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Mixed-Stack Architecture and Solvatomorphism of Trimeric Perfluoro-*ortho*-Phenylene Mercury complexes with Dithieno[3,2-*b*:2',3'-*d*]thiophene

Raúl Castañeda,^a Victor N. Khrustalev,^{a,b} Alexandr Fonari,^c Jean-Luc Bredas,^d Yulia A. Getmanenko^{a,c} and Tatiana V. Timofeeva^{*a,e}

^a *Department of Chemistry & Biology, New Mexico Highlands University, 803 University Ave., Las Vegas, NM 87701, USA*

^b *Peoples' Friendship University of Russia, 6 Miklukho-Maklay St., Moscow, 117198, Russian Federation*

^c *School of Chemistry & Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, 901 Atlantic Drive NW, Atlanta, GA 30332, USA*

^d *Division of Physical Sciences and Engineering and Solar and Photovoltaics Engineering Research Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia*

^e *Department of Engineering Photonics, ITMO University, St. Petersburg 197101, Russia*

tvtimofeeva@nmhu.edu

Abstract

The formation of the mixed-stack donor-acceptor complex of dithieno[3,2-*b*:2',3'-*d*]thiophene (**1**) and trimeric perfluoro-*ortho*-phenylene mercury (**I**) has been investigated under different conditions. Two solvatomorphs – mixed-stack complexes with a 1:1 donor-acceptor ratio and different solvent molecules in the solid state (dichloromethane (**2**) and dichloroethane (**3**)) have been obtained and characterized by experimental methods (FT-IR spectroscopy, differential thermogravimetric analysis, and X-ray crystallography) and quantum-chemical calculations at the density functional theory level. The differences in the solid state packing, thermal stability and potential charge-transfer properties of **2** and **3** are discussed.

Keywords: dithieno[3,2-*b*:2',3'-*d*]thiophene / trimeric perfluoro-*ortho*-phenylene mercury / secondary interactions / solvatomorphism / X-ray diffraction / quantum chemistry

1. Introduction

Mixed-stack donor-acceptor co-crystals recently attracted attention as charge-transporting materials for organic electronics [1-5] and as room-temperature ferroelectrics [6]. Their semiconducting properties are also a subject of theoretical studies [2, 7]. The prediction [2] and demonstration [8] of balanced, efficient ambipolar charge transport in these systems make them an intriguing class of materials in addition to ambipolar molecular [9, 10] and polymeric [11, 12] organic semiconductors.

Dithieno[3,2-*b*:2',3'-*d*]thiophene (DTT) **1**, a donor [13] with a planar core, had been extensively used in the construction of oligomeric [14-23] and polymeric [24-26] semiconductors. While DTT has been extensively used in covalently linked donor-acceptor architectures [14, 15, 24], there is a single example charge-transfer (CT) complex with DTT as a donor and 7,7,8,8-tetracyanoquinodimethane (TCNQ) as an acceptor described in 1983 [27]. Here, we report the X-ray single crystal analysis of the DTT and its mixed-stack complexes with trimeric perfluoro-*o*-phenylene mercury (**I**) (Chart 1), an acceptor known to form mixed-stack co-crystals with a variety of donors [28-30]. Unexpectedly, two different mixed-stack complexes **2** and **3** were obtained from carbon disulfide-dichloromethane (DCM) and carbon disulfide-dichloroethane (DCE) solutions, respectively; in both cases the chlorinated solvent co-crystallized with the DTT-macrocycle **I** co-crystals.

Chart 1. Molecular structures of the trimeric perfluoro-*o*-phenylene mercury (**I**) acceptor and DTT (**1**) donor used in this study.

The thermal properties of the new solvatomorphs **2** and **3** were studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA); the influence of the solvent on the thermal stability and electronic structure of these complexes was also investigated computationally. Differential pulse voltammetry (DPV) was performed for the acceptor **I** to estimate the acceptor strength of this macrocycle.

2. Experimental Section

2.1. General methods

All solvents were purchased from Aldrich Chemical (HPLC grade) and used without any further purification. Dithieno[3,2-*b*:2',3'-*d*]thiophene **1** [31] was provided by Solvay, Inc. Trimeric perfluoro-*o*-phenylene mercury (**I**) was prepared according to the procedure described earlier by Sartori and Golloch [32] and purified by recrystallization from DCM [33]. DTA coupled with TGA experiments were performed under nitrogen with a Hitachi STA7200 SII NanoTechnology instrument (an aluminum crucible (45 μ L) was used; heating rate was 10 $^{\circ}$ C/min). Powder infrared (IR) spectra of finely ground crystals were recorded in attenuated total reflection (ATR) mode at room temperature (22 $^{\circ}$ C) on Magna-IR 550 FT-IR spectrometer (Thermo Nicolet) with the Linear Baseline Correction.

Differential pulse voltammetry for macrocycle **I** was carried out under nitrogen in an anhydrous deoxygenated dichloromethane solution in 0.1 M tetrabutylammonium hexafluorophosphate using a BAS Potentiostat, a glassy carbon working electrode, a platinum auxiliary electrode, and, as a pseudo-reference electrode, a silver wire anodized in 1 M aqueous potassium chloride. Potentials were referenced to ferrocenium / ferrocene ($\text{Cp}_2\text{Fe}^{+/0-}$) as an internal standard.

2.2. Crystallization of dithieno[3,2-*b*:2',3'-*d*]thiophene (**1**)

Single crystals of DTT suitable for X-ray diffraction analysis were obtained by slow evaporation of a solvent mixture of methanol and dichloromethane. IR (cm^{-1}): 3095.2 (s), 3074.0 (m), 1355.7 (s), 696.2 (s), 600.0 (s) (for FT-IR spectroscopy details, see Supporting Information).

2.3. Crystallization of **I**•DDT•DCM (**2**)

Stoichiometric amounts of **I** (18.1 mg, 17.3 μ mol) and DTT (3.4 mg, 17.3 μ mol) were dissolved in a ~2:1 mixture of carbon disulfide and dichloromethane (5.5 and 2.0 mL, respectively) in separate tubes using ultrasonication. The contents of the tubes were mixed carefully and then left for slow evaporation of the solvents. Complex **2** was obtained as colorless prismatic crystals. IR (cm^{-1}): 3116.4 (m), 3093.3 (m), 2921.6 (m), 2852.2 (m), 1469.5 (s), 1415.5 (s), 1286.3 (m), 1081.9 (s), 1002.8 (s), 815.7 (s), 713.5 (m) (for FT-IR spectroscopy details, see Supporting Information).

2.4. Crystallization of **I**•DTT• $\frac{1}{2}$ DCE (**3**)

Stoichiometric amounts of **I** (18.1 mg, 17.3 μ mol) and DTT (2.8 mg, 17.3 μ mol) were

dissolved in a ~1:1 mixture of carbon disulfide and dichloroethane (4.5 and 2.0 mL, respectively) in separate tubes using ultrasonication. The contents of the tubes were mixed carefully and then left for slow evaporation of the solvents. Complex **3** was obtained as colorless prismatic crystals. IR (cm^{-1}): 3112.5 (m), 3093.3 (m), 2958.3 (m), 2923.6 (m), 2858.0 (m), 1496.5 (s), 1415.5 (s), 1286.3 (m), 1078.0 (s), 1002.8 (s), 813.8 (s), 703.9 (s) (for FT-IR spectroscopy details, see Supporting Information).

2.5. X-ray crystallography

Data for **1**, **2** and **3** (Table 1) were collected on a Bruker SMART APEX-II CCD diffractometer ($\lambda(\text{MoK}\alpha)$ -radiation, graphite monochromator, ω and ϕ scan mode) and corrected for absorption using the *SADABS* program [34]. The structures were solved by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$). All calculations were carried out using the *SHELXTL* program package [35].

Crystallographic data for **1**, **2** and **3** have been deposited with the Cambridge Crystallographic Data Center; CCDC 1025419 (**1**), 1024867 (**2**) and 1024868 (**3**). These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

2.6. Computational methodology

Electronic band-structure calculations were performed on the basis of the experimental structures of **2** and **3** at the Density Functional Theory (DFT) level with the B3LYP density functional as implemented in CRYSTAL14 [36]; the 6-31G basis set was used for all atom types except mercury, for which effective core potential was employed [37]. The Brillouin zone was sampled using a Γ -centered uniform k -point mesh with 68 k -points. The molecular electronic structures of **2** and **3** were computed using Gaussian [38].

Table 1. Crystallographic data for **1-3**.

Compound	1	2	3
Empirical formula	C ₈ H ₄ S ₃	C ₂₇ H ₆ Cl ₂ F ₁₂ Hg ₃ S ₃	C ₂₇ H ₆ ClF ₁₂ Hg ₃ S ₃
Fw	196.29	1327.17	1291.72
<i>T</i> , K	100(2)	100(2)	100(2)
Crystal size, mm	0.10×0.15×0.20	0.10×0.12×0.15	0.10×0.15×0.20
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>C</i> 2/ <i>m</i>
<i>a</i> , Å	10.277(4)	7.1085(8)	22.018(10)
<i>b</i> , Å	3.9383(14)	12.8594(15)	18.152(8)
<i>c</i> , Å	19.313(7)	16.7182(19)	7.123(3)
α , deg.	90	74.740(2)	90
β , deg.	102.528(5)	87.431(2)	99.541(7)
γ , deg.	90	86.354(2)	90
<i>V</i> , Å ³	763.1(5)	1470.7(3)	2808(2)
<i>Z</i>	4	2	4
<i>d</i> _c , g · cm ⁻³	1.709	2.997	3.056
<i>F</i> (000)	400	1196	2324
μ , mm ⁻¹	0.886	16.112	16.782
2 θ _{max} , deg.	60.1	58.0	56.7
Index range	-14 ≤ <i>h</i> ≤ 14 -5 ≤ <i>k</i> ≤ 5 -26 ≤ <i>l</i> ≤ 26	-9 ≤ <i>h</i> ≤ 9 -17 ≤ <i>k</i> ≤ 17 -22 ≤ <i>l</i> ≤ 22	-29 ≤ <i>h</i> ≤ 28 -24 ≤ <i>k</i> ≤ 24 -9 ≤ <i>l</i> ≤ 9
No. of rflns collected	11077	15686	13392
No. of unique rflns (<i>R</i> _{int})	2245 (0.0601)	7755 (0.0315)	3595 (0.0461)
No. of rflns with <i>I</i> > 2 σ (<i>I</i>)	1718	6823	2963
Data/restraints/parameters	2245 / 0 / 100	7755 / 0 / 424	3595 / 1 / 214
<i>R</i> ₁ ; <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0350; 0.0729	0.0271; 0.0582	0.0335; 0.0653
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.0550; 0.0817	0.0333; 0.0598	0.0475; 0.0703
GOF on <i>F</i> ²	1.017	0.991	1.013
<i>T</i> _{min} ; <i>T</i> _{max}	0.843; 0.917	0.196; 0.296	0.134; 0.285

3. Results and Discussion

3.1. Molecular and crystal structures

The crystals of **1**, **2** and **3** were investigated by single-crystal X-ray diffraction (the molecular structure of **1** and the symmetrically independent units of complexes **2** and **3** are shown in Figures S1-S3 along with the atomic numbering schemes, see Supporting Information). Selected bond lengths and angles are listed in Table 2.

Table 2. Selected bond lengths (Å) and bond angles (°) for **1-3**.

Compound	1	2	3*
Hg—C		2.060(5), 2.067(5) 2.071(4), 2.078(4) 2.079(4), 2.081(5)	2.061(4) 2.066(5) 2.067(5)
S—C	1.719(2), 1.722(2) 1.726(2), 1.730(2) 1.739(2), 1.740(2)	1.724(4), 1.725(5) 1.730(5), 1.732(5) 1.745(4), 1.749(5)	1.706(5) 1.717(5) 1.751(5)
C—Hg—C		175.09(19), 175.44(17) 176.10(18)	175.1(2) 175.60(18)
C—S—C	90.45(10), 91.05(10) 91.09(10)	90.7(2), 91.3(2) 91.4(2)	90.2(3) 90.9(2)

* The complex occupies a special position on the mirror plane.

The molecules of DTT (**1**) are nearly planar (r.m.s. deviation of 0.014 Å) and packed into columns consisting of paired stacks along the crystallographic *b* axis (Figure 1). The stacks in the columns are linked by secondary S...S interactions (Table S1, see Supporting Information). The molecules within the stacks are arranged face-to-face and separated by a distance of 3.544(1) Å indicating the presence of $\pi\cdots\pi$ interactions. It should be noted that molecules of different stacks in the same column are arranged at an interplane angle of 51.73(3)° (Figure S4, see Supporting Information).

Fig. 1. Crystal structure of **1** demonstrating the stacks toward [010] (a projection along the *b* axis). Dashed lines indicate the secondary S...S interactions.

The crystal packing of **1** is very similar to that of the related 3,3'-bis(dithieno[3,2-*b*:2',3'-*d*]thiophene) [39], in which molecules form analogous face-to-face π -stacked columns. The columns in the structure of 3,3'-bis(dithieno[3,2-*b*:2',3'-*d*]thiophene) are separated by the distance of 3.57 Å, with short intermolecular S...S interactions between the columns of 3.49 Å, similar to what is observed for DTT (Table S1).

Molecule of DTT (**1**) has three donor sulfur centers separated by the distances of (3.9403(15), 4.1747(13) and 4.1762(12) Å), which are similar to the distances between three acceptor mercury centers in the macrocycle **I** (the average values are 3.607, 3.607 and 3.654 Å). As a result, it is expected that in the mixed-stack complex [**1**...**I**] each sulfur atom of **1** could interact with one different mercury atom of macrocycle **I**.

Remarkably, crystallization of **1** and macrocycle **I** using carbon disulfide-dichloromethane or carbon disulfide-dichloroethane solvent mixtures gave rise to the two different complexes [**1**...**I**]•DCM (**2**) and [**1**...**I**]•DCE (**3**) representing different solvatomorphs. It is important to note that the bond lengths and angles of the individual molecules **1** and **I** in complexes **2** and **3** remained nearly identical to those of pure **1** and **I** (Table 2).

A common feature of solvatomorphs **2** and **3** is the parallel disposition of molecules **1** and **I** (the interplane angles between mean planes are 2.89(6) and 2.39(7)°, respectively), which are held together by the secondary Hg...S and π - π stacking interactions (Figures S2 and S3, Table S1). As expected, the sulfur triangle of **1** is arranged almost above the mercury triangle of **I**. However, in complex **2**, the sulfur and mercury atoms of neighboring molecules of **1** and **I** are shifted by 0.948(1) Å toward the Hg3...Hg1 line (the virtual S3...Hg3...Hg1 angle is 73.47(2)°, Figure S2), whereas in complex **3** these atoms are arranged practically above each other (the virtual S2...Hg2...Hg2A angle is 92.92(2)°, Figure S3). Such structural peculiarity of the complex **2** results in additional secondary Hg... π interactions (Table S1), which are complimentary to the attractive

Hg...S interactions. The observed differences between complexes **2** and **3** are dictated by the intrinsic symmetry of the complexes (**2**: triclinic crystal system, space group *P*-1, one independent formula unit in the crystal lattice; **3**: monoclinic crystal system, space group *C*2/*m*, the [**1...I**] complex occupies a special position on the mirror plane) and determined by the various intermolecular secondary interactions with the participation of solvate molecules. It should be pointed out that the space group *C*2/*m* is rather unusual for molecular crystals (only 1,517 out of 673,278 crystal structures, excluding disordered ones, were found in the CCDC [40]). Because of the geometric peculiarities the whole molecule or associate in this case should have intrinsic *C*_{2h} (2/*m*) symmetry; in our case, the associate {[**1...I**]•DCE•[**1...I**]} possesses this symmetry, *i.e.*, a solvate DCE molecule has intrinsic *C*_{2h} symmetry and the complex [**1...I**] has the intrinsic *C*_s symmetry.

Both donors (D) and acceptors (A) in complexes **2** and **3** form infinite DADADA co-facial stacks along the crystallographic *a* and *c* axes, respectively. The molecular complexes [**1...I**] in compounds **2** and **3** are organized into the stacks by secondary Hg...S, Hg... π , S... π , and π ... π stacking interactions (Table S1).

Moreover, the infinite [**1...I**]_n stacks in both complexes **2** and **3** are linked into paired columns by strong F...S interactions (F...S distances are 2.925(3) and 2.967(3) Å in **2** and 2.911 Å in **3**, Table S1, Figure 2). These F...S contacts are significantly shorter than the equilibrium distance found via quantum-chemical computations equilibrium for F...S interactions (~3.4 Å [41]). Further, the columns are bound by F...S and F...F (for **2**) and F...S (for **3**) interactions into a three-dimensional framework. Interestingly, the crystal structure of **3** does not contain any additional intermolecular F...F short contacts. The solvate DCM and DCE molecules in compounds **2** and **3** are arranged in the free space between the paired columns, to which they are linked via secondary S...Cl and F...Cl interactions (Table S1, Figure 2). In the crystal structure of **2**, each solvate DCM molecule is surrounded by three molecular complexes [**1...I**], while in the crystal structure of **3** each solvate DCE molecule is surrounded by six molecular complexes [**1...I**] (Figure 2). Such an arrangement of the solvate DCE molecules determines the denser crystal packing of **3** (3.056 g/cm³) compared to **2** (2.997 g/cm³). Despite the fact that the solvate DCM molecule in **2** has a smaller amount of tightly bound neighbors, it is held more strongly in the crystal in comparison to the DCE molecule owing to the stronger character of all secondary interactions. This observation is confirmed by the different thermal stabilities of complexes **2** and **3** (*vide infra*). The strong secondary S...Cl interactions between molecular complex [**1...I**] and the solvate DCM molecules in **2** are also responsible for the structure of the former.

Fig. 2. Surrounding of the solvate dichloroethane molecules in the crystals of **2** (top) and **3** (bottom). Thick dashed lines indicate the secondary Hg...S interactions; thin dashed lines indicate the secondary S...Cl and F...Cl interactions.

The oxidation potential of alkylated version of DTT was reported at +0.66 V in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane [13]. An absorption band in the visible-NIR region is typically observed in CT materials [42]; however complexes **2** and **3** are colorless crystals; from TD DFT the first excited state is a CT-localized dark state (~0.0 oscillator strength).

3.2. Quantum-chemical calculations

In mixed-stack donor-acceptor crystals, the HOMO-LUMO gap is related to the difference between the energy of the highest occupied molecular orbital (HOMO) of the donor ($E_{\text{DTT,HOMO}}$) and the energy of the lowest unoccupied molecular orbital (LUMO) of the acceptor ($E_{\text{I,LUMO}}$). Frontier orbitals and corresponding energies of DTT (**1**) and macrocycle **I** are shown in Figure 3. The HOMO of **I** is delocalized over the fluorinated phenyl rings, while the LUMO is mainly localized around the mercury atoms. The HOMO-LUMO gap of the complex, that would be estimated from the difference between $E_{\text{DTT,HOMO}}$ and $E_{\text{I,LUMO}}$, is 3.19 eV.

Fig. 3. Frontier molecular orbitals and corresponding energies of DTT (**1**) (top) and Hg-macrocycle **I** (middle) and donor-acceptor complex (bottom).

For an isolated complex, extracted from the crystal structure, HOMO–LUMO gap is 4.36 eV. Unlike in the previously studied donor-acceptor systems [2, 7], the frontier orbitals of the complex do not describe a complete charge-transfer and have localized character mixed-in (Figure 3). As a result, obtained energy gap is higher than the energy gap (2.36 eV) calculated from the electrochemical measurements of the oxidation potential of DTT (**1**) and reduction potential of macrocycle (**I**) in solution or the HOMO–LUMO gap (3.19 eV) estimated from $E_{\text{DTT,HOMO}}$ and $E_{\text{I,LUMO}}$.

The valence and conduction bands of **2** and **3** are shown in Figure 4; the energy band gaps are 4.33 eV and 4.32 eV, which is in agreement with the observation that crystals are colorless.ⁱ

Fig. 4. Valence and conduction bands of complexes **2** (left) and **3** (right) in red solid lines. Valence and conduction bands with the solvent molecules removed from the unit cell are shown in dashed black lines. The points of high symmetry in the first Brillouin zone are labeled as follows: $\Gamma = (0,0,0)$, $X = (0.5,0,0)$, $Y = (0,0.5,0)$, $B = (0,0,0.5)$, $C = (0.5,0.5,0)$, $A = (0.5,0,0.5)$, $E = (0.5,0.5,0.5)$ and $D = (0, 0.5, 0.5)$, all in crystallographic coordinates. The zero of energy is taken as the top of the valence band.

ⁱ For triphenylene, see [28], and the larger aromatic hydrocarbons, see [43]. Co-crystals with macrocycle **I** were reported as white solid. No charge-transfer bands were reported for ferrocene and nickelocene in co-crystals with macrocycle **I** [44].

The HOMO and LUMO energies of DCM [DCE] are: -8.48 eV and -0.01 eV [-8.22 eV and 0.52 eV], suggesting that in both crystals the solvent frontier orbitals are located deep into occupied [empty] bands of the crystal and do not participate in the valence [conduction] bands of the crystal. In order to confirm this, we calculated the band structure with the solvent molecules removed from the unit cell. Valence [conduction] bands of complex **2** and solvent-free DTT-**I** crystals, indeed, overlap almost perfectly. In the case of **3**, the removal of the solvent results in a slight increase of the energy gap (by 0.05 eV). Both valence and conduction bandwidths in **2** are very small (<0.1 eV), thus there is insignificant band dispersions. The valence bandwidth of **3** is around 0.1 eV and conduction bandwidth is 0.2 eV, somewhat larger in comparison with those of **2** due to additional interactions between overlapping acceptor molecules **I** along the *c*-axis. These values are comparable to the bandwidths found in anthracene-TCNQ and tetracene-TCNQ crystals [7]. As a result of such large band gaps and almost flat bands, charge transport in these co-crystals is not expected to be efficient; further modification of the electronic properties of the donor and/or acceptor is required.

3.3. TGA and DTA analyses

DTA analysis of DTT (**1**) (Figure 5a) shows two features at 70 °C and 239 °C, the first event corresponds to the melting point, which is consistent with literature result [45]. The second event at 239 °C corresponds to a decomposition process with decomposition temperature determined by the TGA analysis at 5% weight loss at 168 °C.

TGA thermograms of complexes **2** and **3** (Figures 5b and 5c, respectively) show that these complexes have different thermal stability. In complex **2**, a 5%ⁱⁱ weight loss at 72 °C corresponds to the loss of DCM, which occurs at higher temperature than the boiling point of DCM (39.6 °C). The second event at 255 °C in the DTA measurement (Figure 5b) possibly corresponds to a decomposition of DTT molecules in complex **2** (by TGA analysis, 5% loss after the initial loss of solvent takes place at 208 °C).

Fig. 5. TGA (blue) and DTA (red) thermographs (10 °C/min heating rate) for a) DTT **1**, b) complex **2**, and c) complex **3**.

ⁱⁱFrom the crystallographic data for **2** the DCM content is 6.4%.

For complex **3**, the solvent DCE loss occurs at 85 °C (by TGA analysis, the % weight loss is 3.3 %ⁱⁱⁱ), thus at the temperature close to the boiling point of DCE (84 °C). The second event for **3** observed at *ca.* 229.5 °C by DTA (Figure 5c) is not clearly detected by TGA (a 5% loss after the initial loss of solvent takes place at 187 °C). These observations suggest that in the crystal lattice of **2**, solvent DCM interacts stronger with the DTT (**1**) and macrocycle **I** in comparison with DCE in the crystal lattice of **3**.

4. Conclusion

Two solvatomorphic mixed-stack donor-acceptor complexes of donor dithieno[3,2-*b*:2',3'-*d*]thiophene **1** and acceptor trimeric perfluoro-*ortho*-phenylene mercury **I** with 1:1 ratio and dichloromethane (**2**) and dichloroethane (**3**) as solvates have been obtained. Both complexes **2** and **3** are colorless indicating the lack of charge-transfer character, which is consistent with the large energy gaps (4.33 eV and 4.32 eV) between valence and conduction bands calculated at the DFT level. In the crystal, both complexes **2** and **3** form extended columns consisting of π - π stacks in which molecules **1** and **I** alternate. This fact indicates that the formation of the primary [**1**...**I**]_n chain is not significantly affected by the solvate molecules. However, the relative positions of the donor and acceptor molecules in the stacks, interstack interactions and electronic properties are affected by the solvate molecules as a result of different interplays of intermolecular secondary interactions. While for both complexes the valence and conduction bandwidths are small, and, as a result, the charge-transport properties are not expected to be efficient, an increase in bandwidths could possibly be achieved by changing the solvate in the co-crystals, which provides an additional tool for fine-tuning the electronic properties improving the charge-transport properties of mixed-stack systems.

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Supporting Information

Full crystal data for **1-3**, FT-IR spectroscopy for **I** and **1-3**, and electrochemical analysis of **I**. This material is available free of charge *via* the Internet.

ⁱⁱⁱ From the crystallographic data for **3** the DCE content is 3.8%.

References

- [1] T. Hasegawa, K. Mattenberger, J. Takeya, B. Batlogg, *Phys. Rev. B* 69 (2004).
- [2] L.Y. Zhu, Y.P. Yi, Y. Li, E.G. Kim, V. Coropceanu, J.L. Bredas, *J. Am. Chem. Soc.* 134 (2012) 2340-2347.
- [3] J. Zhang, H. Geng, T.S. Virk, Y. Zhao, J.H. Tan, C.A. Di, W. Xu, K. Singh, W.P. Hu, Z.G. Shuai, Y.Q. Liu, D.B. Zhu, *Adv. Mater.* 24 (2012) 2603-2607.
- [4] T. Wakahara, P. D'Angelo, K.i. Miyazawa, Y. Nemoto, O. Ito, N. Tanigaki, D.D.C. Bradley, T.D. Anthopoulos, *J. Am. Chem. Soc.* 134 (2012) 7204-7206.
- [5] S.K. Park, S. Varghese, J.H. Kim, S.J. Yoon, O.K. Kwon, B.K. An, J. Gierschner, S.Y. Park, *J. Am. Chem. Soc.* 135 (2013) 4757-4764.
- [6] A.S. Tayi, A.K. Shveyd, A.C.H. Sue, J.M. Szarko, B.S. Rolczynski, D. Cao, T.J. Kennedy, A.A. Sarjeant, C.L. Stern, W.F. Paxton, W. Wu, S.K. Dey, A.C. Fahrenbach, J.R. Guest, H. Mohseni, L.X. Chen, K.L. Wang, J.F. Stoddart, S.I. Stupp, *Nature* 488 (2012) 485-489.
- [7] L.Y. Zhu, Y.P. Yi, A. Fonari, N.S. Corbin, V. Coropceanu, J.L. Bredas, *J. Phys. Chem. C* 118 (2014) 14150-14156.
- [8] H.-D. Wu, F.-X. Wang, Y. Xiao, G.-B. Pan, *J. Mater. Chem. C* 1 (2013) 2286-2289.
- [9] X. Kong, X. Zhang, D.M. Gao, D.D. Qi, Y.L. Chen, J.Z. Jiang, *Chem Sci* 6 (2015) 1967-1972.
- [10] K. Zhou, H.L. Dong, H.L. Zhang, W.P. Hu, *Phys Chem Chem Phys* 16 (2014) 22448-22457.
- [11] A.J. Kronemeijer, E. Gili, M. Shahid, J. Rivnay, A. Salleo, M. Heeney, H. Sirringhaus, *Adv Mater* 24 (2012) 1558-1565.
- [12] J. Lee, A.R. Han, J. Kim, Y. Kim, J.H. Oh, C. Yang, *J. Am. Chem. Soc.* 134 (2012) 20713-20721.
- [13] S. Barlow, S.A. Odom, K. Lancaster, Y.A. Getmanenko, R. Mason, V. Coropceanu, J.L. Bredas, S.R. Marder, *J. Phys. Chem. B* 114 (2010) 14397-14407.
- [14] L.E. Polander, S.P. Tiwari, L. Pandey, B.M. Seifried, Q. Zhang, S. Barlow, C. Risko, J.L. Bredas, B. Kippelen, S.R. Marder, *Chem. Mater.* 23 (2011) 3408-3410.
- [15] C. Kim, M.C. Chen, Y.J. Chiang, Y.J. Guo, J. Youn, H. Huang, Y.J. Liang, Y.J. Lin, Y.W. Huang, T.S. Hu, G.H. Lee, A. Facchetti, T.J. Marks, *Org. Electron.* 11 (2010) 801-813.
- [16] L. Zhang, L. Tan, W.P. Hu, Z.H. Wang, *J. Mater. Chem.* 19 (2009) 8216-8222.
- [17] M.C. Chen, Y.J. Chiang, C. Kim, Y.J. Guo, S.Y. Chen, Y.J. Liang, Y.W. Huang, T.S. Hu, G.H. Lee, A. Facchetti, T.J. Marks, *Chem. Commun.* (2009) 1846-1848.
- [18] M. Melucci, L. Favaretto, C. Bettini, M. Gazzano, N. Camaioni, P. Maccagnani, P. Ostoja, M. Monari, G. Barbarella, *Chem. Eur. J.* 13 (2007) 10046-10054.

- [19] M.D. Iosip, S. Destri, M. Pasini, W. Porzio, K.P. Pernstich, B. Batlogg, *Synthetic. Met.* 146 (2004) 251-257.
- [20] J.J. Morrison, M.M. Murray, X.C. Li, A.B. Holmes, S.C. Morratti, R.H. Friend, H. Sirringhaus, *Synthetic. Met.* 102 (1999) 987-988.
- [21] X.C. Li, H. Sirringhaus, F. Garnier, A.B. Holmes, S.C. Moratti, N. Feeder, W. Clegg, S.J. Teat, R.H. Friend, *J. Am. Chem. Soc.* 120 (1998) 2206-2207.
- [22] L.T. Dou, J.B. You, Z.R. Hong, Z. Xu, G. Li, R.A. Street, Y. Yang, *Adv. Mater.* 25 (2013) 6642-6671.
- [23] K.H. Kim, S.Y. Bae, Y.S. Kim, J.A. Hur, M.H. Hoang, T.W. Lee, M.J. Cho, Y. Kim, M. Kim, J.I. Jin, S.J. Kim, K. Lee, S.J. Lee, D.H. Choi, *Adv. Mater.* 23 (2011) 3095-3099.
- [24] X.W. Zhan, Z.A. Tan, B. Domercq, Z.S. An, X. Zhang, S. Barlow, Y.F. Li, D.B. Zhu, B. Kippelen, S.R. Marder, *J. Am. Chem. Soc.* 129 (2007) 7246-+.
- [25] K. Lu, C.A. Di, H.X. Xi, Y.Q. Liu, G. Yu, W.F. Qiu, H.J. Zhang, X. Gao, Y. Liu, T. Qi, C.Y. Du, D.B. Zhu, *J. Mater. Chem.* 18 (2008) 3426-3432.
- [26] J. Li, F. Qin, C.M. Li, Q.L. Bao, M.B. Chan-Park, W. Zhang, J.G. Qin, B.S. Ong, *Chem. Mater.* 20 (2008) 2057-2059.
- [27] D. Zobel, G. Ruban, *Acta Crystallogr., Sect. B: Struct. Sci* 39 (1983) 638-645.
- [28] M.R. Haneline, M. Tsunoda, F.P. Gabbaï, *J. Am. Chem. Soc.* 124 (2002) 3737-3742.
- [29] I.A. Tikhonova, D.A. Gribanyov, K.I. Tugashov, F.M. Dolgushin, A.S. Peregodov, D.Y. Antonov, V.I. Rosenberg, V.B. Shur, *J. Organomet. Chem.* 695 (2010) 1949-1952.
- [30] A.S. Filatov, A.K. Greene, E.A. Jackson, L.T. Scott, M.A. Petrukhina, *J. Organomet. Chem.* 696 (2011) 2877-2881.
- [31] J. Frey, A.D. Bond, A.B. Holmes, *Chem. Commun.* (2002) 2424-2425.
- [32] P. Sartori, A. Golloch, *Chem Ber-Recl* 101 (1968) 2004-2009.
- [33] A.S. Filatov, E.A. Jackson, L.T. Scott, M.A. Petrukhina, *Angew. Chem., Int. Ed. Engl.* 48 (2009) 8473-8476.
- [34] G.M. Sheldrick, in, *Bruker AXS, Madison, Wisconsin*, 2003.
- [35] G.M. Sheldrick, *Acta Crystallogr A* 64 (2008) 112-122.
- [36] R. Dovesi, R. Orlando, A. Erba, C.M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noel, M. Causa, M. Rerat, B. Kirtman, *Int J Quantum Chem* 114 (2014) 1287-1317.
- [37] P.J. Hay, W.R. Wadt, *J Chem Phys* 82 (1985) 270-283.
- [38] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A.J. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, I. Gaussian, in, *Pittsburgh, PA*, 2003.
- [39] L. San Miguel, W.W. Porter, A.J. Matzger, *Org. Lett.* 9 (2007) 1005-1008.

- [40] F. Allen, *Acta Crystallogr., Sect. B* 58 (2002) 380-388.
- [41] N.E. Jackson, B.M. Savoie, K.L. Kohlstedt, M. Olvera de la Cruz, G.C. Schatz, L.X. Chen, M.A. Ratner, *J. Am. Chem. Soc.* 135 (2013) 10475-10483.
- [42] K.R. Leight, B.E. Esarey, A.E. Murray, J.J. Reczek, *Chem Mater* 24 (2012) 3318-3328.
- [43] A.S. Filatov, A.K. Greene, E.A. Jackson, L.T. Scott, M.A. Petrukhina, *J. Organomet. Chem.* 696 (2011) 2877-2881.
- [44] M.R. Haneline, F.P. Gabbai, *Z. Naturforsch., B: Chem. Sci.* 59 (2004) 1483-1487.
- [45] F.M. Stoyanovich, B.P. Fedorov, *Zh. Org. Khim.* 1 (1965) 1282-1292.

Highlights

1. The formation of donor-acceptor complexes by trimeric perfluoro-*ortho*-phenylene mercury was observed.
2. Two solvatomorphic mixed-stack donor-acceptor structures were obtained.
3. The differences between the solvatomorphs were studied by FT-IR spectroscopy, DTA, X-ray diffraction and quantum chemistry.
4. Stacks structure and electronic properties result from interplay of intermolecular secondary interactions.
5. The formation of the stacks is not significantly affected by the solvate molecules.

to

Mixed-Stack Architecture and Solvatomorphism of Trimeric Perfluoro-*ortho*-Phenylene Mercury complexes with Dithieno[3,2-*b*:2',3'-*d*]thiophene

Raúl Castañeda,^a Victor N. Khrustalev,^{a,b} Alexandr Fonari,^c Jean-Luc Bredas,^d
Yulia A. Getmanenko^{a,c} and Tatiana V. Timofeeva^{*a,e}

^a *Department of Chemistry & Biology, New Mexico Highlands University, 803 University Ave.,
Las Vegas, NM 87701, USA*

^b *Peoples' Friendship University of Russia, 6 Miklukho-Maklay St., Moscow, 117198, Russian
Federation*

^c *School of Chemistry & Biochemistry and Center for Organic Photonics and Electronics,
Georgia Institute of Technology, 901 Atlantic Drive NW, Atlanta, GA 30332, USA*

^d *Division of Physical Sciences and Engineering and Solar and Photovoltaics Engineering
Research Center, King Abdullah University of Science and Technology, Thuwal 23955-6900,
Kingdom of Saudi Arabia*

^e *Department of Engineering Photonics, ITMO University, St. Petersburg 197101, Russia*

Fig. S1. Molecular structure of **1** (hydrogen atoms are arbitrarily small).

Fig. S2. Molecular structures of all components of **2** (hydrogen atoms are arbitrarily small). Thick dashed lines indicate the secondary Hg...S interactions; thin dashed lines indicate the secondary Hg...C and $\pi\cdots\pi$ stacking interactions.

Fig. S3. Molecular structures of all components of **3**. Thick dashed lines indicate the secondary Hg...S interactions; thin dashed lines indicate the secondary Hg...C and π ... π stacking interactions. The notations A denote symmetry equivalent atoms relative to the mirror plane (in the case of the main complex) or the inversion center (in the case of the solvate dichloroethane molecule).

Fig. S4. Crystal structure of **1** demonstrating the stacks toward [010] (a projection along the *c* axis). Dashed lines indicate the secondary S...S interactions.

Table S1. Intermolecular contacts (Å) for **1-3**.

DTT 1			
S1...S2 ^a	3.5657(10)	S2...S2 ^a	3.5372(11)
Complex 2			
Hg1...S1	3.4513(12)	F10...F17 ^f	2.816(4)
Hg1...S2 ^b	3.7105(11)	F11...S2 ^g	2.967(3)
Hg1...C21 ^b	3.244(4)	F14...S2 ^g	2.925(3)
Hg1...C22	3.499(4)	F15...C12 ^h	3.208(3)
Hg1...C22 ^b	3.652(4)	F16...F17 ⁱ	2.793(4)
Hg2...S2	3.7528(12)	C1...C22 ^b	3.421(6)
Hg2...S2 ^b	3.5900(12)	C2...S1 ^b	3.482(5)
Hg2...C24	3.456(4)	C2...C3 ^d	3.380(6)
Hg3...S3	3.3334(12)	C3...C3 ^d	3.426(6)
Hg3...C24 ^b	3.370(4)	C5...S3 ^b	3.299(5)
Hg3...C25 ^b	3.208(4)	C6...C23 ^b	3.403(6)
Hg3...C26	3.651(4)	C7...C26	3.399(6)
Hg3...C26 ^b	3.584(4)	C12...C25	3.464(6)
Hg3...Cl1 ^c	3.8387(15)	C17...C19	3.373(6)
F4...S1 ^d	3.121(3)	C18...C22	3.460(6)
F8...Cl1 ^e	3.226(3)	S3...Cl1 ^c	3.4687(19)
Complex 3*			
Hg1...Hg1 ⁱ	3.7890(14)	F4...Cl1 ^k	3.245(3)
Hg1...S1	3.360(2)	F5...S2 ^j	2.940(3)
Hg2...S1 ^j	3.6893(19)	C6...C11	3.488(7)
Hg2...S2	3.3420(18)	C7...C13 ^j	3.364(6)
Hg2...C11 ^j	3.324(5)	C8...S2 ^j	3.476(5)
Hg2...C12 ^j	3.302(5)	S2...Cl1	3.568(2)
F2...S1 ^d	2.911(3)		

* The complex occupies a special position on the mirror plane.

Symmetry transformation used to generate equivalent atoms: **a**: (1-x, 0.5+y, 0.5-z); **b**: (-1+x, y, z); **c**: (1-x, 1-y, -z); **d**: (-x, 1-y, -z); **e**: (-1+x, -1+y, z); **f**: (x, -1+y, z); **g**: (1-x, -y, 1-z); **h**: (1-x, 1-y, 1-z); **i**: (-x, 1-y, 1-z); **j**: (x, y, 1+z); **k**: (0.5-x, 0.5-y, 1-z).

FT-IR of DTT **1**, macrocycle **I**, and complexes **2** and **3** were recorded. The C-H stretching aromatic bands of the pure DTT were observed at 3095 and 3074 cm^{-1} . A hypochromic shift for these bands is observed in **2** (3116 and 3093 cm^{-1} , respectively) and **3** (3112 and 3093 cm^{-1} , respectively). The macrocycle **I** C-C stretching bands at 1248 cm^{-1} and 818 cm^{-1} [A.S. Filatov, E.A. Jackson, L.T. Scott, M.A. Petrukhina, *Angew. Chem., Int. Ed. Engl.* 48 (2009) 8473-8476] are slightly shifted in complex **2** (1253 and 816 cm^{-1}) and complex **3** (1253 and 814 cm^{-1}).

Electrochemical analysis of **I**

The reduction peak for the macrocycle **I** was observed at -1.70 V, and the estimated electron affinity (EA) is 3.4 eV¹ (a similar electron affinity of 3.4 eV was reported previously for this macrocycle [S.M. Tekarli, T.R. Cundari, M.A. Omary, *J. Am. Chem. Soc.* 130 (2008) 1669-1675]; however, the conditions for the electrochemical measurements were not reported).

Fig. S5. Differential pulse voltammogram of macrocycle **I** in 0.1 M tetrabutylammonium hexafluorophosphate-e in dichloromethane ($\text{Cp}_2\text{Fe}^{0/+}$ as internal reference).

¹ EA = ($eE^{0/-}$ + 5.1 eV) [C.M. Cardona, W. Li, A.E. Kaifer, D. Stockdale, G.C. Bazan, *Adv Mater* 23 (2011) 2367-2371].