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Breaking Infinite Cu^I Carboxylate Helix Held by Cuprophilicity into Discrete Cu_n Fragments (n = 6, 4, 2)

Yulia Sevryugina[a] **and Marina A. Petrukhina***[a]

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A new copper(I) carboxylate complex with 3,5-bis(trifluoromethyl)benzoate ligands, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**), has been prepared in high yield and fully characterized. An X-ray diffraction study revealed a remarkable infinite double-helical chain motif held together by cuprophilic interactions ranging from 2.69 to 3.14 Å. Both left- and right-handed helices are present in the unit cell of the centrosymmetric structure of **1** thus making the crystalline compound racemic. Complex **1** shows bright emission at ca. 594 nm upon UV/Vis radiation in the solid state (λ_{ex} = 350 nm). The Cu···Cu contacts in **1** are easily broken in the gas phase to afford copper clusters of ascertained nuclearity upon sublimation with various polyaromatic hydrocarbons. Several polyarenes such as fluoranthene ($C_{16}H_{10}$), pyrene ($C_{16}H_{10}$), and coronene ($C_{24}H_{12}$) were selected to cover a broad temperature range from 130 to 220 °C for the gas-phase co-deposition reactions. As a result of the successive temperature increase, cleavage of the infinite copper(I) chain into $[Cu_n(O_2C(3,5\text{-}CF_3)_2C_6H_3)_n]$ fragments of decreasing nuclearity, n = 6, 4, and 2, has been achieved. The isolation of these units represents the first instance where various polynuclear copper(I) complexes are prepared and structurally characterized for the same carboxylate ligand.

Introduction

Copper(I) carboxylates attract special attention due to numerous catalytic applications[1] and rich photoluminescence properties.[2] They are known to exhibit a remarkable structural diversity for only a few structurally confirmed complexes. The synthetic routes toward copper(I) carboxylate complexes have been well developed,[3] but the ease of disproportionation, hydrolysis, and oxidation of these compounds in solutions[4] thwarted the isolation of single crystalline products and the study of their physical and chemical properties. Thus, crystallographic characterization of copper(I) carboxylates has been so far limited to $[Cu_2(O_2CCH_3)_2]_\infty$[5] (Scheme 1, **a**), $[Cu_4(O_2CC_6H_5)_4]$[6] (**b**), $[Cu_4(O_2CCF_3)_4]_\infty$[7] (**c**), and $[Cu(O_2CC(CH_3)_3)]_\infty$[8] (**e**). We have recently expanded the copper(I) carboxylate family with the goal of examining the influence of bridging carboxylate ligands on the solid-state structure of the resulting complexes. Specifically, we focus on fluorinated carboxylate ligands to yield volatile copper(I) products, because that allowed us to avoid the above-mentioned solution problems and to perform crystallization by sublimation-deposition procedures in the gas phase. Using solvent-free conditions for crystal growth, we have recently accomplished the preparation and structural characterization of $[Cu_2(O_2C(2,6\text{-}CF_3)_2C_6H_3)_2]_\infty$[9] (Scheme 1, **a**), $[Cu_4(O_2C(3\text{-}F)C_6H_4)_4]$ and $[Cu_4(O_2C(2,3,4\text{-}F)_3C_6H_2)_4]$[10] (**b**), $[Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2]_\infty$[10] (**c**), and $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6]$[11] (**d**). Thus, the known structural types of copper(I) carboxylates range from discrete[6,10,11] to infinite motifs,[5,7–9] based on mono-,[8] di-,[5,9] tetra-,[6,7,10] or hexanuclear[11] copper(I) units.

Such structural diversity is fascinating but not well rationalized so far. Only a few general observations can be made at this point. For example, we noticed that very electron-withdrawing carboxylate ligands such as trifluoroacetate and pentafluorobenzoate enhance intermolecular Cu···O interactions between the tetracopper units to afford extended motifs in contrast to discrete tetracopper(I) complexes formed by mono- and trifluorobenzoates.[10] Surprisingly, in contrast to the above-mentioned benzoate ligands that resulted in the tetracopper(I) clusters, 3,5-difluorobenzoate afforded a remarkable hexanuclear copper(I) complex, the first such example in the series.[11] At the same time, copper(I) pivalate was found to exhibit a unique double helical polymeric structure (Scheme 1, **e**). Its formation was explained by a delicate balance between the cuprophilicity and the steric effect of the bulky *t*Bu groups.[8] Then, one might speculate that the cuprophilicity could be enhanced when bulky but more electrophilic carboxylates than pivalates are employed. However, the use of 2,6-bis(trifluoromethyl)benzoate has afforded an extended polymeric product structurally similar to that of copper(I) acetate.[9]

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[a] Department of Chemistry, University at Albany, State University of New York,
1400 Washington Avenue, Albany, New York 12222, USA
Fax: +1-518-442-3462
E-mail: marina@albany.edu

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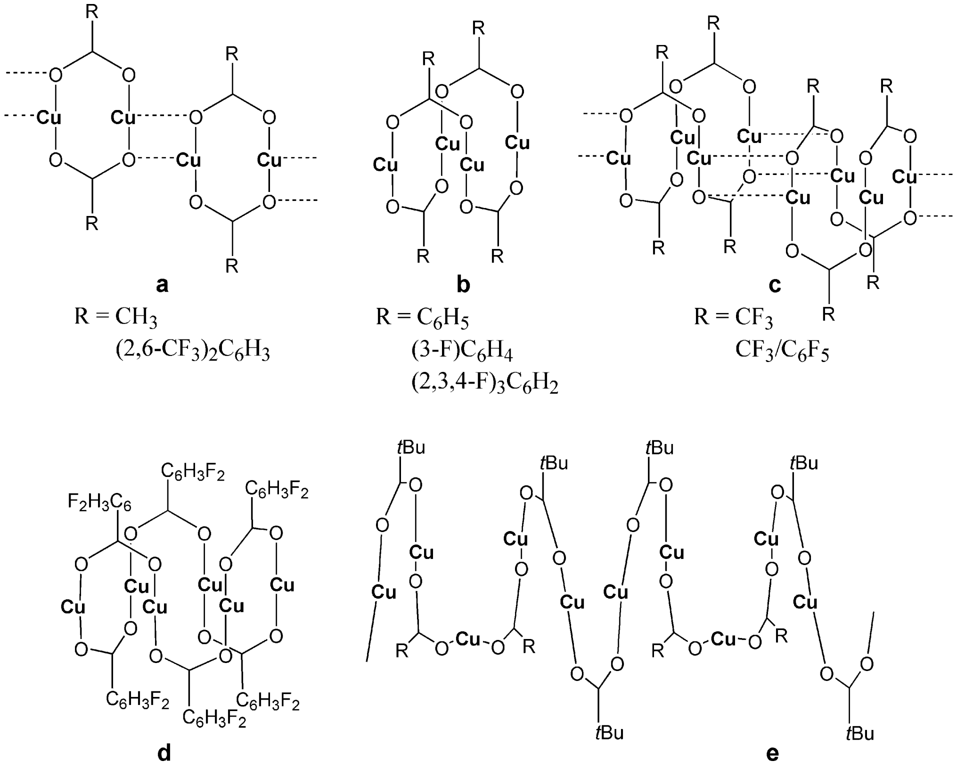


Scheme 1. Schematic representation of structural types for copper(I) carboxylates.

These results show that our ability to control the formation of a specific polynuclear copper(I) core based on the nature of the bridging carboxylate ligands is still very limited. Further expansion of this family to incorporate new members should provide better rationalization of the observed structural variety which is a key to understanding of their properties and reactivity. In this work, we report the synthesis, X-ray structural characterization, and photoluminescence of a new copper(I) carboxylate, namely 3,5-bis(trifluoromethyl)benzoate. In addition, its gas phase fragmentation studies have been performed using various polyaromatic hydrocarbons as weak complexing ligands and temperature controlling agents.

Results and Discussion

Synthesis of Copper(I) 3,5-Bis(trifluoromethyl)benzoate (1)

The preparation of the title copper(I) carboxylate, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**), was accomplished by a modification of the common ligand-exchange procedure developed earlier by Edwards and Richards.[3a] In contrast, we have started with the $[Cu_4(O_2CCF_3)_4]$ complex and substituted the trifluoroacetate groups by 3,5-bis(trifluoromethyl)benzoate ligands. The resulting product was contaminated with excess carboxylic acid, which was removed by several benzene washings and repetitive re-sublimations under dynamic vacuum and mild heating. The crude powder of **1** obtained by the above procedures is readily soluble in coordinating solvents such as acetonitrile or tetrahydrofuran. However, the dissolution process is accompanied by the formation of a yellow precipitate and change of the solution color to blue within a few minutes, which is indicative of a rapid disproportionation.[4]

Because the title complex is volatile, the sublimation-deposition approach can be used for crystal growth and reactivity studies. It was proven to be effective for the isolation of single crystalline products of electrophilic complexes without any exogenous ligands and interfering solvent effects.[7,9–11] Thus, crystals of **1** in the form of colorless thin needles are readily accessible by the gas-phase sublimation of the crude powder in the temperature range of 140–190 °C in a sealed evacuated Pyrex tube.

The compositions of the crude powder and the single crystalline product both correspond to the general formula, $[Cu(O_2C(CF_3)_2C_6H_3)]$. However, our attempts to correlate the X-ray powder diffraction spectrum of the purified polycrystalline material, prior to its sublimation, with the calculated pattern for the single crystalline sample, revealed their unambiguous difference (see Supporting Information, Figure S1). This result indicates that the structures of single crystals of **1** obtained by sublimation-deposition and of the crude powder isolated initially from the carboxylate-exchange reaction are not identical. It is important to mention, however, that the crystals of **1** were produced in high yield, and only those have been further used for characterization and all reactivity tests.

X-ray Structure of Copper(I) 3,5-Bis(trifluoromethyl)benzoate (1)

The X-ray crystallographic study of new copper(I) 3,5-bis(trifluoromethyl)benzoate, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**), has revealed a remarkable structural motif. Compound **1**, crystallizing in the monoclinic space group $P2_1/n$ ($Z = 28$ for the empirical formula), contains seven Cu atoms in an asymmetric unit ($Z = 4$ for the heptanuclear unit) which are bridged by the carboxylate groups in consecutive fashion (Figure 1).

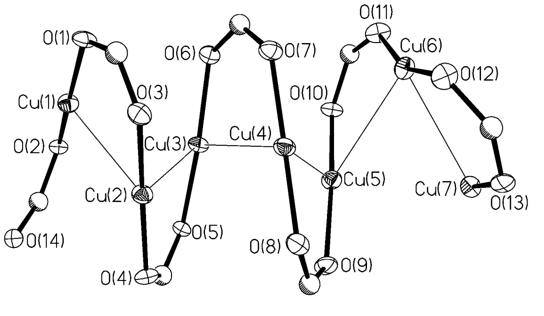


Figure 1. Thermal ellipsoid representation of an asymmetric unit of **1** drawn at the 30% probability level. This ORTEP scheme is used in all figures. The $(3,5\text{-}CF_3)_2C_6H_3$ groups are omitted for clarity.

The Cu···Cu distances between the μ_2-bridged copper atoms in **1** vary in the wide range of 2.693(2)–3.143(2) Å (Δ = 0.45 Å). Specifically, four of the unique seven copper–copper distances, Cu(1)···Cu(2), Cu(2)···Cu(3), Cu(3)···Cu(4), and Cu(7)···Cu(1), are very close, averaging to 2.803(2) Å. The longest intermetallic separation, Cu(5)···Cu(6), of 3.143(2) Å is neighbored by the shorter Cu(4)···Cu(5) and Cu(6)···Cu(7) contacts of 2.730(2) and 2.693(2) Å, respectively. This discrepancy in metal–metal distances is also reflected in the geometry of the carboxylate bridge between Cu(5) and Cu(6), which results in the Cu(5)–O(10)–C and Cu(6)–O(11)–C angles being 128.1(7) and 135.3(8)°, respectively. At the same time, the average value for the rest of the Cu–O–C angles is 124.8(7)°.

The revealed structural type of **1** is close to the recently reported helical structure of copper(I) pivalate, $[Cu(O_2CC(CH_3)_3)]$ (**2**). In contrast to **1**, complex **2** crystallizes in the triclinic space group $P\bar{1}$ ($Z = 10$ for the empirical formula) and has five Cu atoms in an asymmetric unit ($Z = 2$ for the pentanuclear unit). Selected bond lengths and angles for **1** and **2** are listed in Table 1. A close comparison of **1** and **2** shows that the range of Cu···Cu carboxylate-bridged distances is greater in **1** (Δ = 0.45 Å) than in **2** (2.850(2)–2.897(2), Δ ≈ 0.05 Å). At the same time, the seesaw coordination of each Cu-center in **1** results in Cu–Cu–Cu angles of 60.77(5)° on average, which are comparable to those in **2** [62.64(5)°].

In copper(I) 3,5-bis(trifluoromethyl)benzoate (**1**), each of the seven copper atoms, Cu(*n*), besides being in proximity with the adjacent carboxylate-bridged Cu(*n*±1) atoms, has close contacts to the non-bridged Cu(*n*±2) atoms. The range of these Cu(*n*)···Cu(*n*±2) distances in **1** [2.818(2)–3.008(2) Å] falls within that for the μ_2-bridged Cu(*n*)···Cu(*n*±1) contacts [2.693(2)–3.143(2) Å], which essentially eliminates any difference between the bridged- and non-bridged copper–copper separations. In copper(I) pivalate (**2**), however, the μ_2-bridged Cu(*n*)···Cu(*n*±1) contacts are distinguishable from the unsupported Cu(*n*)···Cu(*n*±2) distances.

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

$[Cu(O_2CR)]_\infty$, R =	$(3,5\text{-}CF_3)C_6H_3$ **1**	$C(CH_3)_3$ **2**[8]
$Cu\cdots Cu_{carb-bridged}$	2.693(2)–3.143(2)	2.850(2)–2.897(2)
$Cu\cdots Cu_{non-bridged}$	2.818(2)–3.008(2)	2.891(2)–3.125(2)
$Cu–O_{carb}$[a]	1.858(8)	1.850(7)
Cu–Cu–Cu[a]	60.77(5)	62.64(5)

[a] Averaged.

In the crystal structure of **1**, the crystallographically unique seven Cu atoms represent a repetitive fragment of a polymer that is formed by further bridging of the Cu(7) and Cu(1) atoms with the symmetry equivalent Cu(1A) and Cu(7A) centers, respectively (Figure 2). Due to a similarity between the supported and unsupported copper–copper distances in **1**, we suggest to view the polymer as if it consisted of two infinite chains of Cu(*n*±2) atoms, in which the Cu(*n*–2)–Cu(*n*)–Cu(*n*+2) angles are averaged to 157.57(7)° (Scheme 2). The two parallel Cu(*n*±2) chains running along the [100] direction are paired up by the carboxylate ligands, which bridge the Cu(*n*±1) atoms belonging to different chains. In addition, these parallel and bridged copper(I) strings twist around the [100] axis to form a helix (Scheme 2) with a period of 9.11 Å.

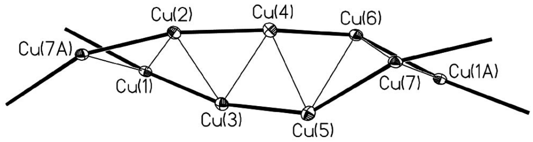
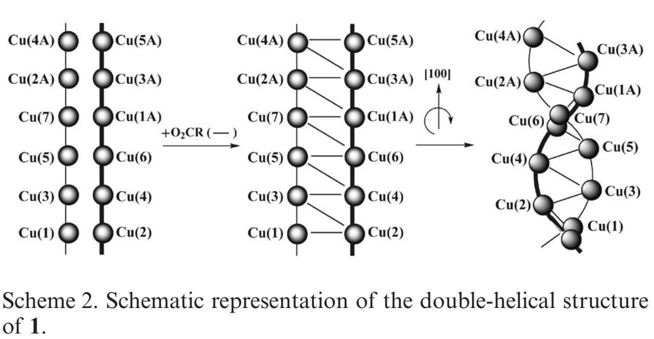


Figure 2. A fragment of the infinite double-helical structure of **1**. Only copper atoms are shown.



Scheme 2. Schematic representation of the double-helical structure of **1**.

In the crystal lattice of **1**, the infinite double-helical units stack together in parallel columns of constant but different helicity. The presence of both left- and right-handed helices in the centrosymmetric structure of **1** makes the crystalline compound racemic (Figure 3).

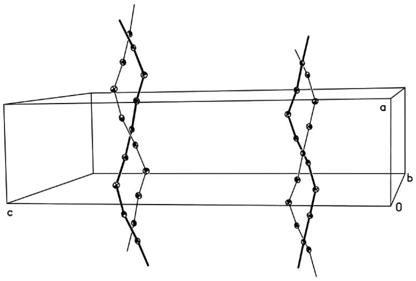
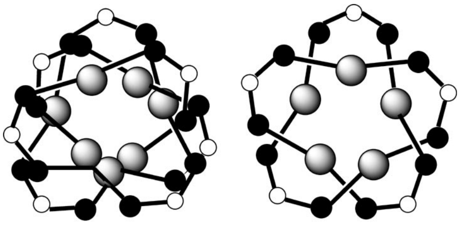


Figure 3. The left- and right-handed helices in the centrosymmetric structure of **1** (two helices out of four are shown). Only copper atoms are shown.

The structure of the previously reported copper(I) pivalate (**2**) can also be regarded as a double helix. The Cu(*n*–2)–Cu(*n*)–Cu(*n*+2) angles in **2** of 143.66(6)° imply that the helical twist in **2** is greater than that in **1**. A projection array perpendicular to the *a* axis in **2** exhibits a perfect pentagon of copper atoms. In contrast, a similar projection in **1** does not indicate any symmetry elements (Scheme 3).



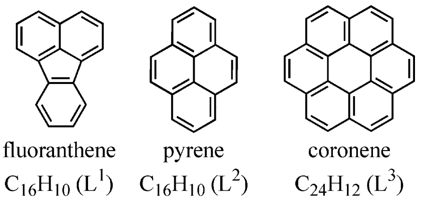
Scheme 3. Schematic representation of projections perpendicular to the *a* axis for the structures of **1** and **2**. Cu shaded spheres, O black, C white. The $C(CH_3)_3$ and $(3,5\text{-}CF_3)_2C_6H_3$ groups are omitted for clarity.

The helical shape is a common natural motif. The similarity between the double helices of **1** and **2** and those of nucleic acids is particularly attractive. Materials of such type are expected to exhibit a wide range of potential applications in the fields of supramolecular chemistry,[12] asymmetric catalysis,[13] and nonlinear optics.[14] Although discrete copper(I) double-helices supported by oligopyridine and oligophenanthroline ligands are known,[15] complex **2** reported by Awaga[8] and complex **1** prepared in our laboratory are the only copper(I) carboxylates with the infinite helical architectures. A few other extended copper(I) chains and infinite arrays held by cuprophilicity should be mentioned here.[16]

It has been previously observed that π-stacking interactions between aromatic rings play an important role in stabilizing the double-helical geometry.[15] However, a thorough analysis of the solid state packing of $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]_\infty$ (**1**) revealed only very weak intramolecular π-π stacking interactions of 4.33–4.74 Å between the adjacent benzene rings of carboxylate moieties (dihedral angles in the range of 11.1–35.1°). Such weak intramolecular contacts could not be a major driving force in the formation of a helix. For comparison, the analogous contacts are in the range of 3.71–4.16 Å for the discrete tetranuclear $[Cu_4(O_2CR)_4]$ (R = $(2,3,4\text{-F})_3C_6H_2$ and $(3\text{-F})C_6H_4$) and hexanuclear $[Cu_6(O_2C(3,5\text{-F})_2C_6H_3)_6]$ complexes. An analysis of the H···F interactions in **1** has shown them to fall in the 2.29–2.84 Å range with the C–H···F angles varying from 131 to 168°. However, one should keep in mind that the trifluoromethyl groups in the crystal structure of **1** are disordered over two or three rotational orientations. Noteworthy, copper(I) 2,6-bis(trifluoromethyl)benzoate reported earlier,[9] having the same molecular formula $[Cu(O_2C(CF_3)_2C_6H_3)]$ but differently positioned trifluoromethyl substituents (2,6- instead of 3,5-) on the benzene rings, forms a different solid state assembly (Scheme 1, **a**).

Fragmentation Studies of Copper(I) 3,5-Bis(trifluoromethyl)benzoate (1)

Crystals of copper(I) 3,5-bis(trifluoromethyl)benzoate, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]$ (**1**), can be quantitatively resublimed in the 140–190 °C range. At these temperatures, the deposited product has been confirmed to have the same infinite double-helical polymeric structure, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]_\infty$. We hypothesized that in the gas phase this compound exists in the form of some discrete molecular species, the isolation and characterization of which turned out to be a synthetic challenge. We reasoned that polycyclic aromatic hydrocarbons (PAHs) may be appropriate π-donor agents for crystallization of the copper(I) carboxylate fragments from the vapor phase. We have recently observed that co-deposition of the hexanuclear copper(I) carboxylate complex with coronene from the gas phase did not change the nuclearity of the copper(I) core in its crystalline adduct.[11] The choice of ligands, fluoranthene ($L^1 = C_{16}H_{10}$), pyrene ($L^2 = C_{16}H_{10}$), and coronene ($L^3 = C_{24}H_{12}$) (Scheme 4), was based on their different volatility that covers a broad temperature range for co-deposition reactions (melting points are 105 °C for fluoranthene, 146 °C for pyrene, and 428 °C for coronene). In addition, the copper(I) binding toward π-donor substrates has been long considered important in molecular recognition processes for many biological and artificial systems,[17] as well as in catalysis of aromatic cross-coupling reactions.[18] However, only two copper(I) carboxylate–arene adducts have been structurally characterized to date,[11,19] with only the recent work attempting to interpret the bonding in such systems.



Scheme 4. Schematic representation of polycyclic hydrocarbons L^1–L^3.

Using the gas-phase deposition approach that we found to be very effective for utilizing intermolecular metal–π-arene interactions for the controlled preparation of discrete

Table 2. Selected bond lengths (Å) and angles (°) for complexes **3**–**6**.

L (name):	fluoranthene	fluoranthene	pyrene	coronene
L (formula):	$C_{16}H_{10}$	$C_{16}H_{10}$	$C_{16}H_{10}$	$C_{24}H_{12}$
$[Cu_n(O_2CR)_n]L_m$:	**3**, $n = 6$, $m = 2$	**4**, $n = 4$, $m = 1$	**5**, $n = 4$, $m = 1$	**6**, $n = 2$, $m = 1$
$Cu\cdots Cu_{carb\text{-}bridged}$	2.6973(13)–2.8280(13)	2.7203(15)–2.7475(16)	2.7028(6), 2.7344(6)	2.5678(15)
$Cu\cdots Cu_{non\text{-}bridged}$	2.8547(18)–2.9407(13)	2.8410(14)	2.8315(8)	
$Cu–O_{carb}$[a]	1.858(5)	1.856(5)	1.862(2)	1.876(4)
$Cu\cdots C$	2.82(2)–3.26(3)	2.895(10)–3.234(8)	2.862(3), 3.044(3)	2.783(9)–3.230(11)
Cu–Cu–Cu	115.73(4), 175.37(4), 65.58(3)	117.47(5)[a], 62.53(4)[a]	117.210(16), 62.763(16)	
O–Cu–O[a]	172.1(2)	175.8(3)	175.99(11)	169.73(16)

[a] Averaged.

Table 3. Data collection and structure refinement parameters for **1**, **3**–**6**.

	1	**3**	**4**	**5**	**6**
Formula	$C_9H_3CuF_6O_2$	$C_{86}H_{38}Cu_6F_{36}O_{12}$	$C_{52}H_{22}Cu_4F_{24}O_8$	$C_{52}H_{22}Cu_4F_{24}O_8$	$C_{42}H_{18}Cu_2F_{12}O_4$
Fw	320.65	2328.40	1484.86	1484.86	941.64
Color	colorless	yellow	yellow	yellow	yellow
Crystal size [mm]	0.28 × 0.03 × 0.02	0.09 × 0.07 × 0.02	0.09 × 0.07 × 0.07	0.20 × 0.06 × 0.05	0.17 × 0.13 × 0.02
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P2_1/c$
a [Å]	9.1145(8)	9.9582(8)	17.7712(10)	15.7991(10)	17.204(3)
b [Å]	23.718(2)	12.9219(10)	20.9291(12)	17.8081(11)	8.1182(15)
c [Å]	35.093(3)	17.7942(14)	15.1217(9)	18.6724(12)	12.557(2)
α [°]		71.889(1)			
β [°]	90.614(2)	73.817(1)	114.099(1)	96.366(1)	101.025(3)
γ [°]		89.921(1)			
V [Å^3]	7585.9(12)	2080.9(3)	5134.1(5)	5221.1(6)	1721.4(6)
Z	28	1	4	4	2
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-3}]	1.965	1.858	1.921	1.889	1.817
μ [mm^{-1}]	2.089	1.650	1.779	1.749	1.348
Min./max. transmission	0.5924/0.9594	0.8657/0.9677	0.8563/0.8856	0.7212/0.9176	0.8032/0.9735
$2\theta_{max}$	50.20	50.32	49.98	56.50	50.14
Unique data	13468	7329	9001	6161	3047
Observed data [$I > 2\sigma(I)$]	8975	4592	5652	5261	1945
Parameters refined	1212	615	856	468	277
Goodness-of-fit[a] on F^2	1.122	1.046	1.106	1.026	1.055
$R1$,[b] $wR2$[c] [$I > 2\sigma(I)$]	0.0988, 0.2071	0.0761, 0.1813	0.0863, 0.1636	0.0487, 0.1220	0.0683, 0.1589
$R1$,[b] $wR2$[c] [all data]	0.1443, 0.2261	0.1222, 0.2106	0.1390, 0.1850	0.0563, 0.1278	0.1143, 0.1876
Residual $\rho_{max,\ min}$ [e Å^{-3}]	0.839, –0.773	1.124, –0.611	0.704, –0.563	1.005, –0.725	1.515, –0.539

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

complexes and extended organometallic networks in a solvent-free environment,[20] we have isolated several new products, each incorporating a certain molecular fragment, $[Cu_n(O_2C(3,5\text{-}CF_3)_2C_6H_3)_n]$.

These compounds, namely $[Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{16}H_{10})_2$ (**3**), $[Cu_4(O_2C(3,5\text{-}CF_3)_2C_6H_3)_4](C_{16}H_{10})$ (**4**), $[Cu_4(O_2C(3,5\text{-}CF_3)_2C_6H_3)_4](C_{16}H_{10})$ (**5**), and $[Cu_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2](C_{24}H_{12})$ (**6**), were isolated in the form of air-stable but slightly moisture sensitive crystals of pale yellow color. Their IR spectra are very similar in the 2000–500 cm^{-1} range and indicate the presence of aromatic and carboxylate functions. Additionally, the composition of the newly prepared compounds **4**–**6** was confirmed by elemental analysis. The molecular structures of **3**–**6** have been determined by X-ray diffraction analysis. The X-ray crystal data for **1**, **3**–**6** as well as selected bond lengths and angles for **3**–**6** are listed in Tables 2 and 3, respectively.

Reaction with Fluoranthene: The reaction of copper(I) 3,5-bis(trifluoromethyl)benzoate (**1**) with fluoranthene (L^1) afforded a mixture of two new products of stoichiometries Cu/L^1 = 6:2 (**3**) and 4:1 (**4**) that were deposited in different parts of the same ampule. The big yellow blocks of the latter compound were mainly found in the "hot" end, where the sublimation temperature was set at 137 °C, while thin yellow plates of the former adduct were located in the "cold" end having a ca. 5 °C lower temperature. In the middle part of the ampule, co-deposition of both types of crystals was observed but their different visual appearance allowed for their manual separation.

Compound $[Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{16}H_{10})_2$ (**3**) crystallizes in the triclinic space group $P\bar{1}$ ($Z = 1$). The building blocks in the structure are a planar hexagon of six copper atoms bridged by carboxylate ligands and two fluoranthene molecules (Figure 4). The hexagon resides on an inversion center with only three copper atoms and the halves of two fluoranthene molecules being crystallographically independent. The 3,5-bis(trifluoromethyl)benzoate ligands support the [Cu$_6$]-core in an alternate manner by positioning above and below the hexacopper plane.

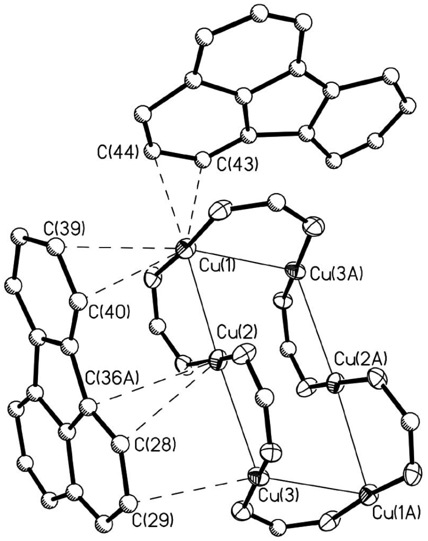


Figure 4. Building blocks of **3**. The (3,5-CF$_3$)$_2$C$_6$H$_3$ groups and the H atoms are omitted for clarity.

Importantly, the [Cu$_6$] unit present in the structure of **3** is only the second example of a hexanuclear core for the whole copper(I) carboxylate series; the first one was discovered recently for copper(I) 3,5-difluorobenzoate, [Cu$_6$(O$_2$C(3,5-F)$_2$C$_6$H$_3$)$_6$].[11] Herein, this hexanuclear fragment was isolated from the sublimation-deposition of the polymeric compound **1** and fluoranthene at the lowest temperature for the series of experiments, namely at 130 °C. This may be indicative of the existence of the [Cu$_6$] fragment in the vapor phase at the above temperature.

The geometry of the [Cu$_6$] core in **3** is very similar to that in copper(I) 3,5-difluorobenzoate. The copper–copper distances for the μ_2-bridged Cu atoms range from 2.6973(13) to 2.8280(13) Å (2.7064(8)–2.8259(8) Å in copper(I) 3,5-difluorobenzoate) and the interior Cu–Cu–Cu angles are 115.73(4), 175.37(4), and 65.58(3)° [123.48(3), 170.27(3), and 66.15(2)° for copper(I) 3,5-difluorobenzoate].

The solid-state structure of **3** can be viewed as a 2D network running in the *ab* plane. In the layer, fluoranthene molecules adopt different orientations around the hexanuclear copper complex. The details of the solid state packing are described in the Supporting Information (Figures S8, S9). The shortest contact of 2.82(2) Å is found between Cu(1) and C(44) (Figure 4). Several Cu···C contacts in the range of 3.014(18)–3.26(3) Å exceed the sum of the van der Waals radii r_{vdW} for Cu and C [Σr_{vdW}(Cu,C) = 3.10 Å].[21] For comparison, the range of Cu···C distances in [Cu$_4$(O$_2$CCF$_3$)$_4$](C$_6$H$_6$)$_2$[19] is 2.7–3.0 Å, while the bonding Cu···C distances in copper(I) cation–arene π complexes with ligands other than carboxylates range from 2.09 to 2.92 Å.[22]

In our recent work we have demonstrated that the nature of communication between the hexanuclear copper(I) carboxylate complex and the polyaromatic system of coronene is described by strong electrostatic ion-induced dipole interactions.[11] DFT calculations confirmed an absence of any bonding interactions and suggested that the [Cu$_6$(O$_2$C(3,5-F)$_2$C$_6$H$_3$)$_6$](C$_{24}$H$_{12}$) adduct be treated as a product of cocrystallization rather than a coordination compound. In contrast, in the recent theoretical work[23] the η^6 complex between the naked Cu(+)-cation and benzene was characterized by strong 3d-π*(C$_6$H$_6$) back-bonding. However, the η^6-binding was not experimentally observed in the solid state and all crystallographically confirmed examples of π-arene complexes of Cu$^{\mathrm{I}}$ are based on η^1 or η^2-type of interactions. In line with our findings for the latter, we will consider compounds **3**–**6** as products of cocrystallization, discussing the short copper-to-carbon distances as non-bonding contacts.

The second product with fluoranthene, [Cu$_4$(O$_2$C(3,5-CF$_3$)$_2$C$_6$H$_3$)$_4$](C$_{16}$H$_{10}$) (**4**), crystallizes in the monoclinic space group $P2_1/c$ (Z = 4). The structural block is a planar tetragon of four crystallographically unique copper atoms bridged by 3,5-bis(trifluoromethyl)benzoate groups and one fluoranthene molecule (Figure 5).

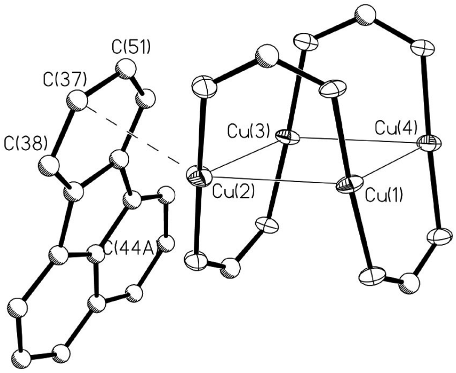


Figure 5. Building block in the structure of **4**. The (3,5-CF$_3$)$_2$C$_6$H$_3$ groups and the H atoms are omitted for clarity.

The tetracopper core of the molecular complex **4** is structurally similar to those of the several previously reported [Cu$_4$(O$_2$CR)$_4$] complexes [R = CF$_3$,[7] C$_6$H$_5$,[6] (3-F)-C$_6$H$_4$,[10] (2,3,4-F)$_3$C$_6$H$_2$,[10] and CF$_3$/C$_6$F$_5$[10]]. The average copper–copper distances [2.7372(16) Å] and angles [117.47(5) and 62.53(4)°] fall in the same range as for the other [Cu$_4$]-core carboxylates. The fluoranthene molecule exhibits a shortest Cu(2)···C(37) distance of 2.895(10) Å, while the adjacent Cu(2)···C(38) and Cu(2)···C(51) separations are noticeably longer [3.173(10) and 3.182(11) Å, respectively].

It is convenient to consider **4** as a polymeric zigzag-type ribbon (Figure 6) built on intermolecular copper–carbon interactions, namely the Cu(2)···C(37) and Cu(4)···C(44A) contacts (Figure 5). The latter of 3.234(8) is, however, considerably longer than the former [2.895(10) Å].

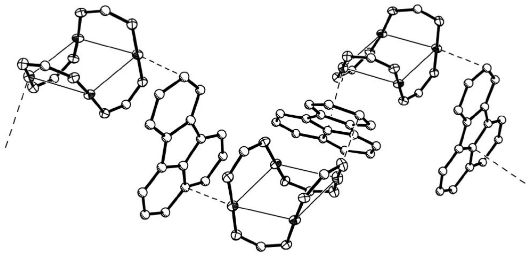


Figure 6. A fragment of a polymeric zigzag chain in **4**. The (3,5-$CF_3)_2C_6H_3$ groups and the H atoms are omitted for clarity.

Reaction with Pyrene: The reaction of **1** with pyrene (L^2) at 160 °C produced the new copper(I) 3,5-bis(trifluoromethyl)benzoate complex with a Cu/L^2 = 4:1 composition. Compound $[Cu_4(O_2C(3,5\text{-}CF_3)_2C_6H_3)_4](C_{16}H_{10})$ (**5**), crystallizing in the monoclinic space group $C2/c$ (Z = 4), has a twofold rotation axis at the center of the $[Cu_4]$-core. The main structural unit contains four copper atoms, two of which are crystallographically independent, and one pyrene molecule (Figure 7).

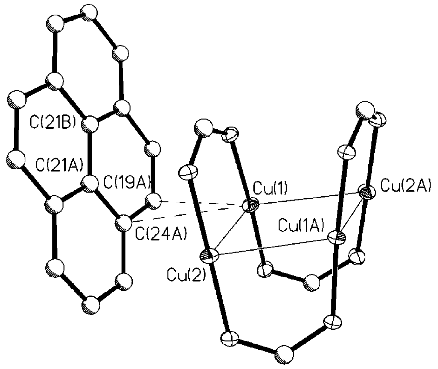


Figure 7. Building block in the structure of **5**. The (3,5-$CF_3)_2C_6H_3$ groups and the H atoms are omitted for clarity.

Although the tetranuclear motif is common among copper(I) carboxylates, the structure of **5** is the first example having almost equal and parallel Cu···Cu sides of 2.7028(6) and 2.7344(6) Å, which make a parallelogram core. The interior Cu–Cu–Cu angles of 117.210(16) and 62.763(16)° are the same as in the tetragonal core of compound **4**. Only one of the two crystallographically independent Cu atoms has contacts of 2.862(3) and 3.044(3) Å with two carbon atoms of pyrene, C(19A) and C(24A), respectively.

Compound **5** can be viewed as an infinite 1D linear network propagating along the [010] direction (Figure 8). Repetitive units are related by an inversion center at the midpoint of the C(21A)···C(21B) bond of pyrene.

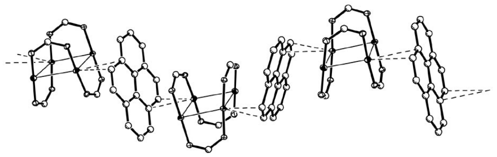


Figure 8. A fragment of a polymeric 1D chain in **5**. The (3,5-$CF_3)_2$-C_6H_3 groups and the H atoms are omitted for clarity.

Reaction with Coronene: Complex $[Cu_2(O_2C(3,5\text{-}CF_3)_2\text{-}C_6H_3)_2](C_{24}H_{12})$ (**6**) of the stoichiometry Cu/L^3 = 2:1 was obtained at sublimation temperature 220 °C by reacting $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]_\infty$ (**1**) with coronene (L^3). Compound **6** crystallizes in the monoclinic space group $P2_1/c$ (Z = 2) and has an inversion center at the midpoint of the Cu(1)···Cu(1A) separation. The main structural block is the dicopper(I,I) carboxylate unit with one coronene molecule (L^3) (Figure 9).

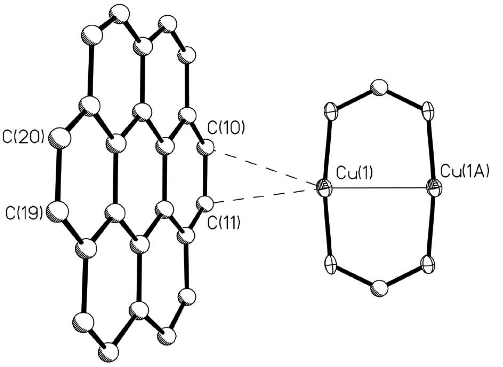


Figure 9. Building block in the structure of **6**. The (3,5-$CF_3)_2C_6H_3$ groups and the H atoms are omitted for clarity.

The Cu(1)···Cu(1A) bond length of 2.5678(15) Å within a dimetal unit is significantly shorter than copper–copper distances for polynuclear compounds **1** and **3**–**5** but comparable to those for analogous dicopper(I)-based acetate[5] [2.556(2) Å] and 2,6-bis(trifluoromethyl)benzoate[9] [2.563(2) Å].

Each Cu atom in **6** is directed toward the C–C π bonds of two different coronene molecules. In the [001] direction the Cu···C distances range from 2.783(9) to 2.950(11) Å and are within the sum of the van der Waals radii for copper and carbon [Σr_{vdW} (Cu, C) = 3.10 Å].[21] In the [010] direction, the Cu···C contacts of 3.100(10)–3.230(11) Å are longer. It is convenient to consider **6** as a 2D layer running in the *bc* plane, that consists of alternating dicopper units and coronene molecules (Figure 10).

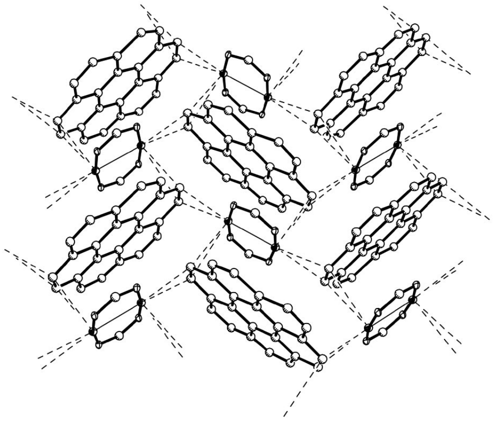


Figure 10. A fragment of the 2D infinite layer in **6**. The (3,5-$CF_3)_2$-C_6H_3 groups and the H atoms are omitted for clarity.

It should be mentioned here that in the polymeric complex $[Ag_4(C_{24}H_{12})_3(ClO_4)_4]_\infty$, the interaction between Ag^I and coronene is so strong that it results in a bent conformation of the latter [Ag···C contacts range from 2.402(4) to 2.517(4) Å].[24] In complex **6**, however, the geometrical parameters of coronene are unchanged as compared to the uncoordinated molecule.[25]

The isolation and structural characterization of adducts **3**–**6** revealed an interesting trend: an increase in the reaction temperature is accompanied by a controlled fragmentation of the infinite helical chain of **1** to form $[Cu_6]$-, $[Cu_4]$- and, finally $[Cu_2]$-based units, cocrystallized with the corresponding polyarene. This clearly illustrates the effect of reaction conditions on the outcome of the co-deposition reactions and gives a tool for controlling the nuclearity of copper(I) clusters.

Photoluminescence

Considerable attention has been paid to understanding the photophysical behavior of polynuclear copper(I) halides, chalcogenides, acetylides, and pyrazolates.[26] However, the only reference to photoluminescent properties of copper(I) carboxylates is dated back to 1981.[2] The emission maxima for a series of aliphatic copper(I) carboxylates were reported in the range of 535–660 nm at room temperature (λ_{ex} = 305–325 nm), but these data were not supported by structural characterization of the complexes.

Our recent findings showed that copper(I) clusters display strikingly different emissive behavior.[9–11] Similar to other copper(I) carboxylates,[9–11,2] complex **1** exhibits photoluminescence (PL) upon exposure to UV radiation (λ_{ex} = 350 nm). The PL spectrum of **1** in the solid state at room temperature displays an emission maximum centered at ca. 594 nm (yellow color). It should be noted that 3,5-bis(trifluoromethyl)benzoic acid is also luminescent in the solid state with an emission peak at ca. 493 nm (λ_{ex} = 350 nm) (see Supporting Information, Figure S10). In contrast, copper(I) 2,6-bis(trifluoromethyl)benzoate having a $[Cu_2]$-based polymeric structure held by Cu···O intermolecular interactions (Scheme 1, **a**) showed green photoluminescence centered at ca. 560 nm under the same conditions. Interestingly, the structurally similar to **1** copper(I) pivalate was reported as nonluminescent.[8] The infinite helical structure of the latter held together by cuprophilicity was suggested as a possible explanation for the nonradiative decay. However, now that does not provide a rationale for the different luminescent behavior of **1** and **2**. The overall subtle structural differences as well as the nature of the bridging carboxylate ligands both seem to affect the emission properties of the copper(I) carboxylate complexes.

None of the copper(I) carboxylate adducts with polyarene ligands (**3**–**6**) exhibit detectable emission in the solid state. The PL spectra recorded for **3**–**6** in the range of 400–700 nm at room temperature are featureless. Under a stream of liquid nitrogen, however, weak and feeble photoluminescence can be hardly observed with the naked eye as a red-color emission. The PL spectrum for compound **5**, $[Cu_4(O_2C(3,5\text{-}CF_3)_2C_6H_3)_4](C_{16}H_{10})$, has, therefore, been recorded in the IR range at room temperature, and the position of an emission maximum was determined at 1363 nm (λ_{ex} = 515 nm). The fact that the emission band for the adduct **5** is significantly red-shifted to the IR region compared to both copper(I) 3,5-bis(trifluoromethyl)benzoate (**1**) and pyrene (that emits radiation at 482 and 515 nm, λ_{ex} = 350 nm) suggests that the copper(I) unit and polyarene are both affected by cocrystallization. The photoluminescence spectra of **5** and free pyrene (L^2) are given in Figure 11 (see also Supporting Information).

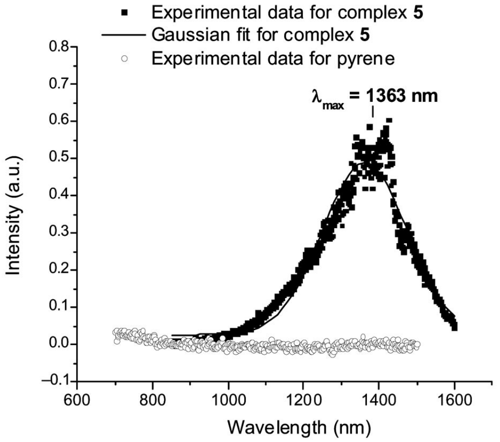


Figure 11. Solid state photoluminescence spectra for **5** and L^2.

We have recently reported[11] that the copper(I) 3,5-difluorobenzoate complex with coronene, $[Cu_6(O_2C(3,5\text{-}F)_2C_6H_3)_6](C_{24}H_{12})$, is also nonluminescent in the visible region at room temperature. In contrast, the photoluminescence for $[Cu_2(CF_3SO_3)_2](C_6H_6)$ was detected at 518 nm (λ_{ex} = 320 nm) and was suggested to originate from the $Cu^I \rightarrow \pi^*$ C_6H_6 MLCT transitions.[27] Besides these, there are no systematic studies discussing the origin of photoluminescence and its dependence on the structural type and π-arene complexation for copper(I) carboxylates, thus thwarting the rationalization of the above-mentioned effects. A full investigation of the luminescent properties of a series of copper(I) carboxylates having different nuclearities and different structural arrangements is currently underway, and that should shed some light on their photophysical behavior.

Conclusions

The isolation and structural characterization of copper(I) 3,5-bis(trifluoromethyl)benzoate, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]_\infty$ (**1**), has added to the copper(I) carboxylate family the second member having a remarkable double-helical structure. In contrast to copper(I) pivalate having a 6.35 Å periodicity and being reported as nonluminescent, the title complex has a period of 9.11 Å and shows bright luminescence in the solid state. The gas phase reactions of the infinite double-helical complex, $[Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)]_\infty$, with fluoranthene, pyrene, and coronene at the temperatures of 137, 162, and 220 °C, afforded hexa- (**3**), tetra- (**4** and **5**), and dinuclear (**6**) copper(I)-core fragments crystallized as adducts with the above polyarenes. Thus, using π-donor aromatic ligands of different volatility, we were able to break the copper(I) 3,5-bis(trifluoromethyl)benzoate helix and isolate several discrete [Cu_n]-clusters, $n = 6$, 4, and 2. In accord with our expectations, the molecular unit of the highest nuclearity is formed at the lowest reaction temperature, while temperature increase results in a further cleavage of the extended motif into smaller copper(I) fragments. This shows that tuning the temperature of gas-phase reactions offers control over the formation of copper(I) clusters of a specific nuclearity. Importantly, the reported system provides the first example where polynuclear [Cu_n]-core complexes have been isolated and structurally characterized for the same carboxylate ligand. All prior structurally confirmed copper(I) carboxylate complexes created an illusion that a specific structure is related to a particular carboxylate ligand. Although crystallized as adducts with polyarenes, compounds **3**–**6** show a more complicated picture and confirm the existence of various structural possibilities for a given carboxylate group. Thus, structures of the known copper(I) carboxylates may depend additionally on the preparation or crystallization conditions, and variation of those would result in the structural changes.

Experimental Section

General: All synthetic reactions and manipulations were carried out under dry dinitrogen or vacuum using standard Schlenk and glovebox techniques. Sublimation-deposition procedures were performed in evacuated (less than 10^{-2} Torr) sealed glass ampules (ca. 7 cm long with an o.d. of 1.1 cm), which were placed in electric furnaces having a small temperature gradient along the length of the tube.

The [$Cu_4(O_2CCF_3)_4$] complex was synthesized according to the literature method.[7] Anhydrous benzene, fluoranthene ($L^1 = C_{16}H_{10}$), and coronene ($L^3 = C_{24}H_{12}$) were purchased from Aldrich, while pyrene ($L^2 = C_{16}H_{10}$) was obtained from Acros. The 3,5-bis(trifluoromethyl)benzoic acid, $(3,5\text{-}CF_3)_2C_6H_3COOH$, was purchased from SynQuest Fluorochemicals and used as received.

The infrared spectra were recorded using KBr pellets with a Nicolet Magna 550 FTIR spectrometer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Canada. The photoluminescence spectrum of **1** was collected with 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 Sub-micro Fluorometer cell, which was mounted in a standard single cell holder. The photoluminescence spectrum of **5** was collected at the College of Nanoscale Science and Engineering, University at Albany, using the following setup. The Ar^+ laser was used as an excitation source. Light emitted from the sample was focused by a lens on the input slit of a monochromator (1 mm). The Ge *p*-i-*n* photodiode attached to the output slit of a monochromator (1 mm) was used as a detector.

[$Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)$] (1): The title compound was prepared by an overnight reflux of [$Cu_4(O_2CCF_3)_4$] (0.902 g, 1.27 mmol) and $(3,5\text{-}CF_3)_2C_6H_3COOH$ (1.709 g, 6.62 mmol) in benzene (50 mL). The volume of a homogeneous solution was then reduced to 2 mL to initiate a precipitation of a light blue powder. The solution above a precipitate was then decanted. The solid was washed with benzene (3 × 10 mL) and then heated at 90–100 °C overnight under the dynamic vacuum to remove the traces of unreacted acid. This afforded a very pale blue microcrystalline powder of **1**. Yield: 1.147 g (70%). $C_9H_3CuF_6O_2$ (320.7): calcd. C 34.73, H 0.96, O 10.29, F 33.44, Cu 20.58; found C 35.06, H 1.09, O 10.49, F 32.91, Cu 21.01. Crystals of **1** as white thin needles were obtained by sublimation of the crude powder at 140–200 °C for 1–3 d. IR (KBr): $\tilde{\nu}$ = 3095 (w), 2966 (w), 2931 (w), 2857 (w), 1631 (m), 1571 (m), 1549 (m), 1468 (m), 1456 (m), 1438 (m), 1347 (s), 1278 (s), 1180 (s), 1131 (s), 939 (w), 917 (m), 846 (m), 791 (w), 773 (m), 765 (m), 700 (m), 707 (m), 682 (s), 668 (w), 576 (w), 548 (w) cm^{-1}. PL (250–750 nm, λ_{ex} = 350 nm, solid): λ_{max} = 594 nm. $C_9H_3CuF_6O_2$ (320.7): calcd. C 34.73, H 0.96; found C 34.55, H 0.86.

[$Cu_6(O_2C(3,5\text{-}CF_3)_2C_6H_3)_6](C_{16}H_{10})_2$ (3) and [$Cu_4(O_2C(3,5\text{-}CF_3)_2C_6H_3)_4](C_{16}H_{10})$ (4): A mixture of crystals of [$Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)$] (**1**) (0.054 g, 0.174 mmol) with fluoranthene ($L^1 = C_{16}H_{10}$) (0.005 g, 0.025 mmol) was sealed under vacuum in a small glass ampule, which was placed in an electric oven at 137 °C. Over four days, two types of crystals appeared in the tube. Thin pale yellow plates of **3** were found mostly in the "cold" end of the ampule, where the temperature was set at ca. 130 °C. Yield: 0.010 g (15%). IR (KBr): $\tilde{\nu}$ = 3068 (w), 3033 (w), 2924 (w), 2854 (w), 1631 (m), 1572 (m), 1456 (m), 1436 (m), 1348 (s), 1278 (s), 1266 (sh), 1177 (m), 1131 (s), 1106 (sh), 914 (m), 845 (m), 806 (w), 773 (m), 761 (sh), 735 (w), 724 (w), 702 (m), 682 (m), 655 (w), 610 (w), 574 (w), 540 (w) cm^{-1}.

The yellow blocks of **4** were found at the "hot" end of the ampule. Yield: 0.025 g (40%). IR (KBr): $\tilde{\nu}$ = 3088 (w), 3069 (w), 1631 (m), 1574 (m), 1465 (w), 1454 (m), 1436 (m), 1346 (s), 1275 (s), 1264 (sh), 1175 (s), 1135 (s), 1105 (sh), 937 (w), 914 (m), 846 (m), 825 (w), 781 (m), 775 (m), 766 (m), 752 (w), 708 (m), 699 (m), 681 (m), 619 (w), 579 (w) cm^{-1}. $C_{52}H_{22}Cu_4F_{24}O_8$ (1484.9): calcd. C 42.05, H 1.48, O 8.63; found C 42.30, H 1.56, O 9.01.

[$Cu_4(O_2C(3,5\text{-}CF_3)_2C_6H_3)_4](C_{16}H_{10})$ (5): A mixture of crystals of [$Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)$] (**1**) (0.127 g, 0.408 mmol) with pyrene ($L^2 = C_{16}H_{10}$) (0.020 g, 0.099 mmol) was sealed under vacuum in a small glass ampule, which was placed in an electric oven at 162 °C. Over two days, pale yellow blocks of **5** had grown at the "cold" end of the tube. In 10 d the yield of **5** reached 0.040 g (27%). IR (KBr): $\tilde{\nu}$ = 3090 (w), 3046 (w), 1628 (m), 1583 (m), 1466 (m), 1457 (m), 1437 (m), 1347 (s), 1278 (s), 1178 (m), 1170 (m), 1139 (s), 1130 (s), 1105 (sh), 940 (w), 934 (w), 912 (m), 847 (m), 777 (m), 771 (sh), 766 (m), 754 (w), 714 (m), 708 (m), 699 (m), 682 (s), 553 (w) cm^{-1}. PL (250–1700 nm, λ_{ex} = 515 nm, solid): λ_{max} = 1363 nm. $C_{52}H_{22}Cu_4F_{24}O_8$ (1484.9): calcd. C 42.05, H 1.48; found C 42.12, H 1.41.

[$Cu_2(O_2C(3,5\text{-}CF_3)_2C_6H_3)_2](C_{24}H_{12})$ (6): A mixture of crystals of [$Cu(O_2C(3,5\text{-}CF_3)_2C_6H_3)$] (**1**) (0.051 g, 0.164 mmol) with coronene ($L^3 = C_{24}H_{12}$) (0.024 g, 0.080 mmol) was sealed under vacuum in a small glass ampule, which was placed in an electric oven at 220 °C. Over the next six days, yellow plates of **6** had grown in the middle part of the tube. Yield: 0.037 g (50%). IR (KBr): $\tilde{\nu}$ = 2921 (w), 2829 (w), 1628 (m), 1565 (m), 1453 (w), 1429 (w), 1348 (s), 1313 (w), 1279 (s), 1262 (m), 1197 (m), 1131 (s), 1105 (sh), 912 (m), 862 (m), 844 (w), 775 (m), 708 (m), 700 (m), 681 (m), 554 (w) cm^{-1}. $C_{42}H_{18}Cu_2F_{12}O_4$ (941.6): calcd. C 53.56, H 1.91; found C 53.69, H 1.81.

X-ray Crystallography: The X-ray diffraction data for single crystals were collected on a Bruker SMART APEX CCD-based diffractometer by using a Mo-target X-ray tube (λ = 0.71073 Å) operated at 1800 W power. Crystal data and data collection parameters for **1**, **3**–**6** are listed in Table 3. A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 30 s/frame for each experiment. The frames were integrated with the Bruker SAINT software package[28] using a narrow-frame integration algorithm. Analysis of the data showed negligible decay during data collection. The structures were solved by the direct methods and refined with the Bruker SHELXTL (Version 6.1) software package.[29] Data were corrected for absorption effects using the empirical methods SADABS.[30]

All non-hydrogen atoms were refined anisotropically, except for disordered carbon and fluorine atoms. The fluorine atoms of the CF_3 groups in **1**, **3**–**6** were disordered over two or three rotational orientations, and this disorder was modeled individually in each case. In compounds **1** and **3**, in addition to the CF_3 rotational disorder, some benzene rings of the bridging carboxylate groups were disordered over two orientations. Moreover, in complex **3**, both fluoranthene molecules exhibited crystallographically imposed disorder due to internal symmetry elements, and that was modeled individually. A crystallographically imposed disorder of coronene was present in complex **6**. Hydrogen atoms in compound **5** were found in the difference Fourier map and refined independently, while in the structures **1**, **3**, **4**, and **6** all hydrogen atoms were included at idealized positions for structure-factor calculations.

CCDC-656949 (for **1**), -656950 (for **3**), -656951 (for **4**), -656952 (for **5**), -656953 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): X-ray powder diffraction data and single crystal structural details, including the description of disorder in the structure of **3** and ORTEP diagrams for structures **1**, **3**–**6**; photoluminescence data for **1** and 3,5-bis(trifluoromethyl)benzoic acid.

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