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The First Hexanuclear Copper(I) Carboxylate: X-ray Crystal Structure and Reactivity in Solution and Gas-Phase Reactions

Yulia Sevryugina, Andrey Yu. Rogachev, and Marina A. Petrukhina*

Department of Chemistry, University at Albany, 1400 Washington Avenue,
Albany, New York 12222

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The carboxylate ligand-exchange reaction of copper(I) trifluoroacetate by 3,5-difluorobenzoate yielded a new product, $[Cu(O_2C(3,5\text{-}F)_2C_6H_3)]$ (**1**). Single crystals of **1** suitable for X-ray structural characterization were obtained by sublimation-deposition procedures at 230 °C. An X-ray diffraction study revealed a remarkable planar hexanuclear copper(I) core supported by bridging carboxylates, the first such structural type among other known copper(I) carboxylates. The Cu···Cu distances within the core range from 2.7064(8) to 2.8259(8) Å and fall into the category of cuprophillic interactions. The hexacopper unit remains intact upon gas-phase deposition with a planar polyarene, coronene ($C_{24}H_{12}$), to give $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ (**2**). Density functional theory calculations suggest the latter compound to be a cocrystallization product having electrostatic interactions between the hexacopper complex and coronene. However, cocrystallization affects the photophysical properties of **2**. While copper(I) 3,5-difluorobenzoate (**1**) exhibits photoluminescence at ca. 554 nm ($\lambda_{ex} = 350$ nm) in the solid state, compound **2** is nonluminescent at room temperature in the visible region. Gas-phase and solution reactions of **1** with alkyne ligands, diphenylacetylene ($C_{14}H_{10}$) and 1,4-bis(*p*-tolylethynyl)benzene ($C_{24}H_{18}$), result in the rupture of the $[Cu_6]$ core to afford dinuclear organometallic copper(I) complexes. The latter have a dimetal core cis-bridged by two carboxylate groups with acetylene ligands η^2-coordinated to each copper(I) center.

Introduction

The controlled formation of small clusters and polynuclear copper(I) complexes is of great importance for supramolecular assembly,[1] optoelectronics,[2] catalysis,[3] and structural and chemical mimicking of active sites in metalloenzymes.[4] In particular, copper(I) carboxylate complexes attract special attention due to their rich catalytic[5] and photoluminescence properties.[6] Only a handful of copper(I) carboxylate complexes have been crystallographically characterized to date, all showing unique polynuclear core structures in the solid state. Copper(I) acetate[7] and 2,6-bis(trifluoromethyl)benzoate[8] exhibit one-dimensional polymeric structures based on dicopper units that are further linked by intermolecular copper−oxygen interactions (Scheme 1a). Copper(I) pivalate is an infinite double-helical chain held together by cuprophilicity (Scheme 1d).[9] In contrast, copper(I) benzoate[10] and trifluoroacetate[11] are composed of tetrameric molecules, in which four copper(I) centers are bridged by carboxylate groups alternately above

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* To whom correspondence should be addressed. E-mail: marina@albany.edu.

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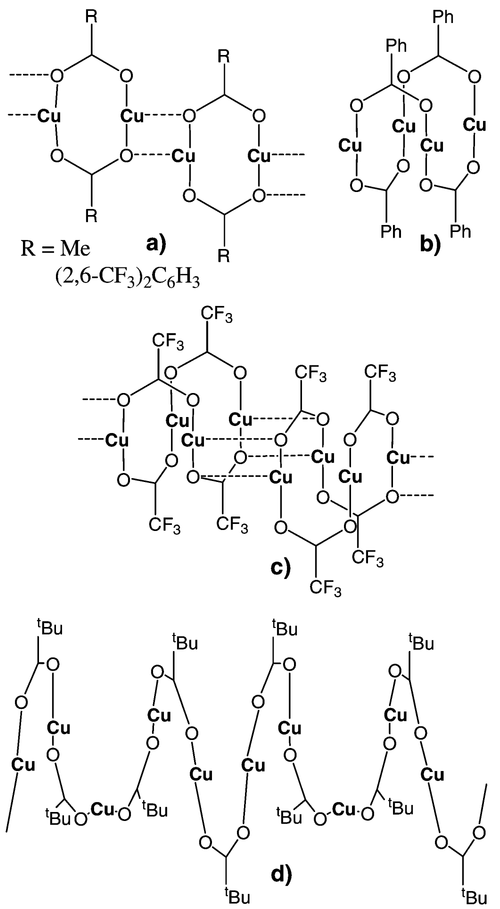
Scheme 1



and below the [Cu_4] plane. However, while the former has discrete tetracopper clusters in the solid state (Scheme 1b), in the latter, the tetranuclear units form a polymeric zigzag ribbon (Scheme 1c). Within this series of copper(I) carboxylates, the intermetallic Cu···Cu separations are the shortest in copper(I) acetate and 2,6-bis(trifluoromethyl)benzoate, in which the neighboring copper(I) centers are doubly bridged by carboxylate ligands. In the rest of the copper(I) carboxylates, the adjacent copper atoms are linked by a single bridge.

This structural diversity for the few copper(I) carboxylate complexes has prompted us to expand this family and pursue the crystallographic characterization of the newly prepared copper(I) 3,5-difluorobenzoate, [$Cu(O_2C(3,5\text{-}F)_2C_6H_3)$]. In addition to the crystal structure, we report the synthesis, photophysical properties, and gas-phase and solution reactivity of this complex toward π-donor arene and alkyne ligands. To get some insights on bonding in a complex polynuclear copper(I)−polyaromatic system, we also look into the nature of copper(I) binding to an aromatic hydrocarbon using density functional theory (DFT) calculations.

Results and Discussion

Synthesis of [$Cu(O_2C(3,5\text{-}F)_2C_6H_3)$] (1). The preparation of the title copper(I) carboxylate was performed by a modification of the common ligand-exchange procedure developed earlier by Edwards and Richards.[12] In contrast, we have started with the [$Cu_4(O_2CCF_3)_4$] complex[11] and substituted the trifluoroacetate groups by 3,5-difluorobenzoate ligands. This resulted in the isolation of a new product, **1**, in quantitative yield. The crude powder was washed with several portions of benzene to remove traces of unreacted acid and then re-sublimed at 90−110 °C to provide a high-purity crystalline product, which is volatile in the temperature range from 210 to 250 °C. At higher temperatures, decomposition was observed with the appearance of a red powder in the “hot” part of the sublimation tube. Single crystals of **1** suitable for X-ray structure determination were obtained by sublimation-deposition procedures carried out at 230 °C.

The colorless dichroic block-shaped crystals of **1** are stable in air at room temperature. They have very limited solubility in benzene and dichloromethane, but in coordinating solvents, such as acetonitrile or tetrahydrofuran (THF), they readily dissolve. However, this process is accompanied by the formation of a yellow precipitate and change of the solution color to blue within a few minutes. While we have not attempted to analyze the yellow precipitate, crystals of the bis-adduct of copper(II) 3,5-difluorobenzoate, [$Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_4(THF)_2$], have been obtained from the above THF solution in good yield and crystallographically characterized.[13] When these crystals of copper(II) complex were dissolved in acetonitrile, the UV−vis spectrum showed peaks at the same positions (ca. 227 and 279 nm) as those obtained by dissolving the title copper(I) complex **1** in acetonitrile. This shows spectroscopically that the blue color of the solution may be associated with the formation of Cu(II) (Supporting Information, Figure S1). The disproportionation of copper(I) complexes to metallic copper and copper(II) derivatives both in solution and in the solid state is a commonly reported main decomposition pathway.[14] Although the observed disproportionation limited the solution studies of the title complex, crystals of **1** have been characterized by X-ray diffraction, elemental analysis, and IR and UV−vis spectroscopy.

The composition of the crude powder as well as that of the single-crystalline material **1** was confirmed by elemental analysis to correspond to the general formula [$Cu(O_2CF_2C_6H_3)$]. In an attempt to correlate the X-ray powder diffraction (XRPD) spectrum of a purified crude powder, prior to its sublimation, with the calculated pattern for the single-crystalline sample, we discovered their essential difference (Supporting Information, Figure S2). The XRPD data indicate that the structure of the single-crystalline product obtained by sublimation-deposition may differ from that of the crude powder isolated initially from the carboxylate-exchange reaction. However, sublimation-deposition

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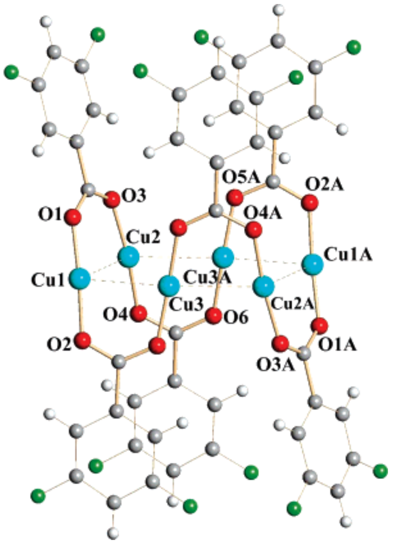

Figure 1. Molecular structure of **1** showing the Cu and O atoms numbering scheme. Color key: Cu, blue; O, red; F, green; C, gray; H, light gray. This color scheme is used in all figures.

reactions yield crystals of **1** in high (ca. 80%) yield, and only these crystals have been further used in all reactivity tests.

Solid-State Structure of 1. The molecular structure of **1** has been determined by single-crystal X-ray diffraction. Copper(I) 3,5-difluorobenzoate (**1**) crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$, which requires the molecule to reside on an inversion center. As shown in Figure 1, the molecule has a planar hexanuclear core comprised of six copper atoms bridged by six fluorinated benzoate ligands alternating above and below the plane. This structural type is unique in the copper(I) carboxylate series.

Intermetallic Cu···Cu distances within the [Cu_6] plane range from 2.7064(8) Å for Cu(1)···Cu(3) to 2.8259(8) Å for Cu(3)···Cu(2A) and are comparable to those in other monocarboxylato-bridged copper(I) complexes with trifluoroacetate and benzoate groups, but not with pivalate ligands (Table 1). The noticeably longer Cu···Cu contacts in the latter may stem from its essential structural difference from others. While three former complexes (Table 1) have discrete polynuclear Cu_n ($n = 6$ and 4) cores, copper(I) pivalate is an infinite Cu_∞-helical chain (Scheme 1d). The Cu···Cu distances in **1** are close to the sum of the van der Waals radii (r_{vdW}(Cu) = 1.40 Å)[15] and can be assigned to the category of metallophilic interactions similar to those in gold(I)[16] or mercury(II)[17] compounds. The interior angles within the [Cu_6] core range from 170.27(3)° for Cu(1)−Cu(3)−Cu(2A) to 123.48(3)° for Cu(1)−Cu(2)−Cu(3A) and to 66.15(2)° for Cu(2)−Cu(1)−Cu(3). This results in additional short Cu···Cu contacts between the nonbridged metal centers, Cu(3)···Cu(3A) of 3.1889(11) Å and Cu(2)···Cu(3) of 2.9621(8) Å. An averaged Cu−O_{carb} distance of 1.851(3) Å is similar to those in the previously reported copper(I) carboxylates.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in the Structures of Complexes [$Cu_n(O_2CR)_n$] (n = 4, R = CF_3, C_6H_5; n = 6, R = (3,5-F)$_2C_6H_3$ (**1**); $n = \infty$, R = $C(CH_3)_3$)

R (ref no.)	(3,5-F)$_2C_6H_3$ **1** (this work)	CF_3 (11)	C_6H_5[b] (10)	$C(CH_3)_3$ (9)
n	6	4	4	∞
Cu···$Cu_{carb-bridged}$	2.7064(8) 2.7215(8) 2.8259(8)	2.719(1)− 2.833(1)	2.709(6)− 2.770(5)	2.850(2)− 2.897(2)
Cu···$Cu_{non-bridged}$	2.9621(8) 3.1889(11)	2.975(1)	2.968(6) 3.180(6)	2.891(2)− 3.1254(18)
Cu−O_{carb}[a]	1.851(3)	1.870(5)	1.840(15)	1.850(7)
Cu···O		2.621(6)		
Cu−Cu−Cu	66.15(2) 123.48(3) 170.27(3)	64.62(4)[a] 115.37(4)	68.4(2) 111.7(2)	59.14(5)− 65.84(5)
O−Cu−O[a]	173.72(13)	172.9(6)	173.6(9)	

[a] Averaged. [b] Averaged for two crystallographically independent units.

The structure of **1** is particularly interesting and merits further discussion. To the best of our knowledge, this is the first instance of a hexanuclear core copper(I) carboxylate. Among other copper(I) compounds, examples are limited to [{$MeC(CH_2PPh_2)_3$}CoP_3]$_2$($CuBr$)$_6$·CH_2Cl_2, which has six copper atoms bridged by bromide ligands,[18] and the phosphido-bridged [$Cu_{12}(PPh)_6(PPh_3)_6$] compound. The latter is built of three interpenetrated planar [Cu_6] units that form a Cu_{12} cuboctahedron.[19] For other coinage metals, the [M_6] moiety (M = Ag^I, Au^I) is present in [Au_6Ag{μ-C_6H_2-($CHMe_2$)$_3$}$_6$]CF_3SO_3,[20] [Au_6(o-$CH_3C_6H_4CS_2$)$_6$],[21] and anionic cluster carbonyls [$Au_6(CO)_n$]$^-$ (n = 0−3).[22]

Due to the absence of an actual bond between the d^{10} metal centers, each copper center of the polynuclear [$Cu_n(O_2CR)_n$] complex is nominally linearly coordinated by two carboxylate oxygen atoms. The proximity of other metal ions, however, reflects the tendency of copper(I) to expand its coordination sphere, especially in the presence of electron-withdrawing ligands. This has been noticed earlier for copper(I) trifluoroacetate,[11] in which copper atoms demonstrate highly distorted trigonal-bipyramidal, tetragonally elongated octahedral, and seesaw-coordination geometries with coordination numbers ranging from four to six. Considering only the adjacent copper atoms in **1**, the Cu(1) and Cu(2) centers display a seesaw coordination, while the geometry around Cu(3) can be viewed as square-planar (Figure 1). However, an inclusion of the additional contacts between nonbridged copper atoms mentioned earlier would make the Cu(2) and Cu(3) atoms become five- and six-coordinate, respectively.

Gas-Phase Reactivity of 1. The title hexanuclear copper(I) complex **1** is readily accessible by deposition from the vapor

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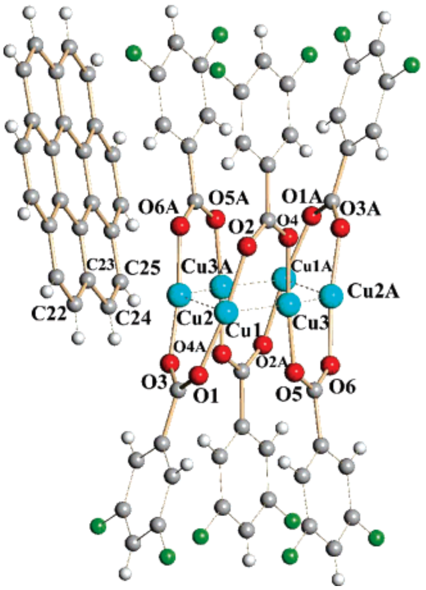

Figure 2. Molecular structure of **2** showing the Cu, O, and selected C atoms numbering scheme.

phase at 210−250 °C. Its very low solubility and instability in solvents limited solution studies, but its volatility allowed us to test the reactivity toward a planar polyaromatic hydrocarbon, coronene, using the gas-phase sublimation-deposition conditions. Deposition of **1** with coronene ($C_{24}H_{12}$) at 248 °C has resulted in the formation of a new product of the $[Cu_6]/C_{24}H_{12} = 1{:}1$ stoichiometry in the single-crystalline form. Its crystal structure was determined to confirm that the hexanuclear units remain intact in the gas phase and can be co-deposited with a polyarene in the solid state to afford $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ (**2**) (Figure 2).

A comparison of the $[Cu_6]$ cores in **2** and the parent complex **1** shows a close similarity with small variations in copper−copper distances and angles (Figure 3). Likewise, a comparison of the geometrical parameters of the coronene ligand in **2** with the corresponding bond lengths and angles in the uncoordinated molecule[23] shows that the two are essentially similar (Table 2).

The significant difference between **1** and **2** is found in their solid-state structures. In contrast to **1** having isolated hexacopper complexes, the $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$ units in **2** exhibit intermolecular Cu···O interactions with neighboring units (Figure 4). The latter contacts of 2.5805(16) Å for Cu(1)···O(2A) in **2** are significantly longer than those in copper(I) acetate (2.310(7) Å)[7] but shorter than those in copper(I) trifluoroacetate (2.621(6) Å).[11] For comparison, the closest intermolecular Cu···O contacts in **1** exceed 4 Å.

The coronene ligand approaches the copper hexamer at the Cu(2)−Cu(3A) side with Cu···C contacts of 2.919(3), 3.211(3), 3.127(3), and 3.259(3) Å to the C(22), C(23), C(24), and C(25) atoms, respectively (Figure 2). The Cu···C separations exceed 3.3 Å for the rest of the carbon atoms.

Although π complexes of copper(I) are common intermediates in catalytic transformations,[24] the only other structurally characterized copper(I) carboxylate complex with an aromatic ligand is the benzene adduct, $[Cu_4(O_2CCF_3)_4]\text{-}(C_6H_6)_2$.[25] It shows the range of Cu···C distances within 2.7−3.0 Å. However, due to large thermal motion of the aromatic rings, the discussion of benzene coordination in the latter compound was not possible. Several copper(I) cation−π-arene complexes such as $(C_6H_6)CuAlCl_4$,[26] $(CuOSO_2CF_3)_2\cdot(C_6H_6)$,[27] $Cu(GaCl_4)\cdot((p\text{-}C_6H_4(CH_2)_3)_2)$,[28] $((C_6H_6)CuCl_3)_2Zr$,[29] and $((C_6H_6)_2Cu)_2Zr_2Cl_{10}\cdot(C_6H_6)$[30] have been structurally characterized to show Cu···C contacts in the 2.09−2.92 Å range and suggest an η^2 binding. Regarding other group 11 metals, bonding Au···C interactions generally are 2.96−3.25 Å[31] (Σr_{vdW} (Au, C) = 3.36 Å), while bonding Ag···C contacts are 2.47−2.76 Å[32] (Σr_{vdW} (Ag, C) = 3.42 Å).[15] In the polymeric silver(I) complex with coronene, $[Ag_4(C_{24}H_{12})_3\text{-}(ClO_4)_4]$,[33] the Ag···C contacts are short and range from 2.402(4) to 2.517(4) Å. In addition, coronene adopts a bent conformation, which indicates strong interactions between Ag^+ cations and the coordinated coronene ligand.

An analysis of the copper−carbon distances in **2** shows them lying barely around the sum of the van der Waals radii for Cu and C (Σr_{vdW} (Cu, C) = 3.10 Å),[15] which raises the question of whether **2** should be considered as a coordination compound.

DFT Description of Bonding in 2. We attempted to address the question of interaction between the hydrocarbon and metal complex by using the DFT computational method.[34] Our study is the first example of the theoretical modeling of a polynuclear copper(I)−polycyclic arene system. Moreover, modeling of the hexanuclear copper(I) complex was also

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[34] Molecular geometry optimizations were performed at the DFT level by using the hybrid Perdew−Burke−Ernzerhof parameters free exchange-correlation functional (PBE0) as implemented in the PC *GAMESS* version of the *GAMESS-US* program package. The Hay and Wadt effective core potential (ECP) and the LANL2DZ basis set were used for Cu atoms, and the 3-21G(d) basis sets were employed for all other atoms. When optimizations were achieved, single-point calculations along with NBO analysis were performed using the same ECP and the same basis set for Cu atoms and the extended 6-311G(d,p) basis sets for all other atoms (see the Supporting Information for details).

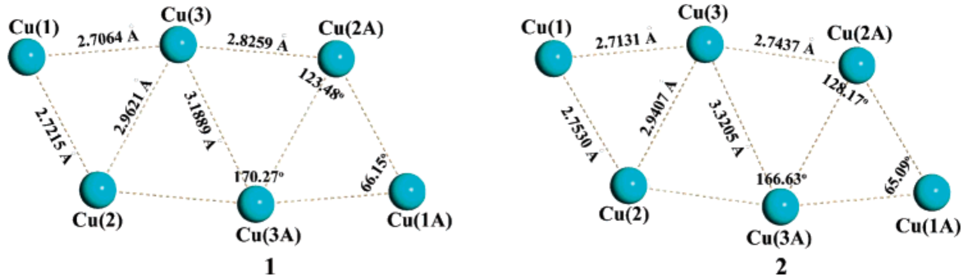
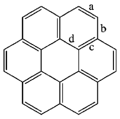


Figure 3. [Cu_6] core structures in **1** and **2**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the Structures of $C_{24}H_{12}$ and Complexes **1** and **2**

	1	2	$C_{24}H_{12}$ [23]
$Cu\cdots Cu_{carb-bridged}$	2.7064(8)	2.7131(4)	
	2.7215(8)	2.7437(4)	
	2.8259(8)	2.7530(4)	
$Cu\cdots Cu_{non-bridged}$	2.9621(8)	2.9407(5)	
	3.1889(11)	3.3205(7)	
	4.8863(10)	4.6179(7)	
$Cu-O_{carb}$[a]	1.851(3)	1.8571(15)	
$Cu\cdots O$		2.5805(16)	
$Cu\cdots C$		2.919(3)	
		3.211(3)	
		3.127(3)	
		3.259(3)	
$Cu-Cu-Cu$	66.15(2)	65.088(12)	
	170.27(3)	166.630(16)	
	123.48(3)	128.167(15)	
$O-Cu-O$[a]	173.72(13)	173.47(8)	
$C-C_{coronene(a)}$[a]		1.373(5)	1.357(3)
$C-C_{coronene(b)}$[a]		1.404(4)	1.421(3)
$C-C_{coronene(c)}$[a]		1.425(4)	1.416(2)
$C-C_{coronene(d)}$[a]		1.414(4)	1.424(2)
$C-C-C_{coronene(a-b)}$[a]		121.5(3)	121.5(2)
$C-C-C_{coronene(b-c)}$[a]		118.5(3)	118.5(2)
$C-C-C_{coronene(c-d)}$[a]		120.0(2)	120.0(2)
$C-C-C_{coronene(b-b)}$[a]		123.0(3)	122.9(2)
$C-C-C_{coronene(d-d)}$[a]		120.0(2)	120.0(2)

[a] Averaged.

carried out for the first time. Prior theoretical works were devoted to tri-[35] and tetranuclear copper(I) clusters[36] only, and the previously found trends[37] may not be applicable to larger systems.

Full geometry optimizations of the molecular structures of **2** and the parent complex **1** were performed at the DFT level of theory using the hybrid Perdew−Burke−Ernzerhof parameters free exchange-correlation functional (PBE0),[38] which is known to better describe coordination compounds of transition metals with weak bonding[39] and polyaromatic systems.[40] Recently, the PBE0 functional was successfully applied for the modeling of a tetranuclear copper cluster.[36b] We also found that the optimized geometries obtained with the use of PBE0 for **1** and **2** reproduce the experimental X-ray structures very closely (Supporting Information, Tables S3 and S4).

A high value of bonding energy for the [$Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ unit, namely, 33.89 kcal/mol, has been calculated. It is comparable to the value of 48.7 kcal/mol calculated for the system comprised of the naked Cu^+ cation and benzene.[41] In contrast, the bonding energies of electrophilic diruthenium(I,I) complexes with a polyarene were found to be only 9.0−11.5 kcal/mol.[42] A detailed analysis of electronic structures in terms of natural bond orbitals (NBO) shows that the bonding between the hexanuclear copper(I) core and coronene in **2** has a strong electrostatic nature. The donor−acceptor interactions in **2** do not exceed 1.00 kcal/mol, indicating a lack of any significant covalent contribution. However, in contrast to the parent [$Cu_6(O_2C\text{-}(3,5\text{-}F)_2C_6H_3)_6$] molecule, which does not display any dipole moment due to symmetry reasons, a noticeable polarization of both the [Cu_6] core and coronene has been found upon their interaction. This fact is clearly illustrated by the charge distribution in the [$Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]/(C_{24}H_{12}) = 1:1$ unit (Supporting Information, Table S5). The positive charges of copper(I) centers in the [Cu_6] core as well as negative charges of carbon atoms in coronene are larger in [$Cu_6(O_2C\text{-}(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$, as compared to free hexacopper molecule and free coronene, generating a dipole moment of 4.36 D in the coronene adduct (Figure 5). Thus, the bonding between the hexanuclear copper(I) cluster and coronene can be best ascribed to an ion-induced dipole interaction.

This bonding description in **2** is in good agreement with recent works,[41,43] where interactions between the Cu^+ cation and benzene were shown to have a similar nature. In accord

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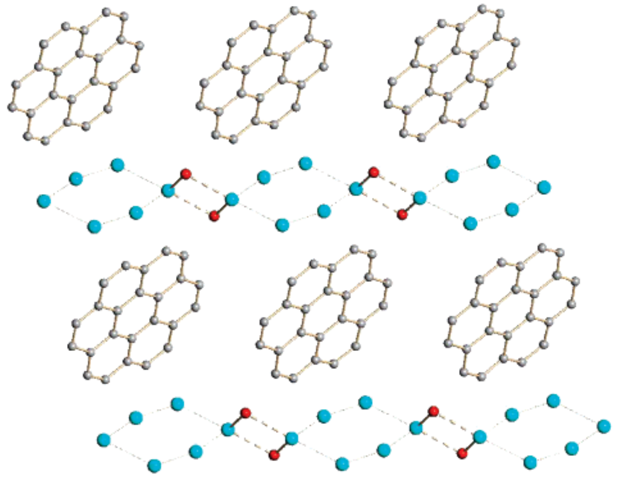

Figure 4. Fragment of the *ab* layer in **2**. The carboxylate groups and H atoms are omitted for clarity. Only the O atoms involved in axial interactions are shown (red).

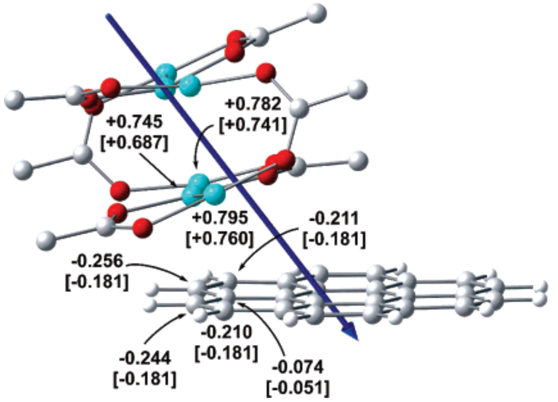

Figure 5. Direction of the dipole moment vector in the $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ adduct (blue arrow) along with selected charges given in comparison to $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$ and $C_{24}H_{12}$ (in square brackets).

with the report of Koch et al.,[43] the nature of interactions between the copper(I) cation and an aromatic system is mainly electrostatic. Moreover, it was shown that η^1, η^2, η^3, and η^6 coordination modes are degenerate, indicating no specific preferences in the coordination of an arene to Cu(I).

A detailed analysis of frontier molecular orbitals for $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$ and $C_{24}H_{12}$ in **2** revealed no symmetry match between them (Supporting Information, Table S7). The energy gap of 6.67 eV between suitable molecular orbitals of the $[Cu_6]$ core and coronene results in the absence of any orbital interactions in the $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ adduct, which makes any consideration of bonding and hapticity for such a system inadequate.

Photoluminescence. Copper(I) carboxylates are known to exhibit rich photoluminescence properties and therefore are of interest as potential optoelectronic materials.[44] The new copper(I) 3,5-difluorobenzoate complex (**1**) exhibits bright green photoluminescence (PL) upon exposure to UV radiation in the solid state. The PL measurements ($\lambda_{ex} = 350$ nm) carried out at room temperature in the range of 250−750 nm using a crystalline sample of **1** determined λ_{max} at ca. 554 nm (Figure 6). It should be mentioned here that 3,5-difluorobenzoic acid emits at 377 nm upon UV radiation at $\lambda_{ex} = 290$ nm, while showing no emission upon excitation at $\lambda_{ex} = 350$ nm. For comparison, the emission maxima were found in the broad range of 535−660 nm at room temperature for copper(I) formate, acetate, propionate, butyrate, valerate, hexanoate, and heptanoate,[6] but those were not correlated with the structures of the complexes. The emission maxima for the structurally similar copper(I) 2,6-bis(trifluoromethyl)benzoate[8] and acetate (Scheme 1a) were measured at 558 and 560 nm at room temperature, respectively.

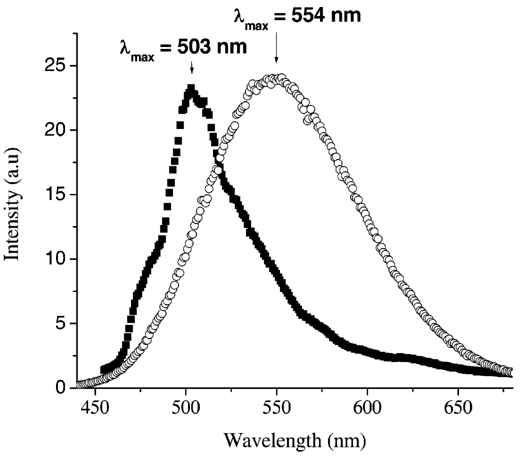

Figure 6. Photoluminescence spectra ($\lambda_{ex} = 350$ nm) of solid samples of **1** (○) and $C_{24}H_{12}$ (■). Compound **2** is nonluminescent.

In contrast to the parent copper(I) 3,5-difluorobenzoate complex **1** and coronene itself, compound **2** is nonluminescent at room temperature in the visible region. Thus, the incorporation of coronene into the copper(I) carboxylate lattice showed a dramatic influence on the photophysical properties of the resultant system.

To our knowledge, no systematic studies discussing the origin of photoluminescence and its dependence on the structural type for copper(I) carboxylate complexes have been done, thus thwarting the rationalization of the above effect for the coronene adduct. A full investigation of the luminescent properties of a series of copper(I) carboxylates is currently underway, and that should shed some light on their photophysical behavior.

Reactivity of 1 Toward Alkynes. To further study the properties of the hexanuclear core complex **1**, its reactivity toward selected alkyne ligands has been tested. To date, only a few copper(I) carboxylate complexes with alkyne ligands have been reported, including $[Cu_2(O_2CC_6H_5)_2(C_{14}H_{10})_2]$,[45] $[Cu_4(O_2CCH_3)_4(C_8H_{18}Si_2)_2]$,[46] and $[Cu_4(O_2CCF_3)_4(C_6H_{10})_2]$.[47]

As a result of refluxing $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$ in benzene with an excess of diphenylacetylene ($C_{14}H_{10}$,

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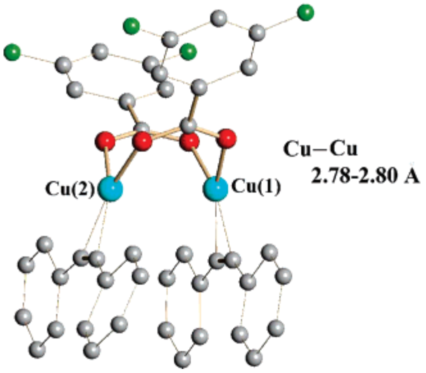
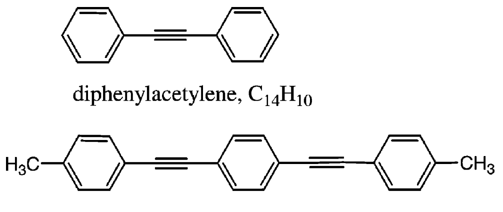


Figure 7. Molecular structure of the $[Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{14}H_{10})_2]$ unit in **3** and **4** showing the Cu atoms numbering scheme. The H atoms are omitted for clarity.

Scheme 2



diphenylacetylene, $C_{14}H_{10}$

1,4-bis(*p*-tolylethynyl)benzene, $C_{24}H_{18}$

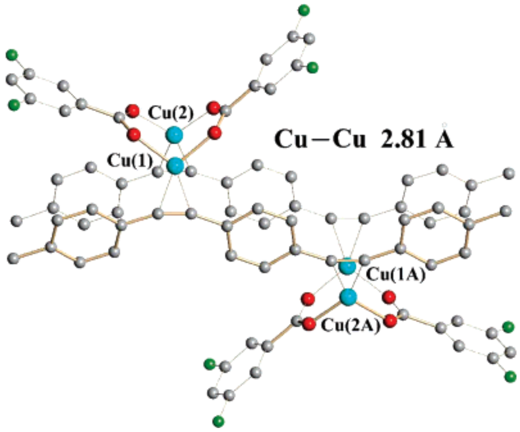


Figure 8. Molecular structure of **5** showing the Cu atoms numbering scheme. The H atoms are omitted for clarity.

Scheme 2), two new crystalline compounds **3** and **4**, having a general formula $[Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{14}H_{10})_2]\cdot$solv, were isolated in crystalline form. Gas-phase reactions with diphenylacetylene were not successful due to a large difference in sublimation temperatures of the reactants and, possibly, due to the vital role of spacers, such as toluene or benzene molecules, in the crystallization of products. Another interesting example of the transformation of the $[Cu_6]$ core is provided by the gas-phase sublimation-deposition reaction of **1** with 1,4-bis(*p*-tolylethynyl)benzene ($C_{24}H_{18}$) (Scheme 2), which resulted in the formation of a new complex **5**, $[Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{24}H_{18})]_2$. In contrast to the hexanuclear copper(I) adduct with coronene, in all new alkyne complexes **3**−**5** we observe the fragmentation of the $[Cu_6]$ core. Complexes **3**−**5** have the dinuclear copper(I) core, regardless whether they were obtained from gas-phase or solution reactions.

The dicopper(I,I) units in **3**−**5** are cis-bridged by two 3,5-difluorobenzoates. In addition, each copper(I) center is involved in an η^2 interaction with the triple bond of an alkyne ligand (Figure 7). The structures of **3** and **4** are similar to that of the previously reported $[Cu_2(O_2CC_6H_5)_2(C_{14}H_{10})_2]$[45] (Supporting Information, Table S1). All three complexes consist of discrete neutral molecules $[Cu_2(O_2CR)_2(C_{14}H_{10})_2]$, in which each copper(I) center coordinates one diphenylacetylene molecule through two alkyne C atoms at averaged distances 1.959(4) and 1.965(5) Å in **3** and **4**, respectively. The composition of complex **5**, however, can be represented as $[Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{24}H_{18})]_2$. Since the 1,4-bis(*p*-tolylethynyl)benzene ligand incorporates two C≡C bonds, each is coordinated to a metal center of two separate copper dimers at an average distance of 1.957(3) Å (Figure 8). Two such dicopper units align two $C_{24}H_{18}$ ligands nearly coplanar with distances between the terminal benzene rings of 3.87 Å and distances between the central ones of 3.93 Å (see the Supporting Information for additional details on the solid-state packing of **3**−**5**). The Cu−C bond distances for **3**−**5** are in the same range as that generally observed for other copper(I)−π-alkyne complexes (1.95−2.01 Å).

A comparison of the geometrical parameters of complexes **3**−**5** reveals an elongation of the copper−copper distances, falling in the 2.7829(8)−2.8149(6) Å range, as compared to those in the parent compound **1** (Tables 1 and Supporting Information, Figure S1). Notably, the presence of innocent solvents, such as benzene or toluene, in the crystal lattices of **3** and **4**, respectively, affects the packing of otherwise similar complexes, which is seen in slightly different Cu···Cu separations within the dimers (2.8033(6) Å in **3** vs 2.7829(8) Å in **4**).

The impact of metal coordination on the length of a carbon−carbon triple bond is worth mentioning. The Cu−C contacts in **3**−**5** are short (average distance 1.960(4) Å) as compared with those in the aforementioned copper(I)−π-arene compounds. As a consequence, the coordinated carbon−carbon bond in **5** is noticeably elongated (1.237(5) Å) as compared with free 1,4-bis(*p*-tolylethynyl)benzene (1.1992(15) Å),[48] indicating that the triple-bond order is reduced as a result of strong interaction with the metal moiety. Due to a variety of bond lengths reported for the carbon−carbon triple bond of free diphenylacetylene (1.192−1.226 Å),[49] we cannot make a similar comparison for complexes **3** and **4**. However, the evaluation of the C−C≡C angles in compounds **3**−**5** and uncoordinated acetylenes supports the tenet of strong π bonding between the copper(I) centers and the C≡C groups (157.4(4)° and 158.8(5)° in **3** and **4** vs 178.0(2)° in free $C_{14}H_{10}$;[49d] 158.3(3)° in **5** vs 179.43(13)° in free $C_{24}H_{18}$).[48]

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Table 3. Crystallographic Data and Structural Refinement Parameters for **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$C_{42}H_{18}Cu_6F_{12}O_{12}$	$C_{66}H_{30}Cu_6F_{12}O_{12}$	$C_{48}H_{32}Cu_2F_4O_4$	$C_{49}H_{34}Cu_2F_4O_4$	$C_{76}H_{48}Cu_4F_8O_8$
fw	1323.80	1624.14	875.82	889.84	1495.30
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	9.4517(8)	9.5577(5)	13.6060(9)	13.4866(10)	7.1445(4)
b (Å)	9.7078(9)	11.9244(6)	18.9596(13)	16.5619(12)	24.6212(12)
c (Å)	11.9872(10)	12.9601(7)	15.3574(11)	18.4314(14)	17.5605(9)
α (deg)	87.4160(10)	81.5120(10)			
β (deg)	70.4870(10)	76.6640(10)	99.9570(10)	98.7990(10)	95.0310(10)
γ (deg)	83.5180(10)	78.8140(10)			
V (Å^3)	1030.06(16)	1401.72(13)	3902.0(5)	4068.5(5)	3077.1(3)
Z	1	1	4	4	2
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
d_{calc} (g·cm^{-3})	2.134	1.924	1.491	1.453	1.614
μ (mm^{-1})	3.163	2.345	1.155	1.109	1.449
θ_{max} (deg)	28.22	28.27	28.27	25.00	28.28
unique data	4648	6336	9139	7152	7254
observed data [$I > 2\sigma(I)$]	3388	5229	5475	4479	5279
params	325	493	517	522	507
GOF^a on F^2	1.027	1.033	1.015	1.013	1.047
R1^b, wR2^c [$I > 2\sigma(I)$]	0.0465, 0.1008	0.0332, 0.0803	0.0533, 0.1196	0.0580, 0.1216	0.0539, 0.1109
R1^b, wR2^c (all data)	0.0701, 0.1091	0.0432, 0.0852	0.1066, 0.1395	0.1059, 0.1425	0.0817, 0.1217
$\Delta\rho_{max,min}$ (e·A^{-3})	0.499, −0.439	0.365, −0.301	0.697, −0.388	0.536, −0.431	0.693, −0.393

[a] $GOF = [\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

The copper(I)−alkyne complexes **3**−**5** showed no luminescence in the visible region at room temperature upon UV−vis radiation. To further characterize complexes **3**−**5**, we studied their ^{13}C NMR spectra in chloroform solution. The general observation was that the ^{13}C NMR resonances of π-coordinated ligands in **3**−**5** display no change in chemical shifts with respect to those of free $C_{14}H_{10}$ and $C_{28}H_{14}$, most probably suggesting the dissociation of ligands even in noncoordinating chloroform. However, when recording the solid-state IR spectra, we found that $\nu_{C\equiv C}$ absorptions for complexes **3**−**5** are shifted to lower wavenumbers ($\nu_{C\equiv C}$ = 1983 (**3**), 1982 (**4**), 1981 (**5**) cm^{-1}) as compared with the uncoordinated ligands $C_{14}H_{10}$ ($\nu_{C\equiv C}$ = 2100−2300 cm^{-1})[50] and $C_{24}H_{18}$ ($\nu_{C\equiv C}$ = 2211 cm^{-1}).[51] This is generally observed for copper(I) η^2-coordinated alkynes[52] and indicates the weakening of the C≡C bond, which is consistent with our solid-state structural observations.

The coordination geometry at each Cu center in **3**−**5** is considered to be nearly trigonal planar with the inclusion of two carboxylate oxygens and a triple C≡C bond. It is important that despite the bifunctionality offered by two ligands (alkyne and arene functions),[53] diphenylacetylene and 1,4-bis(*p*-tolylethynyl)benzene coordinate to copper(I) exclusively by their alkyne parts. The Cu−C interactions in alkyne complexes are considerably stronger than those in copper(I)−arene systems, which certainly affects the nuclearity of the resulting Cu-based units.

Summary. The novel copper(I) complex, $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$ (**1**), having a discrete planar $[Cu_6]$ core, was prepared in good yield and high purity. This is the first example of the hexanuclear structure among the copper(I) carboxylate family. Importantly, the $[Cu_6]$ unit remains intact upon sublimation with polycyclic aromatic coronene to form $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$ (**2**). Detailed structural and DFT analyses suggest that **2** is a product of cocrystallization. First, this is confirmed empirically by the finding of long intermolecular Cu···C distances, all exceeding the sum of the van der Waals radii for copper and carbon. Second, DFT calculations reveal the bonding in **2** to be an ion-induced dipole interaction without any covalent contribution. Interestingly, although no significant structural changes are observed in the hydrocarbon or metal moieties in **2**, its photoluminescence is found to be highly affected by cocrystallization. In contrast to the parent copper(I) 3,5-difluorobenzoate complex (**1**) which shows photoluminescence at 554 nm and coronene, which emits at 503 nm, compound **2** is nonluminescent at room temperature in the visible region. In addition, the reactivity of the hexacopper core in **1** toward alkyne ligands has been tested to confirm its fragmentation to dinuclear copper(I) complexes.

Experimental Section

Materials and Methods. All manipulations were performed under a dinitrogen atmosphere, employing either drybox or standard Schlenk techniques. Sublimation-deposition procedures were carried out in small Pyrex glass ampules of 1.1 cm o.d. and of varied (5−8 cm) length. The ampules equipped with a vacuum adapter were loaded with starting materials in a drybox. They were evacuated to ca. 10^{-2} Torr and sealed under vacuum. The ampules were then placed in electric furnaces having a ca. 5 °C temperature gradient along the length of the tube. The starting material $[Cu_4(O_2CCF_3)_4]$ was synthesized following a reported procedure.[11] Com-

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mercially available coronene ($C_{24}H_{12}$), diphenylacetylene ($C_{14}H_{10}$), and anhydrous benzene and toluene were used as received. 1,4-Bis(*p*-tolylethynyl)benzene ($C_{24}H_{18}$) was prepared by the known method.[51]

Physical Measurements. Elemental analyses were performed by Guelph Chemical Laboratories, Ltd., Canada. The electronic spectra were measured at room temperature on a Perkin-Elmer Lambda 35 UV−vis spectrometer equipped with an integrating sphere for diffuse-reflectance spectroscopy. The NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz for protons, 282 MHz for fluorine, and 75 MHz for carbon. Chemical shifts (δ, ppm) for ^{19}F were referenced to $CFCl_3$, and chemical shifts for ^{13}C and ^{1}H were referenced to $SiMe_4$. The infrared spectra were measured using KBr pellets or Nujol mulls on a Nicolet Magna 550 FTIR spectrometer. The photoluminescence spectra were collected on a Varian Cary Eclipse spectrophotometer, in which the PMT detector was positioned 90° to the incident beam. Default settings (slit widths of 5 nm and integration time of 0.5 s) were applied. The crystalline sample was placed in a Varian Cary Submicro Fluorometer cell, which was mounted in a standard single cell holder.

Preparation of [Cu($O_2C(3,5\text{-}F)_2C_6H_3$)] (1). [$Cu_4(O_2CCF_3)_4$] (0.874 g, 1.23 mmol) and $(3,5\text{-}F)_2C_6H_3COOH$ (0.975 g, 6.17 mmol) were dissolved in 50 mL of benzene. The mixture was then refluxed overnight to yield a light green solution. The volume of the solution was reduced under vacuum to about 2 mL to yield a precipitate. After the remaining solution was decanted, the solid was washed with benzene (3 × 7 mL) and then heated at 90−100 °C overnight under reduced pressure to remove unreacted acid. These sublimation-separation procedures were repeated 2−3 times to finally give a light blue powder of the title complex. Yield: 0.708 g (65%). Anal. Calcd for $C_7H_3F_2O_2Cu$ (crude powder): C, 38.10; H, 1.36; O, 14.51; F, 17.23; Cu, 28.80. Found: C, 38.43; H, 1.77; O, 14.10; F, 16.62; Cu, 28.71. Colorless dichroic crystals of **1** were obtained within 1−3 days by sublimation under vacuum at 210−250 °C (ca. 10^{-2} Torr). IR (KBr, cm^{-1}): 3095 m, 1556 s, 1472 m, 1441 m, 1399 s, 1307 m, 1211 w, 1122 s, 988 s, 962 m, 892 m, 860 m, 770 s, 660 m. IR (Nujol, cm^{-1}): 3093 w, 1561 s, 1474 m, 1436 sh, 1402 s, 1309 m, 1209 w, 1120 s, 987 s, 959 m, 891 m, 860 m, 769 s. PL (250−750 nm, $\lambda_{ex} = 350$ nm, solid, λ_{max}, nm) 554. Anal. Calcd for $C_{42}H_{18}F_{12}O_{12}Cu_6$ (crystals): C, 38.10; H, 1.36; O, 14.51. Found: C, 38.39; H, 1.16; O, 13.92. UV−vis (250−800 nm, solid, λ_{max}, nm): 314, 439.

Preparation of [$Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6$]($C_{24}H_{12}$) (2). A mixture of crystals of **1** (0.065 g, 0.05 mmol) with coronene (0.008 g, 0.03 mmol) was sealed under vacuum in a small glass ampule that was placed in an electric tube furnace at 248 °C. In 1 day, yellow blocks of **2** were deposited in the "cold" end of the ampule together with volatile starting materials. Crystals were manually separated for characterization. Yield: 0.022 g (50%). IR (KBr, cm^{-1}): 3095 w, 1605 sh, 1557 s, 1535 s, 1475 m, 1439 m, 1414 s, 1399 s, 1308 m, 1124 m, 989 m, 961 w, 888 w, 871 w, 856 m, 774 m, 768 m, 666 w, 661 w, 528 w, 519 w, 491 w, 454 w. Anal. Calcd for $C_{66}H_{30}F_{12}O_{12}Cu_6$: C, 48.15; H, 1.69; O, 11.19. Found: C, 48.76; H, 1.85; O, 11.62.

Preparation of [$Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{14}H_{10})_2$]·$C_6H_6$ (3). A mixture of crystals of **1** (0.058 g, 0.04 mmol) with diphenylacetylene (0.070 g, 0.39 mmol) was dissolved in 4 mL of benzene in a round-bottom flask. The heterogeneous reaction mixture was vigorously stirred at room temperature for 1 h and then refluxed for 3 h. The resulting solution was filtered into another Schlenk tube and layered with hexanes. The tube was kept in a freezer at −60 °C. Pale pink crystals formed within several days. Yield: 0.069 g (60%). IR (KBr, cm^{-1}): 3082 w, 3073 w, 3055 w, 3030 w, 3000 w, 1617 m, 1607 sh, 1583 s, 1571 sh, 1489 m, 1481 w, 1469 m, 1443 m, 1435 m, 1395 s, 1324 w, 1301 m, 1179 w, 1117 s, 1071 w, 1026 w, 985 s, 953 m, 917 w, 900 w, 892 w, 881 w, 850 m, 781 s, 769 s, 763 s, 752 s, 757 s, 666 m, 632 m, 621 sh, 595 m, 530 w, 506 m, 469 m, 458 m. ^{1}H NMR ($CDCl_3$, 22 °C): δ 7.71 (m), 7.52 (br), 7.33 (br), 7.17 (s), 6.96 (br). ^{19}F NMR ($CDCl_3$, 22 °C): δ −109.70. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 22 °C): δ 131.56 (PhC), 130.88, 128.37 (PhC), 123.29 (PhC), 89.85 (C).

Preparation of [$Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{14}H_{10})_2$]·$C_6H_5CH_3$ (4). This compound was prepared similarly to **3** but using toluene. Yield: 55%. IR (KBr, cm^{-1}): 3082 w, 3066 w, 3030 w, 3017 w, 2914 w, 2858 w, 1662 w, 1615 s, 1585 s, 1569 sh, 1494 w, 1489 w, 1481 w, 1468 w, 1444 m, 1436 m, 1417 sh, 1392 s, 1324 w, 1301 m, 1208 w, 1180 w, 1156 w, 1118 m, 1070 w, 1029 w, 986 m, 950 w, 916 w, 895 m, 851 m, 781 m, 770 m, 763 s, 754 s, 728 m, 684 m, 664 m, 634 m, 621 sh, 597 m, 531 w, 506 m, 465 m. ^{1}H NMR ($CDCl_3$, 22 °C): δ 7.71 (m), 7.51 (br), 7.31−7.23 (m), 7.19−7.16 (m), 6.92 (br), 2.36 (s). ^{19}F NMR ($CDCl_3$, 22 °C): δ −110.46. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 22 °C): δ 131.54 (PhC), 130.86, 129.02, 128.36 (PhC), 123.29 (PhC), 90.40 (C).

Preparation of [$Cu_2(O_2C(3,5\text{-}F)_2C_6H_3)_2(C_{24}H_{18})$]$_2$ (5). A mixture of crystals of **1** (0.040 g, 0.03 mmol) with 1,4-bis(*p*-tolylethynyl)benzene (0.014 g, 0.05 mmol) was sealed under vacuum in a small glass ampule that was placed in an electric tube furnace at 245 °C. In 11 days, yellow blocks of **5** were deposited in the cold end of the ampule. Yield: 0.020 g (60%). IR (KBr, cm^{-1}): 3077 w, 3030 w, 2913 w, 1615 s, 1591 s, 1511 m, 1466 m, 1436 sh, 1390 s, 1303 m, 1261 w, 1182 w, 1120 s, 1021 w, 989 s, 952 w, 894 m, 851 m, 833 m, 809 m, 784 s, 768 m, 761 s, 664 m, 652 w, 613 w, 586 w, 514 w, 461 m. ^{1}H NMR ($CDCl_3$, 22 °C): δ 7.69 (m), 7.52−7.39 (m), 7.16−7.13 (m), 2.35 (s). ^{19}F NMR ($CDCl_3$, 22 °C): δ −108.02. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 22 °C): δ 138.62 (PhC), 131.52 (PhC), 129.18 (PhC), 123.13 (PhC), 120.00 (PhC), 103.55 (PhC), 91.37 (C), 88.55 (C).

X-ray Structural Determinations. The X-ray data sets were collected for **1**−**5** at −100 °C (Bruker KRYO-FLEX) on a Bruker APEX CCD X-ray diffractometer equipped with a graphite-monochromated Mo Kα radiation source ($\lambda = 0.71073$ Å). Data reduction and integration were performed with the software package *SAINT*,[54] and absorption corrections were applied using the program *SADABS*.[55] In all structures, the positions of the heavy atoms were found via direct methods using the program *SHELXTL*.[56] Subsequent cycles of least-squares refinement followed by difference Fourier syntheses revealed the positions of the remaining non-hydrogen atoms. Crystallographic data and X-ray experimental conditions for **1**−**5** are listed in Table 3. All non-hydrogen atoms in **1**−**5** were refined anisotropically, except for carbon and fluorine atoms of all disordered groups in **3** and **4**. One benzene ring of the carboxylate group in **4** and interstitial benzene and toluene molecules in **3** and **4**, respectively, were found to be disordered. Each disorder was modeled individually. All hydrogen atoms were included at idealized positions for structure−factor calculations, except for those in the structures of **2**, which were found in the difference Fourier map and refined independently. The refinement of hydrogen atoms in the structure of **5** was mixed. Hydrogen atoms of the methyl groups were included at idealized positions for structure−factor calculations. The rest of the hydrogen atoms were found in the difference Fourier map and refined independently.

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Supporting Information Available: Preparative details, including analytical and spectroscopic data, X-ray crystallographic files in CIF format, ORTEP diagrams for structures **1**−**5**, and computational details for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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