Synthesis and Luminescence Studies of a Tethered, Trigonal, Silver(I) *Tris*-Alkyne Complex

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Abstract

The synthesis and characterization of a *tris*-alkyne ligand *tris*-(2-(trimethylsilyl)ethynyl-4-*tert*-butyl-benzyl)amine (**1**), and its silver(I) hexafluorophosphate complex, **1-Ag**, are reported. The solid-state structure and luminescence properties of **1-Ag** indicate relatively strong silver(I)-alkyne interactions between the metal cation and **1**. No significant changes in bond angles or lengths were observed upon metalation of **1** with Ag^+, indicating a relatively unstrained ligand-metal motif. The luminescence properties of **1** and **1-Ag** are also disclosed, showing attenuation in luminescence intensity upon Ag^+ metalation, with Stokes shifts of ~3,700 and ~3,200 cm^{-1}, for **1** and **1-Ag,** respectively. The lifetimes of **1-Ag**, τ_1 = 8.383 ± 0.053 ns and τ_2 = 4.665 ± 0.061 ns, were longer than those of **1** (τ_1 = 6.708 ± 0.085 ns and τ_2 = 3.689 ± 0.025 ns), possibly indicating multiple conformers of **1-Ag** in solution. This new Ag-alkyne platform has potential applications in studies of catalysis, luminescent compounds, and sensing.

Studies of the interactions of Ag^+ cations with alkynes are of interest in the contexts of catalysis, environmental chemistry, and luminescence. In catalysis, Ag^+ is considered one of the most efficient activators of the carbon-carbon triple bond,[1-3] allowing for a variety of alkyne-derived transformations, including cycloadditions,[4,5] (sp)C-H activation,[6,7] alkyne hydrogenation,[8,9] and others.[10-12] A key intermediate formed in these transformations are alkyne π-complexes of the Ag^+ cation.[13,14] In the context of environmental chemistry, the sensing and sequestering of Ag^+ ions in solution is of interest. Silver nanoparticles are used to prevent bacterial growth in textiles,[15] but as clothing is laundered, toxic Ag^+ can be released into wastewater streams or the body.[16,17] Considerable work has been done sensing of Ag^+ cations in solution, which could be achieved by fluorescence quenching.[18,19] Finally, in the context of luminescence, Ag-alkyne complexes have applications in sensing and medical labeling.[20,21] Two multi-metallic examples containing chelating moieties include a *tris*-Ag tweezer complex reported by Custer and coworkers in 2005,[22] and a *tris*-Au-(Ag)-acetylide complex reported by Zhou and coworkers in 2013,[23] the latter of which is shown in **Figure 1**.

Based on such applications, there is interest in the characterization of isolable silver(I)-alkyne organometallic complexes to gain insight into the bonding and electronic structure between π-donating alkyne moieties and π-accepting Ag^+ cations. Examples of recent related Ag-alkyne complexes reported in this context include an [Ag-*tris*(cyclooctyne)][PF_6] complex reported by Dias and coworkers,[13] a *tris*-alkyne *ortho*-oligophenylene ethynylene (**Figure 1**),[24] and a 1,3-diketimine derivative-supported Ag complex [N{(C_3F_7)C(Dipp)N}$_2$]Ag(EtC≡CEt) (Dipp = 2,6-diisopropylphenyl) reported by Kroll and coworkers.[25]

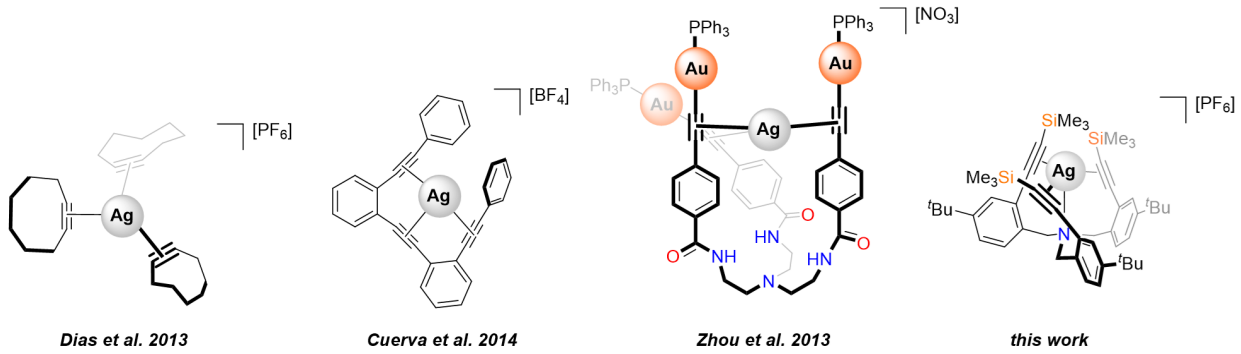
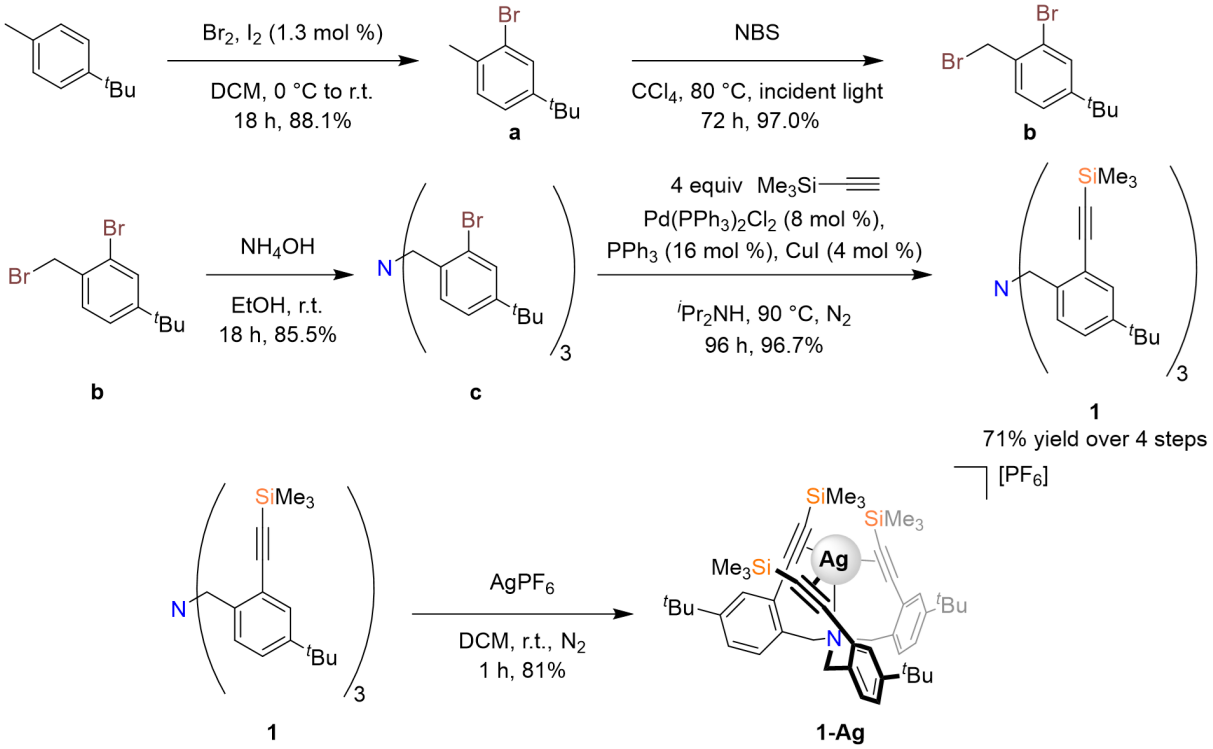


Figure 1. Selected previous silver(I) *tris*-alkyne complexes and structure described in the present work, **1-Ag**.

For the current work, we expected that tethering coordinating *tris*-alkyne moieties to a tripodal moiety would constrain the geometry and flexibility of the heptadentate silver(I)-alkyne complex compared to Ag^+ complexes with multiple bidentate ligands, without forcing an overall planar geometry comprising multiple alkyne moieties (see the *tris*-alkyne *ortho*-oligophenylene ethynylene reported by Cuerva and co-workers, **Figure 1**). This novel structural motif allows for the investigation of the metal-ligand bonding characteristics and electronic properties associated with tethered alkynes and for comparison with flexible, untethered alkynes. Herein, we describe the synthesis and characterization of a novel *tris*-alkyne ligand **1** within a tripodal ligand framework (**Figure 1**). And we report the synthesis of the tethered *tris*-alkyne silver complex **1-Ag** and the electronic, solid-state, and emissive properties of the complex. The synthesis and characterization of **1-Ag** allows for studies of the resulting properties, which indicated relatively strong silver(I)-alkyne interactions.

Synthesis of ligand **1** progressed as shown in **Scheme 1**. Iodine-catalyzed, bromine-S_NAr of 1-*tert*-butyl-4-methylbenzene yielded 2-bromo-4-*tert*-butyl-1-methylbenzene **a**. Radical bromination of **a** with *N*-bromosuccinimide (NBS) furnished 2-bromo-1-(bromomethyl)-4-*tert*-butylbenzene **b**. Ammonium hydroxide condensation of **b** yielded *tris*-benzyl amine product **c**, which was then subjected to Sonagashira cross-coupling conditions to furnish *tris*-alkyne **1** in 71% yield over four steps. X-ray quality crystals of **1** were obtained by cooling saturated chloroform solutions to 0 °C and letting the solutions stand for 18 h. The solid-state structure is shown in **Figure 2A**. The trimethylsilyl-deprotected product *tris*-(2-ethynyl-4-*tert*-butyl-benzyl)amine (**2**), not used further in this work due to its instability under basic conditions, was also isolated and characterized (see Supporting Information).



Scheme 1. Synthetic scheme for ligand **1** and complex **1-Ag**.

With **1** in hand, metalation reactions were investigated with the silver salt: $AgPF_6$. Upon addition of an equimolar dichloromethane solution of $AgPF_6$ to a stirred dichloromethane solution of **1** (**Scheme 1**), a color change from colorless to green-blue was observed. After 1 h, the solvent was removed under reduced pressure and the resultant green-blue solid was washed with pentanes to yield the silver(I) hexafluorophosphate *tris*-alkyne product, **1-Ag**, in 81% yield. Green-blue X-ray quality crystals of **1-Ag** were obtained by layering pentane upon a saturated dichloromethane solution of **1-Ag** and allowing the pentane to diffuse over the course of 24 h at –20 °C, followed by another 48 h at RT. The solid-state structure of **1-Ag** is shown in **Figure 2B**.

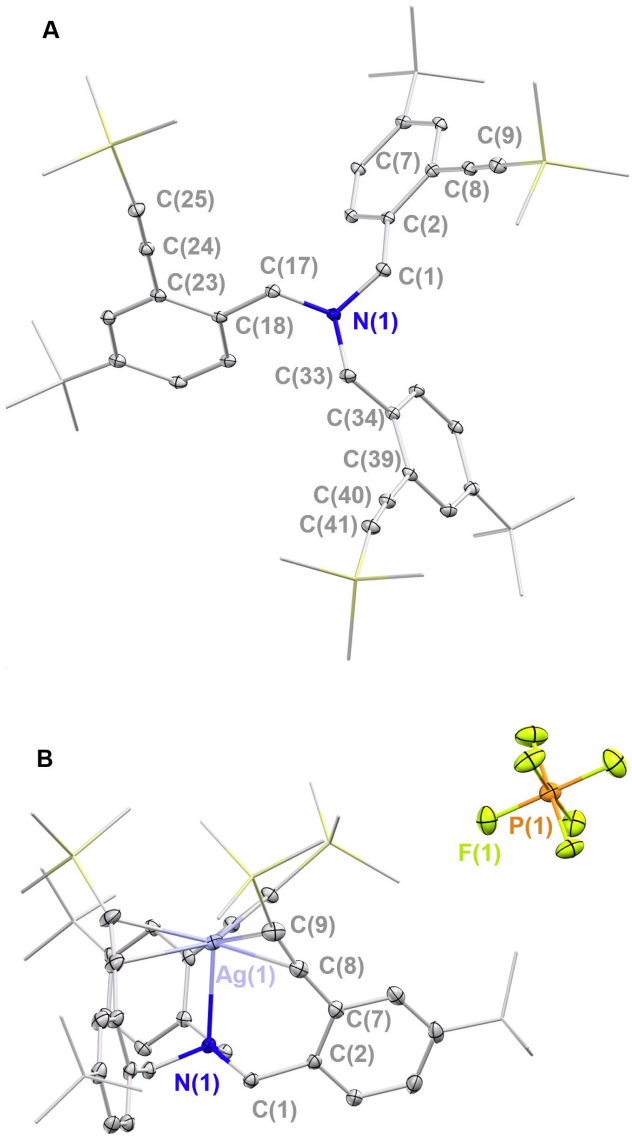


Figure 2. Solid-state structures of **1** (**A**) and complex **1-Ag** (**B**). Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Atoms are presented as thermal ellipsoids at 30% probability. *Tert*-butyl- and trimethylsilyl-groups are presented as 0.05 Å capped sticks.

^{1}H and ^{13}C{^{1}H} NMR spectroscopy of **1-Ag** showed three aromatic proton resonances and six aromatic carbon resonances, consistent with C_3-symmetry (**Figures S3** and **S4**). ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC) (**Figure S8**) allowed for unambiguous identification of three carbon doublets. The two alkyne resonances, centered at δ = 92.88 and 104.19 ppm, display Ag-C coupling constants of J = 10 and 2 Hz, respectively, consistent with reported other Ag-C alkyne coupling constants, ranging from 2-19 Hz.[26-28] The benzylic carbon resonance was also observed to show Ag-C splitting, with a coupling constant J = 1 Hz, consistent

with a two-bond interaction.[26] In sum, the $^{13}C\{^{1}H\}$ NMR is consistent with the structure shown in **Figure 2B**, with central Ag^+ cation bonding to both alkyne carbons and splitting the third benzylic carbon through the bridgehead N-atom. ^{1}H NMR spectroscopy revealed that the benzylic peak, recorded at δ = 3.84 ppm for **1**, was split into two broad doublets at δ = 3.99 and 3.29 ppm for **1-Ag**, consistent with helical chirality introduced to the complex following metalation.

Although direct observation of the ^{109}Ag or ^{107}Ag resonances was impractical due to the long relaxation times and low gyromagnetic ratios associated with these nuclei,[29] a ^{109}Ag chemical shift at δ = 991 ppm was observed using ^{1}H-^{109}Ag heteronuclear single quantum coherence (HSQC) NMR (**Figure S9**). The Ag^+ cation interacted with only one of the two benzylic protons at δ = 3.29. No cross-peaks were observed for the other benzylic proton at δ = 3.99, signifying different chemical environments experienced by the two diastereotopic protons. The ^{109}Ag chemical shift δ = 991 is indicative of a deshielded Ag nucleus, with ^{109}Ag chemical shift values reported at δ = 900-1100 for molecular (electron-withdrawing) Ag carboxylate species,[29-31] δ = 500-800 for σ-donating, π-accepting N-heterocyclic carbene (NHC) Ag^+ complexes,[32,33] and δ = 0-300 for aqueous or DMSO-solvated Ag^+ cations.[29,34] This deshielded Ag^+ cation is characteristic of Ag-alkyne interactions due to the Ag d^{10} electron donation in π-accepting alkyne systems,[35] with representative Ag-alkyne chemical shift values including δ = 988[36] and 856.[37]

The **1-Ag** solid-state structure similarly revealed pseudo C_3-symmetry and heptadentate coordination at the Ag^+ cation. The C≡C average bond distance did not lengthen at a statistically significant level between **1** (1.204(5) Å) and **1-Ag** (1.214(10) Å). No significant changes in either the tripodal N-CH_2-C angle or the aryl-alkyne angle (such as the C(2)-C(8)-C(9) angle) were observed, with average N-CH_2-C angles of 113.1(4)° and 113.5(5)° for **1** and **1-Ag**, respectively, and aryl-alkyne angles of 120.7(3)° and 120.6(6)° for **1** and **1-Ag**, respectively. In contrast, the average alkyne-silicon angle (such as the C(8)-C(9)-Si(1) angle) narrowed by an average of 12.1 degrees, from 172.5(6)° for **1** to 160.4(8)° for **1-Ag**, a phenomenon observed in other silver alkynes upon η^2 coordination (**Table S1**).[25] The Ag^+ cation was also observed to be coordinated by the bridgehead *N*-atom, with an Ag(1)-N(1) bond length of 2.423(3) Å. In sum, these data point to a conformationally unstrained, heptadentate Ag^+ complex.

Infrared (IR) spectroscopy revealed a shift of 66 cm^{-1} of the $\nu_{C\equiv C}$ stretch from 2156 cm^{-1} of the free ligand **1** to 2090 cm^{-1} of complex **1-Ag** (**Figure S16**). This shift lies between the 34-79 cm^{-1} shifts reported by Noonikara-Poyil and coworkers for Ag^+ coordination to acetylene,[38] and larger shifts such as that described by Dias and coworkers upon diethylacetylene coordination (136 cm^{-1}).[25] The change in C≡C stretching frequency is used to determine relative degree of π-

backbonding between electron-rich d^{10} metals and π-accepting alkyne moieties.[25,39] Increased π-donation into a ligand-based π* antibonding orbital decreases the bond order of alkynes, increasing the bond length and decreasing the $\nu_{C\equiv C}$ stretching frequency. The 136 cm^{-1} shift discussed above or the 162 cm^{-1} shift described by Lang and coworkers[39] are some of the largest reported shifts. The comparatively small shift in the present case, coupled with no statistically significant change in C≡C bond length, points to a relatively small degree of Ag π-backdonation to coordinating alkynes compared to other Ag^{+}-alkyne complexes. Compared to other Group 11 metals, Ag is known to exhibit relatively low pi-backdonation with alkynes, and in the present case, the IR shift is smaller than shifts for Au or Cu alkyne complexes, which have been reported to show IR shifts of 175-367 cm^{-1}.[25,40,41]

With the bonding of **1-Ag** established, we next turned to **1-Ag** photoluminescence spectroscopy. UV-visible (UV-vis) spectroscopy showed absorption starting at 650 nm for **1-Ag**, conferring the characteristic green-blue color, and absorption starting at 450 nm for **1** (**Figure 3A**). For photoluminescence experiments, the excitation wavelength 375 nm was selected due to the strong absorption of both compounds in this spectral region. Upon excitation, **1** and **1-Ag** exhibited broad emission bands with emission maxima at 440 and 436 nm with FWHMs of ~3,800 and ~3,600 cm^{-1}, respectively (**Figure 3B**).

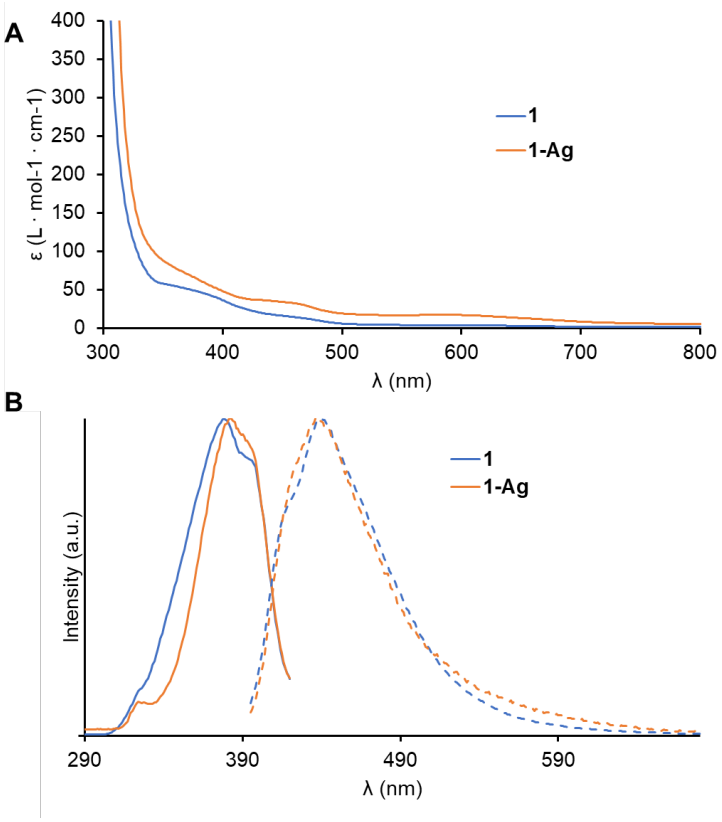


Figure 3. (**A**) UV-Vis spectra of **1** and **1-Ag** in CH_2Cl_2 (10 mM). (**B**) Normalized excitation (solid lines, 440 nm emission wavelength) and emission (dashed lines, 375 nm excitation wavelength) spectra of **1** and **1-Ag** in CH_2Cl_2 (10 mM).

While the normalized emission profiles of **1** and **1-Ag** are similar, the emission intensity of **1-Ag** was attenuated compared to **1**, which can be ascribed to higher self-quenching due to the increased absorptivity at the fluorescence emission maximum wavelength displayed by **1-Ag** compared to **1**. Similar fluorescence quenching has been previously observed in Ag^+-alkyne complexes,[24] as well as other emissive compounds upon addition of Ag^+.[42,43] The corresponding excitation spectra of **1** and **1-Ag** displayed broad excitation bands with excitation maxima located at 378 and 383 nm, respectively. The excitation bands in both spectra contain an intense low-energy shoulder at 400 nm and a weak high energy feature at 326 nm. The Stokes shifts for **1** and **1-Ag** were determined to be ~3,700 and ~3,200 cm^{-1}, respectively. The reduced Stokes shift observed for **1-Ag** suggests that coordination of **1** to the silver ion inhibits nonradiative vibrational relaxation processes. The similarities between the excitation and emission spectra of **1** and **1-Ag** and the energies of the transitions indicate that the luminescent behavior of both species originates from intraligand π–π* transitions, a phenomenon observed in the literature for other aryl organometallic complexes.[44]

Fluorescence lifetime measurements were obtained for **1** and **1-Ag** at 360 nm excitation (**Figures S29** and **S30**). Optimized multi-exponential fits obtained for **1** and **1-Ag** yielded two decay processes for each compound. The lifetimes of **1-Ag**, τ_1 = 8.383 ± 0.053 ns and τ_2 = 4.665 ± 0.061, were longer than those of **1**, τ_1 = 6.708 ± 0.085 ns and τ_2 = 3.689 ± 0.025, and both fell within the range of previously reported lifetimes for arylacetylenes and structurally comparable Group 11 alkyne complexes.[24,45-47] Multiple fluorescence decay lifetimes have previously been observed in OPE foldamers and were attributed to the presence of multiple emissive conformers in solution.[24] Here, a similar mechanism may be operative, in which **1** and **1-Ag** rapidly interconvert between two emissive conformations.

We have disclosed the synthesis and characterization of a tethered, *tris*-alkyne ligand and demonstrated its ability to bind Ag^+ cations. After Ag^+ coordination, few significant changes in ligand bond lengths or angles were observed, speaking to the relatively unconstrained nature of the complex **1-Ag**. Photoluminescence spectroscopy indicated that the luminescent behavior of **1-Ag** likely originated from ligand π–π* transitions, rather than transitions implicating the Ag^+ metal cation. These studies also suggest that the excited state of the complex was relatively long-lived compared to the free ligand, and that multiple emissive **1-Ag** confirmers may exist in **1** and

1-Ag solutions. These results provide insights into the nature of Ag^+/alkyne π-complexes, a common motif in luminescent compounds and catalysis.

Associated Content

The Supporting Information is available free of charge on the ACS Publications website at XXX:

Experimental, NMR/IR/UV-Vis spectra, crystallography, photoluminescence details (PDF).

Accession Codes

CCDC deposition numbers 2345078-2345080 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Acknowledgements

The authors thank the National Science Foundation (CHE-1955724) for financial support of this work. The authors also thank the University of Pennsylvania for support. M.H.F. thanks Cameron B. Berlin and Cassandra D. Vu (Kozlowski Group, University of Pennsylvania) for assistance and advice with organic synthesis and purification.

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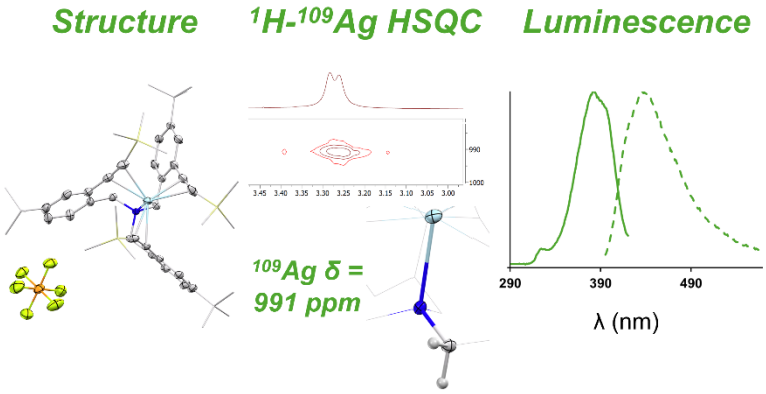
TOC Graphic



Synopsis

The synthesis and characterization of a tethered, trigonal *tris*-alkyne silver(I) complex is presented. Structural, spectroscopic, and luminescence studies offer insights into the nature of the silver-alkyne π-interactions, a motif with interest in the fields of luminescence, separations, and catalysis.