

π -Complexation of Biphenyl, Naphthalene, and Triphenylene to Trimeric Perfluoro-*ortho*-phenylene Mercury. Formation of Extended Binary Stacks with Unusual Luminescent Properties

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Abstract: Trimeric perfluoro-*ortho*-phenylene mercury (**1**) crystallizes from CS₂ as a pure compound. In the crystal, **1** forms staggered cofacial dimers (centroid distance of 3.38 Å). In the dimer, the individual components are associated via long mercury- π interactions (3.443 < Hg...C < 3.650 Å). Interestingly, this arrangement leads to the existence of relatively short intermolecular mercury-mercury distances (3.811 < Hg...Hg < 4.093 Å). In this form, compound **1** is photoluminescent and exhibits a broad emission band with a maximum at 440 nm and a shoulder at 530 nm. Compound **1** interacts with biphenyl, naphthalene, or triphenylene to form **1**-biphenyl (**2**), **1**-naphthalene (**3**), and **1**-triphenylene (**4**), respectively. These adducts have been characterized by elemental analysis and X-ray crystallography. Their structure reveals the existence of stacks in which molecules of **1** and molecules of arenes alternate. In each stack, secondary π -interactions occur between the arene and the mercury centers of **1**. The resulting Hg...C distances range from 3.25 to 3.55 Å and are within the sum of the van der Waals radii. They reflect the presence of secondary polyhapto- π interactions occurring between the electron-rich aromatic molecules and the acidic mercury centers. In the case of the triphenylene adduct **4**, an arene-fluoroarene interaction is also observed (centroid distance of 3.605 Å). Compounds **2**–**4** are photoluminescent. The emission observed for **2** and **3** corresponds to the phosphorescence of the aromatic substrate and suggests the occurrence of a mercury heavy atom effect. In the case of **4**, the emission appears at longer wavelengths than those typically observed for triphenylene.

Introduction

The supramolecular chemistry of polyfunctional Lewis acids^{1–4} is a vibrant area of research with applications in the field of catalysis⁵ and molecular recognition.^{1–15} While different Lewis acidic elements have been employed, those containing mercury

in combination with electron-withdrawing backbones constitute a unique class. These derivatives exhibit fascinating host-guest chemistry with anions.^{1–4,8–10} Depending on the structure of

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Table 1. Crystal Data for Compounds **1**, **2**, **3**, and **4**^a

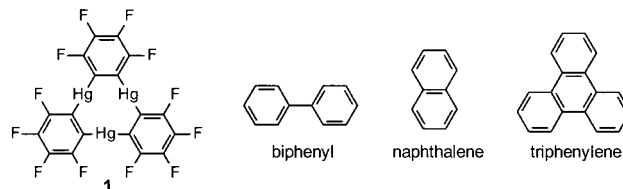
crystal data	1	2	3	4
formula	C ₁₈ F ₁₂ Hg ₃	C ₃₀ H ₁₀ F ₁₂ Hg ₃	C ₂₈ H ₈ F ₁₂ Hg ₃	C ₃₆ H ₁₂ F ₁₂ Hg ₃
<i>M_r</i>	1045.95	1200.15	1194.11	1274.23
crystal size (mm ³)	0.29 × 0.20 × 0.20	0.14 × 0.10 × 0.70	0.15 × 0.23 × 0.35	0.07 × 0.08 × 0.40
crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbcn</i>
<i>a</i> (Å)	10.505(2)	7.3093(15)	19.632(4)	7.2103(14)
<i>b</i> (Å)	8.6105(17)	19.747(4)	7.0170(14)	35.982(7)
<i>c</i> (Å)	20.489(4)	19.450(4)	21.212(4)	11.670(2)
β (°)	97.29(3)	97.17(3)	116.41(3)	
<i>V</i> (Å ³)	1838.2(6)	2785.3(10)	2617.2(9)	3027.7(10)
<i>Z</i>	4	4	4	4
ρ _{calc} (g cm ⁻³)	3.779	2.862	2.980	2.795
μ(Mo Kα) (mm ⁻¹)	25.116	16.597	17.659	15.278
<i>F</i> (000)	1824	2152	2096	2304
data collection				
<i>T</i> /K	293(2)	293(2)	293(2)	180(2)
scan mode	ω	ω	ω	ω
<i>hkl</i> range	-12 → 12 -9 → 9 -23 → 23	-8 → 8 -22 → 23 -23 → 20	-21 → 22 -9 → 8 -24 → 24	-9 → 9 -48 → 47 -13 → 15
measured refl.	15 685	8736	15 732	33 533
unique refl., [<i>R</i> _{int}]	2879 [0.0293]	2451 [0.0966]	3965 [0.0472]	3765 [0.0584]
refl. used for refinement	2879	2451	3965	3765
absorption correction	SADABS	SADABS	SADABS	SADABS
<i>T</i> _{min} / <i>T</i> _{max}	0.072358	0.070697	0.266223	0.316523
refinement				
refined parameters	298	205	388	231
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0403, 0.1130	0.0677, 0.1603	0.0607, 0.1611	0.0384, 0.0710
ρ _{fin} (max/min) (e Å ⁻³)	3.959, -2.374	2.327, -3.969	6.045, -2.476	1.022, -2.056

^a *R*1 = Σ(*F*_o - *F*_c)/Σ*F*_o; *wR*2 = {[Σ*w*(*F*_o² - *F*_c²)²]/[Σ*w*(*F*_o²)²]}^{1/2}; *w* = 1/[σ²(*F*_o²) + (*ap*)² + *bp*]; *p* = (*F*_o² + 2*F*_c²)/3; *a* = 0.0850 (**2**), 0.1178 (**3**), 0.1392 (**4**), 0.0203 (**5**); *b* = 5.37 (**2**), 0 (**3**), 0 (**4**), 42.07 (**5**).

the guest, highly unusual complexes containing hypercoordinated anions can be isolated. In the case of organic substrates such as ethers,¹¹ ketones,¹² formamides,^{12,13} sulfoxides,¹⁴ and nitriles,¹⁵ polydentate mercury Lewis acids form chelate complexes in which the electron-rich terminus of the substrate interacts concomitantly with two, three, and sometimes four of the Lewis acidic mercury centers. In parallel to those studies, we have recently focused on the interaction of polyfunctional organomercurials with arenes.¹⁶

The affinity of mercury for unsaturated substrates is well documented. In addition to the mercuriation of alkenes, alkynes, and aromatic derivatives which reflect this chemical trait, different types of arene-mercury π-complexes have been isolated. While Crabtree has collected solid evidence for the formation of the [Hg(η²-arene)] exciplexes,¹⁷ Hg(I)¹⁸ and Hg(II) complexes have been structurally characterized. In this domain, the contributions of Olah,¹⁹ Dean,²⁰ Kochi,²¹ and more recently Barron²² are especially noteworthy. Interestingly, related, yet weaker, arene π-complexes have been observed in the chemistry of organomercurials. In most cases, π-coordination occurs intramolecularly,^{23,24} although unsupported complexes have been isolated recently.¹⁶ With Hg-C_{arene} distances in the

range of 3–3.4 Å, these interactions are inherently weak. Nevertheless, solution NMR measurements have been performed and suggest an energy range of 1–2 kcal/mol.²⁵ Following the isolation of π-complexes involving *ortho*-bis(chloromercurio)-tetrafluorophenylene and benzene,^{11b} we investigated the interaction of benzene with trimeric perfluoro-*ortho*-phenylene mercury (**1**)²⁶ and observed the formation of compact stacks in which **1** and hexacoordinated benzene molecules alternate.¹⁶ In an extension of these studies, we have now examined the interaction of **1** with biphenyl, naphthalene, and triphenylene and report the structures and luminescent properties of supramolecular stacks formed by the weak π-complexation of the aromatic substrates to the mercury centers of **1**. As part of this work we also report the crystal structure and luminescence of free **1**.



Results and Discussion

Structure and Luminescent Properties of 1. Compound **1** is moderately soluble in CS₂ (3 g/L) and CH₂Cl₂ (7 g/L). Upon slow evaporation of a saturated solution in either of these solvents, clear colorless crystals of **1** as a free acid are readily obtained. These crystals belong to the monoclinic space group *P*2₁/*n* (Table 1). Interestingly, examination of the cell packing

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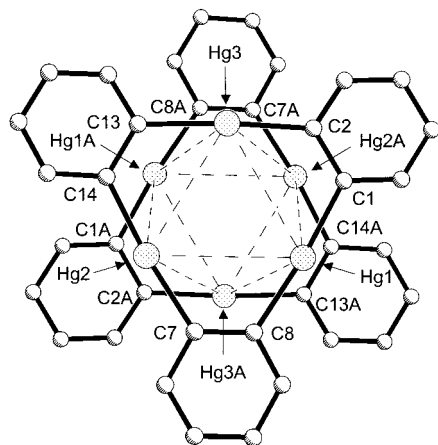


Figure 1. Molecular structure of crystalline **1**. Fluorine atoms are omitted for clarity. Selected intramolecular bond distances [Å] and angles [deg]. Hg(1)–C(1) 2.060(11), Hg(1)–C(8) 2.092(12), Hg(2)–C(14) 2.051(11), Hg(2)–C(7) 2.079(11), Hg(3)–C(2) 2.046(12), Hg(3)–C(13) 2.067(13), C(1)–Hg(1)–C(8) 174.5(5), C(14)–Hg(2)–C(7) 174.2(5), C(2)–Hg(3)–C(13) 175.6(5).

Table 2. Intermolecular Distances (Å) in the Structure of **1**^a

Hg(1)···C(13) ^b	3.479	Hg(2)···C(1) ^b	3.453	Hg(3)···C(7) ^b	3.650
Hg(1)···C(14) ^b	3.514	Hg(2)···C(2) ^b	3.443	Hg(3)···C(8) ^b	3.502
Hg(1)···F(12) ^c	3.295			Hg(3)···F(11) ^c	3.236
Hg(1)···F(16) ^d	3.093			Hg(3)···F(18) ^e	3.440
Hg(1)···Hg(2) ^b	4.018	Hg(2)···Hg(3) ^b	4.093	Hg(3)···Hg(1) ^b	3.811

^a Symmetry operations used to generate the atoms of neighboring units are indicated in the following footnotes. ^b $-x + 1, -y + 2, -z$. ^c $-x + 1, -y + 1, -z$. ^d $x + 0.5, -y + 1.5, z + 0.5$. ^e $-x, -y + 2, -z$.

diagram indicates that molecules of **1** associate into compact cofacial dimers with a centroid distance of 3.38 Å (Figure 1, Table 2). As shown by the relatively short distances observed between the mercury centers and the *ipso*-carbon of the juxtaposed molecule ($3.443 < \text{Hg} \cdots \text{C} < 3.650$ Å, Table 2), mercury–arene interactions are likely responsible for the formation of this dimeric unit. It is interesting to note that, as a result of this arrangement, short intermolecular distances are observed between the mercury atoms ($3.811 < \text{Hg} \cdots \text{Hg} < 4.093$ Å). These distances are longer than those observed intramolecularly (Hg(1)···Hg(2), 3.647 Å; Hg(2)···Hg(3), 3.622 Å, Hg(1)···Hg(3), 3.622 Å) and slightly exceed the range suggested for mercuriphilic interactions.^{27,28} The mercury centers also engaged into mercury–fluorine interactions ($3.093 < \text{Hg} \cdots \text{F} < 3.295$ Å) which are shorter than the sum of the van der Waals radii ($r_{\text{vdw}}(\text{F}) = 1.30\text{--}1.38$ Å,²⁹ $r_{\text{vdw}}(\text{Hg}) = 1.73\text{--}2.00$ Å)^{28,30} and link the dimers into extended chains.

Solutions of **1** in CH₂Cl₂ do not luminesce and feature an absorption band at 275 nm in agreement with the excitation of

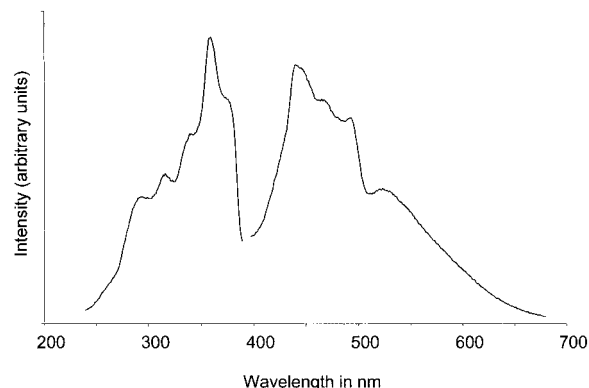


Figure 2. Excitation ($\lambda_{\text{emission}} = 440$ nm) and emission ($\lambda_{\text{excitation}} = 355$ nm) spectra of crystalline **1**.

the tetrafluorophenylene backbone of the complex.³¹ By contrast, when irradiated with UV light in the crystalline state, compound **1** displays an intense orange photoluminescence. Measurement of the emission spectrum at 77 K ($\lambda_{\text{ex}} = 355$ nm) reveals the existence of an extremely broad band featuring a maximum at 440 nm and a broad shoulder at 530 nm that expands far in the visible part of the spectrum (Figure 2). While a rationalization of the luminescent properties of **1** can only be tentatively provided, we note that the presence of metallophilic interactions³² is often associated with unusual luminescent properties.³³ While this phenomenon is especially well characterized in the chemistry of gold(I),³⁴ a recent report by Burini and Fackler demonstrates that increased metallophilic interactions in stacks involving **1** and trinuclear gold complexes result in low energy emissions.³⁵ Hence, the aggregation of molecules of **1** into tight dimers can possibly be held responsible for some features of the visible emission observed in crystals of **1**.

Synthesis of 1·Biphenyl (2), 1·Naphthalene (3), and 1·Triphenylene (4). Following our discovery that **1** complexes benzene, we decided to expand our studies to the case of larger arenes. When a CS₂ or CH₂Cl₂ solution of **1** is mixed with a solution of biphenyl in the same solvent, slow evaporation of the solvent leads to crystallization of a 1:1 adduct (**2**) which is isolated in a pure form. A similar observation is made in the case of naphthalene, which also forms a 1:1 adduct with **1** (**3**). Interestingly, when a CS₂ or CH₂Cl₂ of **1** is mixed with a solution of triphenylene in the same solvent, precipitation of a 1:1 adduct (**4**) occurs spontaneously. Single crystals of **4** can be obtained by slow diffusion of a CH₂Cl₂ solution of **1** into a CH₂Cl₂ solution of triphenylene. The stoichiometry of **2–4** was confirmed by elemental analysis as well as X-ray structural studies (vide infra). Compounds **2–4** are colorless but luminesce when irradiated with UV light.

Structures of 2–4. The crystal structures of **2–4** have been determined. The solid-state structure of these three compounds consists of extended binary stacks in which eclipsed molecules of **1** alternate with the aromatic substrate. In all three cases,

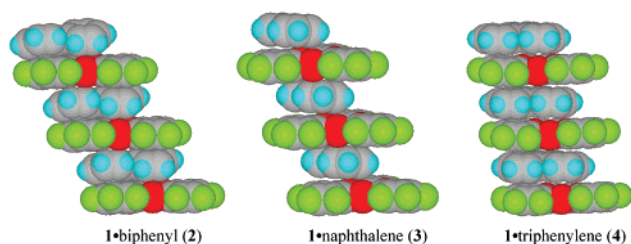
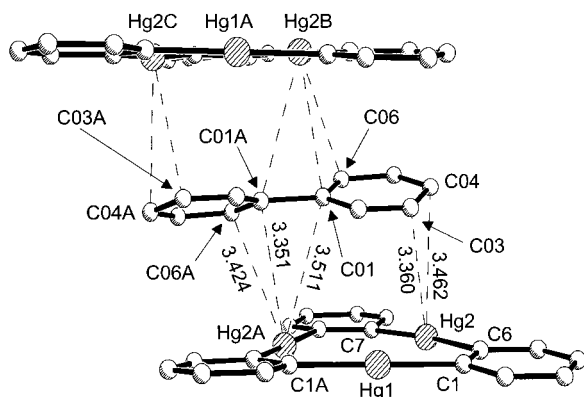
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Table 3. Intermolecular Distances (Å) in the Structures of 2–4^a

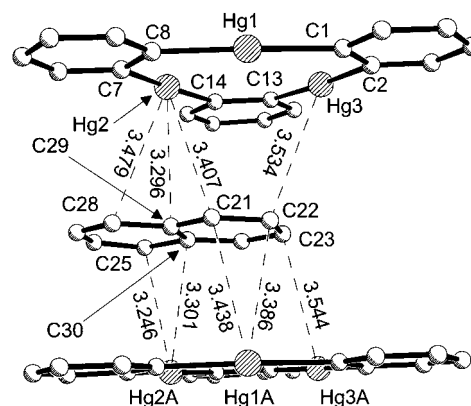
Compound 2			
Hg(2)···C(04)	3.462	Hg(2)···C(01) ^b	3.511
Hg(2)···C(03)	3.360	Hg(2)···C(01) ^c	3.351
		Hg(2)···C(06) ^c	3.424
Compound 3			
Hg(1)···C(21) ^d	3.438	Hg(2)···C(25) ^d	3.246
Hg(1)···C(22) ^d	3.386	Hg(2)···C(30) ^d	3.301
		Hg(3)···C(22)	3.534
		Hg(3)···C(23) ^d	3.544
		Hg(2)···C(21)	3.407
		Hg(3)···F(4) ^e	3.292
		Hg(2)···C(28)	3.478
		Hg(3)···F(10) ^f	3.012
		Hg(2)···C(29)	3.296
Compound 4			
Hg(2)···C(13)	3.511	Hg(2)···C(17) ^g	3.541
Hg(2)···C(14)	3.460	Hg(2)···C(18) ^g	3.465
Hg(1)···F(3) ^h	3.270		
Hg(1)···F(3C) ⁱ	3.270		

^a The symmetry operations used to generate the atoms of neighboring units are indicated in the following footnotes. ^b $-x, y, 0.5 - z$. ^c $x + 1, y, z$. ^d $x, y + 1, z$. ^e $-x + 0.5, y - 0.5, z + 1.5$. ^f $-x + 0.5, -y + 0.5, z + 0.5$. ^g $x - 1, y, z$. ^h $-x + 0.5, -y + 0.5, z - 0.5$. ⁱ $x - 0.5, -y + 0.5, -z + 2$.

**Figure 3.** Space filling models of the binary stacks observed in the structures of 2–4.**Figure 4.** Molecular structure of 2. Fluorine and hydrogen atoms are omitted for clarity. Short contacts and distances are shown. Selected intramolecular bond distances [Å] and angles [deg]. Hg(1)–C(1) 2.070(18), Hg(2)–C(6) 2.075(17), Hg(2)–C(7) 2.063(19), C(1A)–Hg(1)–C(1) 177.4(10), C(7)–Hg(2)–C(6) 174.0(8).

there are no unusual intramolecular bond distances and angles in the structure of the individual components.

Compound 2 crystallizes in the monoclinic space group $C2/c$ with one-half of a molecule of 1 and one-half of a molecule of biphenyl in the asymmetric unit (Table 1). The sandwiched biphenyl molecule is nonplanar and has a dihedral angle of 30.4°. With Hg···C_{biphenyl} distances ranging from 3.351 to 3.511 Å, the biphenyl molecule is weakly π -coordinated to four mercury centers of the neighboring molecules of 1 (Tables 1 and 3, Figures 3 and 4). The carbon atoms C(03) and C(04) engage in a η^2 -interaction with the mercury center Hg(2), while the C(01)–C(01A)–C(06A) portion of the biphenyl is involved

**Figure 5.** Molecular structure of 3. Fluorine and hydrogen atoms are omitted for clarity. Short contacts and distances are shown. Selected intramolecular bond distances [Å] and angles [deg]. Hg(1)–C(1) 2.053(12), Hg(1)–C(8) 2.060(12), Hg(2)–C(14) 2.100(12), Hg(2)–C(7) 2.078(12), Hg(3)–C(13) 2.062(12), Hg(3)–C(2) 2.089(13), C(1)–Hg(1)–C(8) 178.1(5), C(14)–Hg(2)–C(7) 174.6(5), C(13)–Hg(3)–C(2) 175.9(5).

in an η^3 -interaction with Hg(2A) (Table 3). The cohesion of the stacks is further cemented by symmetry-related interactions that involve C(03A)–C(04A) and Hg(2B) as well as C(01A)–C(01)–C(06) and Hg(2C).

Compound 3 crystallizes in the monoclinic space group $P2_1/n$ with one molecule of compound 1 and one molecule of naphthalene in the asymmetric unit (Tables 1 and 3, Figures 3 and 5). The stacks consist of alternating molecules of 1 and naphthalene. Inspection of the packing diagram reveals that the molecules of 1 and naphthalene are not strictly parallel and form an interplane angle of 3.9°. The sandwiched naphthalene molecule engages in a double η^2 -coordination involving C(21)–C(22) and Hg(1A) as well as C(25)–C(30) and Hg(2A). Short distances are also observed between the C(21)–C(29)–C(28) portion of the naphthalene molecule which is η^3 -coordinated to the mercury atom Hg(2). Further contacts involve C(22) and Hg(3) as well as C(23) and Hg(3A). The resulting Hg···C_{naphthalene} distances, ranging from 3.246 to 3.544 Å, are comparable to the Hg···C_{biphenyl} distances in compound 2. In compound 3, one mercury atom (Hg(3)) does not interact with the arene but forms contacts with fluorine atoms of other stacks. These distances are within the sum of the van der Waals radii ($r_{vdw}(F) = 1.30$ – 1.38 Å,²⁹ $r_{vdw}(Hg) = 1.73$ – 2.00 Å)^{28,30} and substantiate the presence of secondary interactions.

Compound 4 crystallizes in the orthorhombic space group $Pbcn$ with one-half of a molecule of 1 and one-half of a molecule of triphenylene in the asymmetric unit. The molecules are essentially planar and parallel to one another (Tables 1 and 3, Figures 3 and 6). The C(13)–C(14) as well as C(17A)–C(18A) portions of the triphenylene are η^2 -coordinated to Hg(2) and Hg(2A), respectively (3.460 > Hg···C_{triphenylene} > 3.541 Å). Symmetry-related interactions occur between C(13A)–C(14A) and Hg(2C) as well as between C(17)–C(18) and Hg(2B). Interestingly, at the difference of compound 2 and 3, arene–fluoroarene interactions occur in the structure of 4. These interactions involve a tetrafluorophenylene and a phenylene ring which result in a centroid distance of 3.605 Å. As in the case of 3, one of the mercury atoms (Hg(1)) does not interact with the arene but forms contacts with fluorine atoms of neighboring molecules.

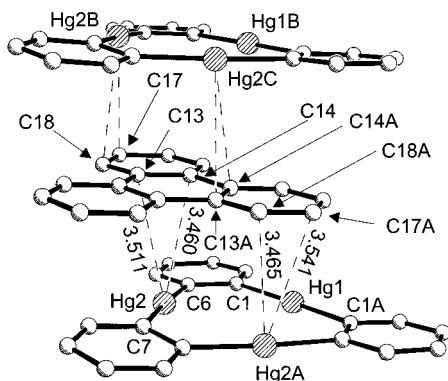


Figure 6. Molecular structure of **4**. Fluorine and hydrogen atoms are omitted for clarity. Short contacts and distances are shown. Selected bond distances [Å] and angles [deg]. Hg(1)–C(1) 2.070(8), Hg(2)–C(6) 2.071(7), Hg(2)–C(7) 2.069(7), C(1A)–Hg(1)–C(1) 175.9(5), C(7)–Hg(2)–C(6) 175.7(3).

While electrostatic forces likely contribute to the stability of these assemblies,³⁵ it is important to note that in all three cases, there are short contacts between the mercury centers of **1** and the aromatic molecules. These contacts range from 3.25 to 3.55 Å and are within the sum of the Waals radius of mercury ($r_{\text{vdw}}(\text{Hg}) = 1.73\text{--}2.00$ Å)^{28,30} and that usually accepted for carbon in aromatic systems ($r_{\text{vdw}}(\text{C}_{\text{aromatic}}) = 1.7$ Å).³⁶ They reflect the presence of secondary polyhaptο- π interactions occurring between the electron-rich aromatic molecules and the acidic mercury centers.^{23–25} Similar distances have been previously observed in **1**•benzene (3.408 and 3.457 Å).¹⁶ Despite the weakness of the individual interactions,²⁵ we note that each aromatic molecule establishes multiple links to neighboring mercury centers thus strengthening the cohesion of each stack. In the case of the triphenylene adduct **4**, an arene–fluoroarene interaction is observed. With a centroid distance of 3.605 Å, this interaction resembles that encountered in several purely organic arene–fluoroarene assemblies.^{37–40} Such interactions have been proposed to result, at least in part, from electrostatic interactions^{41,42} and have been observed in related complexes.^{11b,15c,43} In **2–4**, the coordinated aromatic derivatives do not appear to be affected by their participation in the stacks. While no lengthening of the C–C bond could be confirmed within the error of the crystallographic measurements, the Ph–Ph twist angle of 30.4° in the structure of the biphenyl molecule in **2** is between that observed for free biphenyl in the molten state (25°)⁴⁴ and in solution (32°).⁴⁵ As a final structural remark, we note the structural resemblance that exists between compounds

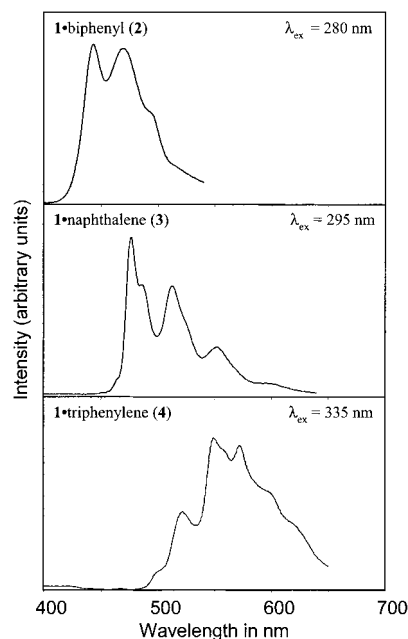


Figure 7. Excitation and emission spectra for solid **2**, **3**, and **4** recorded at room temperature.

2–4 and a series of gold-containing supramolecules reported by Balch⁴⁶ as well as Burini and Fackler.⁴⁷ These supramolecules consist of stacks in which trinuclear gold(I) complexes alternate with organic derivatives such as fluorenones, hexafluorobenzene, and TCNQ. At the difference of **2–4**, the trinuclear gold(I) complexes are electron-rich while the organic substrates are electron-poor. Compounds **2–4**, which contain electron-poor mercury centers and unsubstituted arenes, can therefore be regarded as the charge-reverse analogues of the gold assemblies.

Luminescence Studies on 2–4. Under a hand-held UV lamp, compounds **2–4** display luminescence in the visible region of the spectrum. The emission spectra of compounds **2–4** are shown in Figure 7. In all three cases, the selected excitation wavelength falls within the $S_0 \rightarrow S_1$ absorption band of the pure arene.^{48–51} For **2** and **3**, the resulting emission spectrum corresponds very closely to that expected for the $T_1 \rightarrow S_0$ phosphorescence of biphenyl⁵² and naphthalene,⁵³ respectively. These observations suggest the occurrence of a mercury heavy atom effect, which promotes intersystem spin crossing from the S_1 to the T_1 state of the aromatic derivative. Similar effects have

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been reported for aromatic substrates sequestered in Ti^+ exchanged zeolites.⁵³ In the case of **4**, we note that the emission appears at longer wavelengths than those typically observed for the room-temperature phosphorescence of triphenylene.⁵⁴ While the photophysics of arene–fluoroarene assemblies have not been unraveled, the presence of arene–fluoroarene interactions in the structure of **4** can be tentatively correlated to this red-shifted emission.

Summary

The results reported herein further document the affinity of **1** for aromatic substrates. While the biphenyl and naphthalene adducts **2** and **3** can be isolated upon concentration of the mother liquor, spontaneous precipitation occurs in the case of the largest arene, triphenylene. The structures of adducts **2–4** reveal the existence of stacks in which molecules of **1** and molecules of arenes alternate. In each stack, secondary π -interactions occur between the arene and the mercury centers of **1**, thus providing cohesion to the stacks. It is important to note that DFT calculations carried out on **1** show the existence of a positively charged electrostatic potential surface in the center of the macrocycle.³⁵ Hence, it is probable that electrostatic forces also play a role in the formation of the observed structures. Finally, compounds **1–4** show luminescence in the solid state. While more work is needed to clarify the origin of the photoluminescence in the case of **1** and **4**, the emission observed for **2** and **3** corresponds to the phosphorescence of the aromatic substrate. This observation indicates the occurrence of a heavy atom effect that promotes intersystem spin crossing from the S_1 to the T_1 state. Hence, compound **1** could be used as a luminescence-based sensor for arenes.

Experimental Section

General. Atlantic Microlab, Inc., Norcross, GA, performed the elemental analyses. All commercially available starting materials and solvents were purchased from Aldrich Chemical and used as provided. Compound **1** was prepared according to the published procedure.²⁶ The luminescence spectra were recorded with a SLM/AMINCO, Model 8100 spectrofluorometer equipped with a xenon lamp. Low-temperature measurements were made in a cryogenic device of local design. Collodion was used to attach the powder samples to the holder. The collodion was scanned for a baseline subtraction. Liquid nitrogen was used to obtain the 77 K measurements.

Crystallization of 1·Biphenyl (2). Compound **1** (0.26 g, 0.25 mmol)

was dissolved in CH_2Cl_2 (50 mL). In a separate vial, biphenyl (0.075 g, 0.52 mmol) was dissolved in CH_2Cl_2 (20 mL). The two solutions were mixed. Upon concentration by partial evaporation of the solvent, crystals of **2** formed in a 68% yield (0.20 g, 0.17 mmol). mp 290–293 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{10}\text{F}_{12}\text{Hg}_3$: C, 30.0; H, 0.8. Found: C, 29.76; H, 0.82.

Synthesis of 1·Naphthalene (3). Compound **1** (0.27 g, 0.26 mmol) was dissolved in CH_2Cl_2 (50 mL). In a separate vial, naphthalene (0.080 g, 0.62 mmol) was dissolved in CH_2Cl_2 (20 mL). The two solutions were mixed. Upon concentration by partial evaporation of the solvent, crystals of **3** formed in a 73% yield (0.22 g, 0.19 mmol). mp 305–307 °C. Anal. Calcd for $\text{C}_{28}\text{H}_8\text{F}_{12}\text{Hg}_3$: C, 28.63; H, 0.69. Found: C, 28.77; H, 0.64.

Synthesis of 1·Triphenylene (4). Compound **1** (0.24 g, 0.23 mmol) was dissolved in CH_2Cl_2 (50 mL). In a separate vial, triphenylene (0.11 g, 0.47 mmol) was dissolved in CH_2Cl_2 (20 mL). Upon mixing of the two solutions, a white precipitate formed. The precipitate was washed with a small amount of CH_2Cl_2 to afford pure **4** in a 67% yield (0.20 g, 0.15 mmol). Single crystals of **4** were obtained by allowing slow diffusion of a CH_2Cl_2 solution of **1** into a CH_2Cl_2 solution of triphenylene through an intermediate layer of pristine CH_2Cl_2 . mp 337 °C (sub.). Anal. Calcd for $\text{C}_{36}\text{H}_{12}\text{F}_{12}\text{Hg}_3$: C, 33.93; H, 0.95. Found: C, 33.82; H, 0.94.

Crystal Structure Determinations. X-ray data for **1**, **2**, **3**, and **4** were collected on a Bruker SMART-CCD diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Specimens of suitable size and quality were selected and glued onto a glass fiber with freshly prepared epoxy resin. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Further crystallographic details can be found in Table 1 and in the Supporting Information.

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Supporting Information Available: X-ray crystallographic data for **1–4** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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