193 and 3.359 Å in **3** (see also ref. [27]). The centroid-to-centroid separations between neighboring aromatic rings are exhibiting typical slipped π-π stacking inter-

Table 3. Directional intermolecular interactions in **1** – **3**.

D–H···A	H···A (Å)	D···A (Å)	D–H···A (deg)
1			
C2–H2A···F1 $(1-x, -y, -z)$	2.655	3.377(2)	134.8
C2–H2A···F6 $(1-x, -y, -z)$	2.648	3.331(2)	130.8
C25–H25A···F3 $(x, y, 1+z)$	2.478	3.373(2)	161.5
C28–H28A···O2 $(-x, 1-y, 1-z)$	2.698	3.630(6)	163.8
C23–H23A···O4 $(-x, 1-y, 1-z)$	2.521	3.360(6)	150.1
S2···O2 $(1-x, 1-y, 1-z)$	–	3.237(3)	–
2			
C24–H24A···F6 $(-x, 1-y, 1-z)$	2.612	3.295(5)	130.7
C11–H11A···F5 $(-1-x, -y, 1-z)$	2.600	3.520(2)	170.8
C27–H27A···F2 $(-x, -y, 1-z)$	2.530	3.273(3)	134.3
3			
C25–H25A···F1 $(-1+x, y, z)$	2.616	3.161(2)	118.0
C2–H2A···F4 $(1-x, -y, 1-z)$	2.595	3.427(3)	149.2
C28–H28A···F2 $(1-x, 1-y, -z)$	2.508	3.144(3)	123.8
C18–H18A···O6 $(-1+x, y, z)$	2.533	3.388(5)	152.8

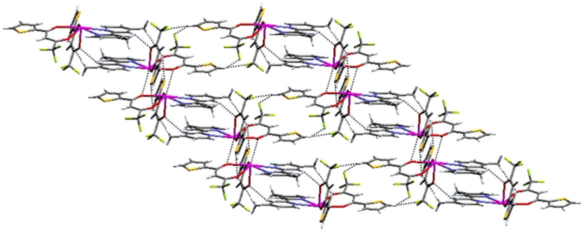

Fig. 4. Packing of the molecules of **1** in the crystal as viewed along the crystallographic *b* axis showing the non-covalent interactions.

actions in an offset fashion. Thus, a three-dimensional hydrogen-bonded and layer-packed network is constructed, as is illustrated for **1** as an example in Fig. 4.

A useful comparison of the result of the present study with those of others is provided by a recent structural study of the thenoyltrifluoroacetonate complex of Pb(II) with 2,2′-bipyridine [28]. Considering the dimeric units alone, there are obvious differences in the relative orientations of the chelate rings (Figs. 1 – 3) and in the types of contacts < 3.5 Å between the atoms in separate units. These differences are reflected in the interactions that can be discerned (on the basis of short atom contacts) between the dimeric species (Table 3).

Experimental Section

Materials and measurements

All chemicals were reagent grade and used without further purification. FT-IR spectra were collected on a Mattson 1000 spectrophotometer using KBr pellets in the range of 4000 – 450 cm^{-1}. Elemental analyses (CHN) were performed using a Carlo Erba model EA 1108 analyzer, ^{1}H-NMR spectra were obtained with a Bruker spectrometer at 250 MHz in [D$_6$]DMSO. Thermal analyses were carried out on a Perkin-Elmer instrument (Seiko Instruments).

*Preparation of [Pb(4,4′-dm-2,2′-bpy)(ttfa)$_2$]$_2$ (**1**)*

4,4′-Dimethyl-2,2′-bipyridine, (0.184 g, 1 mmol) was placed in one arm of a branched tube [29], and lead(II) acetate (0.190 g, 0.5 mmol) and Httfa (0.222 g, 1 mmol) in the other. Methanol and ethanol (ratio 2 : 2) were carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in a bath at 60 °C while the other one was kept at ambient temperature. After 3 d, crystals had deposited in the cooler arm which were filtered off, washed with acetone and ether, and dried in air; yield 70 %. – Analysis: found C 40.5, H 2.2, N 3.4 %; calcd. for $C_{56}H_{40}F_{12}N_4O_8Pb_2S_4$: C 40.3, H 2.4, N 3.4 %. – IR (selected bands, cm^{-1}): ν = 701 (m, C-H), 1018 (m), 1149 (s), 1280 (vs, C-F), 1410, 1473, 1573 (s, aromatic ring), 1610 (vs, C=O), 2985 (w, C-H aliphatic), 3070 (w, C-H aromatic). – ^{1}H NMR ([D$_6$]DMSO): δ = 8.51 (d, 2H, py), 8.21 (s, 2H, py), 7.76 (d, 2H, thiophene-H), 7.71 (d, 2H, thiophene-H), 7.26 (d, 2H, py-H), 7.08 (dd, 2H, thiophene), 5.96 (s, 2H, =CH-), 2.48 (s, 6H, methyl) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 21.15 (methyl), 91.34 (methine), 117.62, 121.81, 122.21, 128.76, 132.77, 147.13 (py), 148.48 (py), 149.37 (py), 155.48 (py), 161.47 (py), 168.45, 179.94 ppm.

*Preparation of [Pb(5,5′-dm-2,2′-bpy)(ttfa)$_2$]$_2$ (**2**)*

Complex **2** was synthesized in the same way as complex **1** using 5,5′-dimethyl-2,2′-bipyridine; yield: 65 %. – Analysis: found C 40.7, H 2.3, N 3.6 %; calcd. for $C_{56}H_{40}F_{12}N_4O_8Pb_2S_4$: C 40.3, H 2.4, N 3.4 %. – IR (selected bands, cm^{-1}): ν = 711 (m, C-H), 1027 (m), 1165 (s), 1298 (vs, C-F), 1420, 1453, 1576 (s, aromatic ring), 1617 (vs, C=O), 2979 (w, C-H aliphatic), 3043 (w, C-H aromatic). – ^{1}H NMR ([D$_6$]DMSO): δ = 8.49 (s, 2H, py), 8.20 (d, 2H, py), 7.73 (m, 2H, py and 4H, thiophene), 7.07 (dd, 2H, thiophene), 5.94 (s, 2H, =CH-), 2.49 (s, 6H, methyl) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 18.51 (methyl), 91.32 (methine), 117.60, 121.54, 122.19, 128.76, 132.77, 134.12 (py), 138.43 (py), 147.13 (py), 150.02 (py), 153.10 (py), 168.50, 179.93 ppm.

*Preparation of [Pb(4,4′-dmo-2,2′-bpy)(ttfa)$_2$]$_2$ (**3**)*

Complex **3** was synthesized in the same way as complex **1** using 4,4′-dimethoxy-2,2′-bipyridine; yield 75 %. – Analysis: found C 38.5, H 2.2, N 3.5 %; calcd. for $C_{56}H_{40}F_{12}N_4O_{12}Pb_2S_4$: C 38.8, H 2.3, N 3.2 %. – IR (selected bands, cm^{-1}): ν = 671 (m, C-H), 1124 (m), 1185 (s), 1254 (vs, C-F), 1462, 1513, 1567 (s, aromatic ring), 1612 (vs, C=O), 2930 (w, C-H, aliphatic), 3056 (w, C-H, aromatic). – ^{1}H NMR ([D$_6$]DMSO): δ = 8.51 (d, 2H, py), 7.91 (m, 2H, py), 7.75 (d, 2H, thiophene), 7.71 (d, 2H, thiophene), 7.13 (m, 2H, py-H), 7.06 (dd, 2H, thiophene), 5.92 (s, 2H, =CH-), 3.89 (s, 6H, methoxy) ppm. – ^{13}C NMR ([D$_6$]DMSO): δ = 55.92 (methoxy), 91.39 (methine), 117.62, 122.21, 124.19, 128.75, 129.79 (py), 132.78, 129.79 (py), 147.09 (py), 150.93 (py), 157.13 (py), 168.00, 179.97 ppm.

Crystallography

Crystallographic data were collected at 100 K with the Oxford Cryosystem Cobra low-temperature attachment. The data were collected using a Bruker Apex2 CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at a detector distance of 5 cm and with APEX2 software [30]. The collected data were reduced using the program SAINT [30], and the empirical absorption corrections were performed using SADABS [31]. The structures were solved by Direct Methods and refined by full-matrix least-squares routines using the SHELXTL software package [32]. All non-hydrogen atoms were refined anistropically, and hydrogen atoms were located and included at their calculated positions. Rigid group, similarity and simulation restraints were applied for the refinement of **1** and **3** due to main residue disorder (**1**: 16 %; **3**: 15 %). Materials for publication were prepared using SHELXTL [32] and ORTEP-III [33].

CCDC 753136 (**1**), 753137 (**2**) and 753138 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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