

Structure and luminescence properties of a well-known macrometallocyclic trinuclear Au(I) complex and its adduct with a perfluorinated fluorophore showing cooperative anisotropic supramolecular interactions†

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The structure and luminescence properties of a well-known trinuclear Au(I) imidazolite complex are determined for the first time along with its interaction with the organic π acid perfluoronaphthalene in the solid state and solution.

Trinuclear Au(I) complexes have been studied since the 1970s and continue to receive current interest from multiple research groups owing to their remarkable structural¹ and photophysical² properties. Interesting chemistries in these materials include π acid–base interactions, aurophilic bonding, excited state Au–Au covalent bonding, and stimulus-sensitive luminescence.^{1–4} Among members of this class, the trinuclear Au(I) complexes [Au(μ -C²,N³-bzim)]₃ (**1**, where bzim = 1-benzylimidazolite) and [Au(μ -C(OEt)=N(*p*-C₆H₄CH₃))]₃ (**2**) have been subject to particularly immense investigations since 1972 by Minghetti, Bonati, Burini, Balch, Fackler and co-workers.^{1,2,5} While the structure⁵ and luminescence properties² of **2** have been determined, the same is not true regarding **1** prior to this work as the compound is usually isolated as a powder that is non-luminescent at room temperature. Several papers by Burini, Fackler, and co-workers showed that these complexes with Au(I) atoms bridged by the -N=C- carbenite and imidazolite ligands form sandwich adducts with a variety of electrophiles (Tl⁺, Ag⁺, an Hg(II) trimer, TCNQ, C₆F₆, etc.) to produce supramolecular chains that exhibit versatile optoelectronic properties influenced by the corresponding electrostatic interaction.^{6,7}

Gabbaï and co-workers reported extensive studies regarding stacking interactions of an electrophilic Hg(II) cyclic trinuclear complex with organic fluorophores, resulting in arene-sensitized phosphorescence with multiple orders of magnitude reduction in radiative lifetime due to spin–orbit coupling enhancement.⁸ Meanwhile, a recent density-functional computational study suggested that trinuclear Au(I) imidazolates such as **1** represent the strongest nucleophiles among the class of cyclic trinuclear d¹⁰ complexes known to date.⁹ Given that **2** forms a stacked adduct with the π -acidic fluorophore F₈-naphthalene (C₁₀F₈),¹⁰ an analogous study for **1**, being a stronger π base, is warranted. This study also includes

solution complexation *via* fluorescence quenching similar to that reported by Gabbaï and co-workers.⁸

Here we report the structure and corresponding luminescence properties of **1** and its reaction product with perfluoronaphthalene, C₁₀F₈ (Chart 1). Synthesis of **1** was performed according to a published procedure.¹¹ X-Ray quality single crystals were obtained by slow evaporation from THF or C₆F₆ solution. On the other hand, the synthesis of the binary π acid–base adduct was accomplished by slow evaporation of a mixed solution composed of a hexane solution of **1** and a dichloromethane solution of C₁₀F₈. This mixture was kept at 25 °C for several days to obtain X-ray quality single crystals in 80% yield. Further synthetic and characterization details are given in the ESI.†

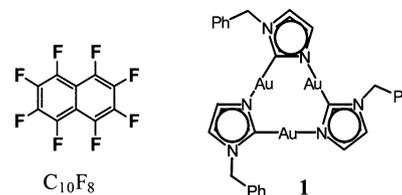


Chart 1

1 crystallizes in the monoclinic space group *C2/c*. Fig. 1 shows that symmetric molecules of **1** associate as dimer-of-trimer units with the shortest intermolecular Au...Au distance

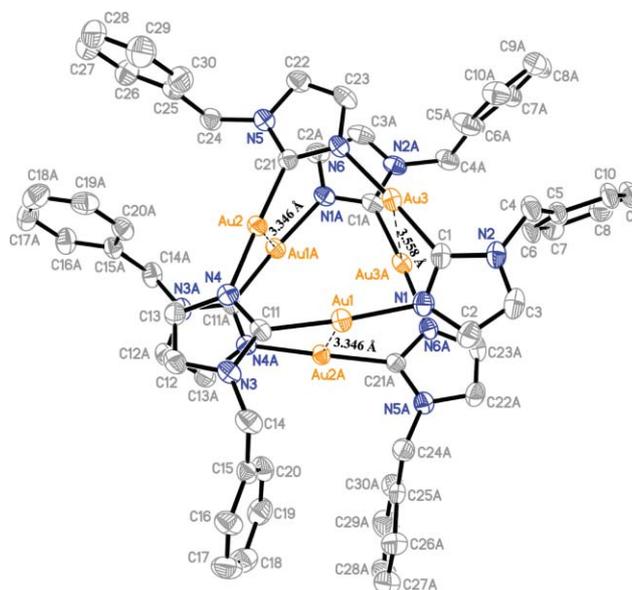


Fig. 1 Crystal structure of **1** showing a dimer-of-trimer repeat unit.

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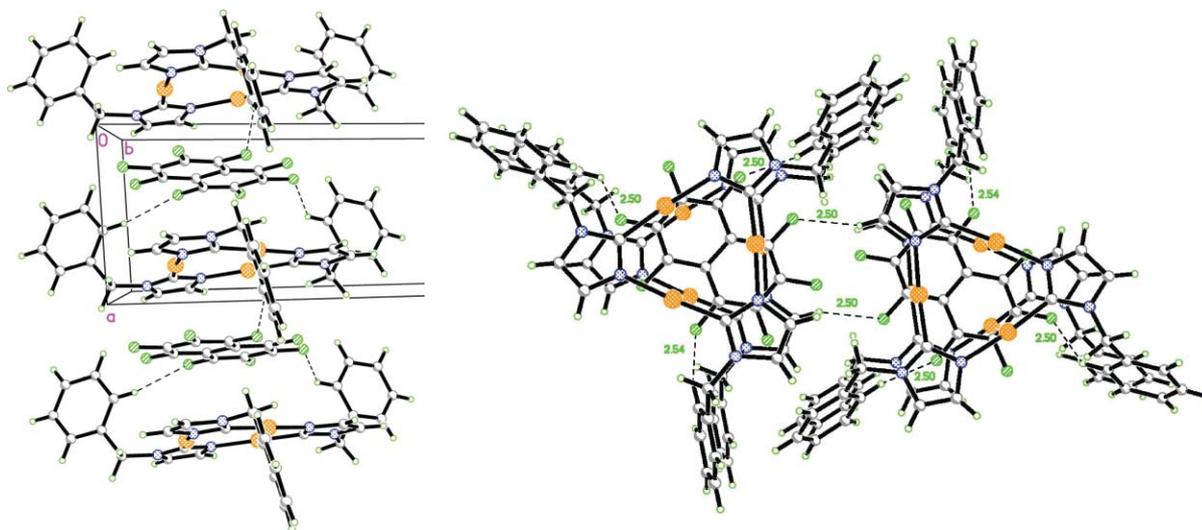


Fig. 2 Portions of the packing of $\{[1][C_{10}F_8]\}_\infty$ crystals showing 1D columnar stacking along the a -axis via π acid–base interactions (left) and 2D sheet structure across the bc planes via $H\cdots F$ interactions (right). Further views of molecular structure and packing are available in the ESI.†

being 3.3465(4) Å, which is even shorter than the intramolecular ligand-assisted aurophilic distances (3.453, 3.458, and 3.465 Å). The hexanuclear dimer-of-trimer units adopt a semi-prismatic conformation with one long (3.558 Å) and two short (3.346 Å) intertrimer aurophilic distances and torsion angles of $\sim 17^\circ$. The intertrimer aurophilic interactions in **1** are stronger than those in the reported structure of **2**, which entails a chair conformation with only two of the three Au atoms engaged in intertrimer aurophilic interaction (3.422 Å).⁵ A prismatic structure is somewhat rare among trinuclear d^{10} complexes and has been reported for polymorphs of $[Au(\mu-C(OMe)=NMe)]_3$,^{3a,12} for which an extended columnar structure was obtained, whereas a more similar situation to the one herein with discrete dimer-of-trimer units has been reported for $\{[3,5-(i-Pr)_2Tz]Au\}_3$,^{4f} as well as charge transfer adducts of $[Au(\mu-C(OEt)=NMe)]_3$.^{3b}

The adduct $1 \cdot C_{10}F_8$ crystallizes as a triclinic ($P\bar{1}$) system. An extended structure with two principal modes of anisotropic supramolecular interaction (Fig. 2) exist: one-dimensional (1D) π acid–base quadrupolar interactions manifest by alternating $C_{10}F_8$ and **1** planar moieties stacked perfectly on top of each other in infinite columns along the a -axis, and two-dimensional (2D) $H\cdots F$ dipole–dipole interactions involving the F atoms of $C_{10}F_8$ and H atoms of both the benzyl and imidazolyl groups of **1** to form extended planar sheets across the bc -planes. The centroids of the π -acidic $C_{10}F_8$ and π -basic **1** are separated by 3.506 Å in the 1D stacks, very similar to that in $2 \cdot C_{10}F_8$ (3.509 Å)¹⁰ and shorter than in $2 \cdot C_6F_6$ (3.565 Å).^{7b} The shortest $Au\cdots C$ ($C_{10}F_8$) distances are 3.395 and 3.436 Å. These distances are close to the sum of the estimated van der Waals radii of Au and C (3.36 Å). The intramolecular $Au\cdots Au$ distances become somewhat longer upon adduct formation (average 3.472 Å vs. 3.459 Å in **1** alone). Overall, the π acid–base stacking interactions are similar to those reported for the adduct of the carbenate analogue **2** with the same fluorophore and with C_6F_6 . However, the same cannot be said regarding the $H\cdots F$ interactions, as only intra-stack $H_{\text{tolyl}}\cdots F$ interactions were described^{7b,10} in those adducts of **2**. In contrast, $1 \cdot C_{10}F_8$ exhibits both intra-stack and inter-stack $H\cdots F$ interactions, including $H_{\text{Ph(benzyl)}}\cdots F$ and $H_{\text{imidazolyl}}\cdots F$ hydrogen

bonds and $H_{\text{CH}_2(\text{benzyl})}\cdots F$ interactions with varying strength (2.50–2.68 Å). All of these $H\cdots F$ interactions are spread in 2D layers that cooperatively stabilize the supramolecular structure along with the columnar π acid–base interactions. Precedents of cooperative aurophilic/ H -bonding interactions exist for other Au(I) species.¹³

Crystals of **1** exhibit bright green luminescence even at room temperature (Fig. 3, I). Cooling leads to enhancement in the intensity and lifetime; the latter increases from $\tau = 7.8 \pm 0.5 \mu\text{s}$ at 298 K to $23.0 \pm 1.5 \mu\text{s}$ at 77 K. The broad/structureless emission profile, large Stokes' shift ($\sim 6500 \text{ cm}^{-1}$), and lifetime magnitude are consistent with an Au-centered phosphorescent emission from a largely distorted excimeric triplet state. The strong intertrimer

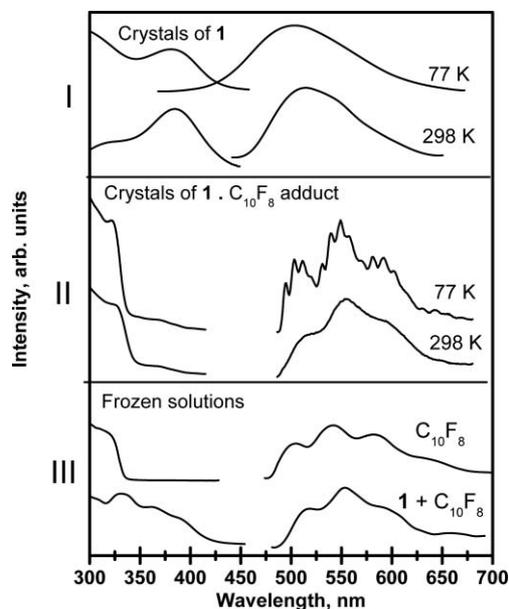


Fig. 3 Normalized photoluminescence excitation (left) and emission (right) spectra for crystals of **1** (I), crystals of $1 \cdot C_{10}F_8$ (II), and deaerated THF frozen solutions of $C_{10}F_8$ and 1 : 1 molar mixture of **1** and $C_{10}F_8$ (III).

interactions in the crystal structure of **1** support this assignment. The aurophilic association in the crystal imparts a significant red shift in the excitation bands for the solid ($\lambda_{\text{exc}} \sim 390$ nm) compared to the electronic absorption bands in dilute solution, which occur at $\lambda_{\text{max}} \sim 250$ nm in dichloromethane, assignable to metal-to-ligand charge transfer (MLCT) in monomeric **1** units.⁶ The solid powder of **1** is non-luminescent at room temperature but exhibits weak luminescence at 77 K with the same emission and excitation profile as in the crystals (Fig. S8[†]), suggesting the same crystallographic form for the microcrystalline powder.

The Au-centered green unstructured phosphorescence of **1** crystals changes qualitatively in the **1**·C₁₀F₈ solid adduct, which exhibits bright yellow emission with a structured profile. The vibronic structure becomes more resolved upon cooling to 77 K. These features are characteristic of the triplet state emission of the C₁₀F₈ arene, which alone exhibits the same emission only at cryogenic temperatures. There is no significant shift in the phosphorescence energy of **1**·C₁₀F₈ crystals vs. uncomplexed C₁₀F₈ (Fig. 3). At ambient temperature, the yellow organic-based luminescence is very bright for **1**·C₁₀F₈ but undetectable for solid octafluoronaphthalene, similar to the observation made for the analogous **2**·C₁₀F₈ adduct.¹⁰ Lifetime measurements verify that the yellow luminescence of **1**·C₁₀F₈ is phosphorescence with $\tau = 1.8 \pm 0.05$ ms at 298 K, also within the same order of magnitude obtained for the analogous **2**·C₁₀F₈ adduct. The luminescence intensity and lifetime both increase upon cooling to 77 K ($\tau = 3.8 \pm 0.08$ ms). This is expected because of the corresponding nonradiative depopulation of the emitting T₁ state of the organic π acid. The excitation bands for solid **1**·C₁₀F₈ are red-shifted from the absorption bands of the C₁₀F₈ and **1** isolated components, suggesting a charge-transfer excitation route promoted by the cooperative electrostatic attraction forces discussed above. Such a route also has been invoked in literature precedents with Au₃,¹⁰ Hg₃,⁸ and Ag₃,^{4f} triplet sensitizers. The photoluminescence spectra of frozen 2-Me-THF solutions containing equimolar amounts of **1** and C₁₀F₈ exhibit only a yellow emission with a structured profile, assigned to C₁₀F₈ monomer phosphorescence with $\tau = 12.5 \pm 0.2$ ms compared to 0.4 s for the pure C₁₀F₈ (see Fig. 3). The T₁ emission of C₁₀F₈ is drastically enhanced because the three gold centers per molecule in **1**·C₁₀F₈ provide a significant external heavy-atom effect with substantial spin-orbit coupling ($\xi_{\text{5d}} = 5100$ cm⁻¹).¹⁴

The excitation spectra for the single crystal form of $\{[\mathbf{1}][\text{C}_{10}\text{F}_8]\}_n$ or a frozen solution of a 1:1 molar admixture of **1** and C₁₀F₈ reveal a red-shifted feature that covers the spectral range of ~ 340 to 400 nm (Fig. 3). This excitation band is assignable to a charge transfer (CT) transition in the ground state adduct because it appears at lower energy than the absorption bands for dilute solutions of **1** and of C₁₀F₈, which represent monomers of these species (see ESI[†]). This CT assignment is consistent with the strongly nucleophilic character of the trinuclear Au(I) imidazolite complex, which acts as a π -base^{7c,10} that donates electron density to the π -acid C₁₀F₈. The luminescence excitation spectra suggest that this CT transition represents an additional excitation route that leads to the yellow phosphorescence of the crystalline adduct. However, while significant, this CT route is somewhat minor to the conventional route that governs the excitation mechanism of the free arene C₁₀F₈ (*i.e.*, S₀ → S_n followed by intersystem crossing to T₁)¹⁵ based on analysis of relative intensities of excitation bands.

Finally, in order to investigate possible charge transfer adducts in fluid solution, we monitored the fluorescence spectrum of dilute solutions of C₁₀F₈ in CH₂Cl₂ upon titration with **1**. Gradual quenching of arene fluorescence was observed upon incremental addition of **1**. Stern–Volmer analysis¹⁶ yields a K_{SV} value of 374 ± 5 M⁻¹ (Fig. 4). The quenching data suggest static rather than dynamic quenching, as the lifetime remains constant during the titration experiment (Fig. 4). These data suggest the formation of a *ground-state complex in solution*, *i.e.* [**1**·C₁₀F₈], with an association constant equalling K_{SV} . This complex undergoes photoexcitation as an integral binary unit, which is substantiated by the appearance of the CT excitation band in the 1:1 molar admixture of **1** and C₁₀F₈ in dichloromethane (albeit that was for a frozen solution while the fluorescence quenching is for a fluid solution). The solution quenching results here are qualitatively similar to those for naphthalene quenching by fluorinated Hg₃ and Ag₃ π -acidic complexes that have been reported by Gabbaï *et al.*⁸ and Dias *et al.*,^{4h} respectively. Solution quenching was not reported for C₁₀F₈ quenching by the π -basic Au₃ complex **2** in the preceding study by Fackler *et al.*²

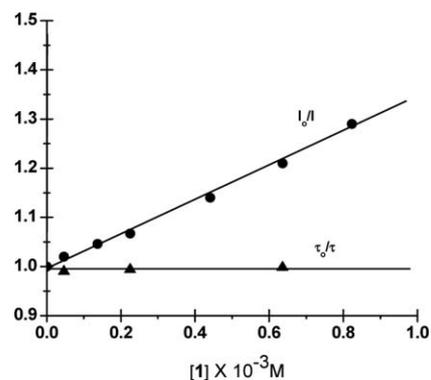


Fig. 4 Stern–Volmer plots for fluorescence quenching of C₁₀F₈ by **1**.

To conclude, this work reports an uncommon prismatic dimer-of-trimer aurophilic association for a trinuclear Au(I) imidazolite complex whose crystal structure has alluded researchers investigating this complex since the 1970s. Metal-centered green phosphorescence typical of aurophilic systems is exhibited only by single crystals of the trinuclear complex, whereas the non-crystalline material isolated in the synthesis does not exhibit detectable luminescence. Upon complexation of the electron-rich complex with perfluoronaphthalene, the aurophilic interactions are replaced by cooperative π acid–base quadrupolar and H \cdots F dipolar interactions, which in turn lead to yellow arene-centered monomer phosphorescence in the solid state or frozen solution and arene fluorescence quenching in solution.

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