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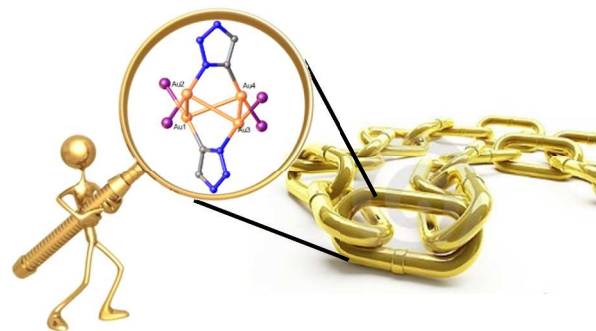
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Cluster formation via multiple gold-gold bonds provides sufficient thermodynamic driving force to overcome entropic penalties to link multiple units and create solution stable organogold oligomers.



ARTICLE

Organogold oligomers: exploiting iClick and aurophilic cluster formation to prepare *solution* stable Au₄ repeating units.

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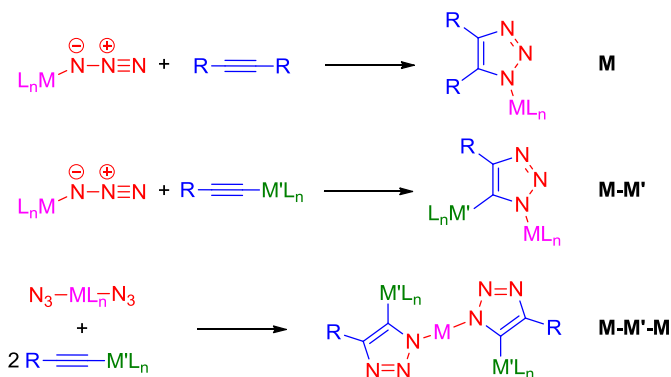
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A novel synthetic method to create gold based metallo-oligomers/polymers via the combination of inorganic click (iClick) with intermolecular aurophilic interactions is demonstrated. Complexes [PEt₃Au]₄(μ-N₃C₂C₆H₅) (**1**) and [PPhMe₂Au]₄(μ-N₃C₂C₆H₅) (**2**) and {[PEt₃Au]₄[(μ-N₃C₂)₂-9,9-dihexyl-9H-fluorene]}_n (**8**) have been synthesized via iClick. The tetranuclear structures of **1** and **2**, induced by aurophilic bonding, are confirmed in the solid state through single crystal X-ray diffraction experiments and in solution via variable temperature NMR spectroscopy. The extended 1D structure of **8** is constructed by aurophilic induced self-assembly. ¹H DOSY NMR analysis reveals that the aurophilic bonds in **1**, **2**, and **8** are retained in the solution phase. The degree of polymerization within complex **8** is temperature and concentration dependent, as determined by ¹H DOSY NMR. Complex **8** is a rare example of a solution stable higher ordered structure linked by aurophilic interactions.

Introduction

Building complex molecules and materials¹⁻⁵ from simple building blocks is an important component of modern synthetic chemistry, and is one of the principle design features of Click chemistry.⁶ Critical in the pursuit of building complexity is the precise control of bond forming events and is particularly exemplified by the Cu^I catalyzed azide-alkyne cycloaddition reaction (CuAAC).⁷⁻⁸

Scheme 1. iClick reactions.



Taking a new approach, we recently demonstrated the cycloaddition between a metal-azide with a metal-acetylide to form triazolate bridged dinuclear (M-M')⁹ and trinuclear (M-M'-M)¹⁰ complexes (Scheme 1), which are already rather prevalent reactions,¹³⁻²⁵ and the subject of reviews.²⁶⁻²⁷ It is

reasonable to expect many other reactions within a coordination sphere, that serve to link subunits and build complexity, can be categorized as iClick reactions.

Another fascinating linkage is the gold-gold bond. Characterized as only having the approximate strength of a hydrogen bond,²⁸ the aurophilic interaction is not necessarily the first choice a chemist employs to build higher ordered structures or add complexity. Within the confines of the solid state though, Au-Au bonds can support higher ordered structures in the form of coordination polymers, clusters, and networks.²⁹⁻³⁰ The structures fall into three distinct categories. One type involves main chain gold-gold linkages between mono-nuclear gold units that feature small ligands. Prototypical examples include [(TPA)₂Au][Au(CN)₂] and (TPA)AuCl (TPA = 1,3,5-triaza-7-phosphaadamantane),³¹ and (RNC)AuCN (R = Me,³² ^tBu,³³ ⁱPr,³⁴ Cy,³⁴ ⁿBu³⁴). Phosphine gold acetylide complexes also provide this type of structure in the solid state. Recently, Lima et al. reported the gold complex [Au{7-(prop-2-ine-1-yloxy)-1-benzopyran}(DAPTA)] (DAPTA = 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane) which has a zigzag 1D chain self-assembled via aurophilic interactions.³⁵

For the second type, organic linking units separate the gold atoms within the main chain. Common linkers include diphosphines, diacetylides and diisocyanides.³⁶ Lima et al. reported the polymeric complex [(dppe)Au₂(C≡CC₅H₄N)]_n (dppe = diphenylphosphine ethane) in which the dppe ligand serves as the bridge.³⁷ Puddephatt reported the polymeric gold complexes {[PMe₃Au]₂R}_n (R = 1,4-diacetylide-2,5-dimethyl benzene) and [(PhC≡C)AuRAu(PhC≡C)]_n

(R = 1,4-diisocyanide-2,5-*t*-butyl benzene) that feature diacetylide and diisocyanide linkers, respectively.³⁸⁻³⁹

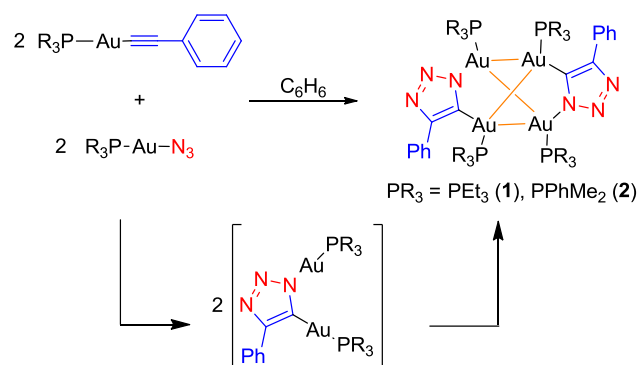
For the third type, the main chain of the polymer consists of only gold atoms, similar to the first type, however; instead of having mono-nuclear gold complexes as building blocks, the linking units contain multiple Au ions. An example by Eisenberg et al. of a di-gold repeat unit that aggregates in the solid state via aurophilic interactions is $[\text{Au}_2(\mu\text{-TU})(\mu\text{-dppm})](\text{CF}_3\text{COO})$ (TU = 2-thiouracil, dppm = diphenylphosphine methane). It is interesting to point out that the gold atoms in the polymer chain have a helical arrangement.⁴⁰ For tri-nuclear complexes, Balch et al. demonstrate that $[\text{Au}_3(\text{py})_3]$ (py = pyridine) units self-associate through two types of intermolecular aurophilic interactions to provide a stair-like extended structure in the solid state.⁴¹ In solution however, only a few oligomeric compounds featuring Au-Au linkages as the primary propagating backbone bond have been reported;⁴²⁻⁵⁰ but they are either unstable at ambient temperature, or lack conclusive data supporting higher ordered structures.

Understandably, in solution large entropic penalties to self-assemble units overwhelm the weak enthalpy of the aurophilic interaction and the units break apart. This work combines iClick synthesis and the manipulation of aurophilic interactions to build higher ordered structures. For the first time, cluster formation via multiple gold-gold bonds provides sufficient thermodynamic driving force to overcome entropic penalties to link multiple units and create solution stable organogold oligomers, even at 50 °C.

Results and discussion

Prior to realizing the synthesis of higher ordered compounds, it was important to first understand the strength of gold-gold bonds within a Au-cluster, and the ancillary ligand size requirements to permit oligomerization. Treating $\text{PR}_3\text{AuC}\equiv\text{CC}_6\text{H}_5$ ⁵¹⁻⁵² with one equiv of PR_3AuN_3 (R = Et,¹⁵ PhMe₂) in benzene (25 °C) provides the tetranuclear clusters $[\text{PR}_3\text{Au}]_4(\mu\text{-N}_3\text{C}_2\text{C}_6\text{H}_5)_2$ (PR₃ = PEt₃ (**1**), PPhMe₂ (**2**); Scheme 2). Both **1** and **2** precipitate from benzene as off-white crystalline powders in good yield (83%; **1**, 82%; **2**). During the reaction, the azide-acetylide cycloaddition product (iClick) forms initially, and then dimerization via aurophilic interactions generates the tetranuclear gold clusters. The preparation of **1** and **2** mirrors the previously reported synthesis of the nitro-substituted analog $[\text{PR}_3\text{Au}]_4(\mu\text{-N}_3\text{C}_2\text{C}_6\text{H}_5\text{NO}_2)_2$ (**1-NO₂**).¹⁰

Scheme 2. Synthesis of tetranuclear clusters **1** and **2** via iClick.



Single crystals of both **1** and **2** grow via slow diffusion of pentane into a methylene chloride solution of the complexes. Single crystal X-ray diffraction experiments performed on crystals of **1** and **2** provide their unambiguous assignment as tetranuclear gold clusters (Figure 1). The metric parameters for both complexes are similar, thus only complex **1** will be discussed in detail (see ESI for full details). Complex **1** crystallizes in the orthorhombic Pna2₁ space group. Holding the cluster together are four Au-Au bonds that create a C₂-symmetric distorted tetrahedron geometry. The Au¹-Au¹ contacts that range from 3.0334(4) Å for Au³-Au⁴ to 3.1318(4) Å for Au²-Au³, and average of 3.0678(4) Å, are within the acceptable length of a Au¹-Au¹ bond.⁵³⁻⁵⁴ The distortion from a pure tetrahedron is a consequence of two gold ions being held apart and across the triazolide bridge. For example, the distance between Au¹-Au³ and Au²-Au⁴ are 3.938 (4) Å and 3.973 (4) Å, respectively, and are beyond the distance recognized for aurophilic interactions (3.6 Å).

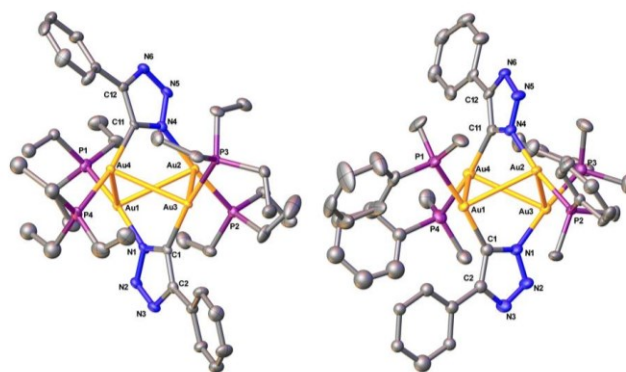


Figure 1. Crystal structures of **1** (left) and **2** (right). H atoms and disordered atoms are removed for clarity.

Consistent with the solid state C₂-symmetric structure, the ³¹P{¹H} NMR spectrum of complex **1** exhibits two resonances at 20.64 and 31.69 ppm corresponding to the PAuN and PAuC atoms, respectively. For **2**, the corresponding PAuN and PAuC signals shift upfield to -1.50 and 11.79 ppm. A consequence of the low symmetry within complex **2** is the methyl groups within the PPhMe₂ ligands are diastereotopic and appear as four distinct doublets (ESI figure S6). The diastereotopic methyl groups are conclusive evidence that the cluster remains intact in

solution because dissociation into the C_2 -symmetric digold intermediate would manifest only two doublets. Though it is likely many tetragold complexes are stable in solution, only a few are conclusively characterized.⁵³⁻⁵⁶

^1H DOSY NMR experiments performed on complexes **1** and **2** in CDCl_3 provide diffusion coefficients D of $6.96 \pm 0.03 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for **1** and $6.25 \pm 0.03 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ for **2**. Employing the modified Stokes-Einstein equation,⁵⁷⁻⁵⁸ the experimentally determined values of D for **1** and **2** convert into hydrodynamic radii (r_H) of 6.50 and 7.12 Å, respectively. These hydrodynamic radii values match well with the calculated values of 6.60 and 6.63 Å, as determined by the volume of the complexes obtained from the X-ray data (Table 1). Matching the experimentally determined hydrodynamic radii from DOSY and X-ray data serve to calibrate the NMR technique and provide a measure of confidence for subsequent evaluation of oligomeric species that do not have solid state characterization.

Table 1. ^1H DOSY NMR determined diffusion coefficients and estimates of hydrodynamic radii (r_H).

Complex	Diffusion Coeff. (D)	Hydrodynamic radius (r_H) ^c
1 ^a	$6.96 \pm 0.03 \times 10^{-10} \text{ m}^2\text{s}^{-1}$	6.50 (6.60) Å
2 ^a	$6.25 \pm 0.03 \times 10^{-10} \text{ m}^2\text{s}^{-1}$	7.12 (6.63) Å
8 ^b	$0.35 \pm 0.01 \times 10^{-10} \text{ m}^2\text{s}^{-1}$	89.9 (n/a) Å

^aExperiments performed in CDCl_3 at 25 °C and 50 μM . ^bExperiment performed in C_6D_6 at 25 °C and 50 μM . ^cValue determined by diffusion coefficient D (value estimated from X-ray crystal structure).

It is possible however to purposely break apart the cluster in solution. Dissolving complex **1** in polar $\text{DMSO-}d_6$ causes dissociation and equilibrium establishes between the tetranuclear cluster and the corresponding digold intermediate. Increasing the temperature beyond 80 °C completely dissociates the tetranuclear cluster. A variable temperature NMR experiment and analysis yields $\Delta H = 13.48 \pm 0.22 \text{ kcal}\cdot\text{mol}^{-1}$ and $\Delta S = 45.71 \pm 0.70 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the dissociation process (Figure 2). The large and positive entropic term is consistent with an increase in entropy as the cluster breaks into two parts and is unfavorable at lower temperatures. Considering the rarity of tetranuclear gold clusters that remain intact in solution, it is interesting to note that dissociation of **1** in DMSO actually becomes non-spontaneous at temperatures below 21.7 °C. Remarkably, only about 20% of **2** dissociates at 80 °C in $\text{DMSO-}d_6$. Unfortunately, variable temperature experiments do not provide thermodynamic parameters for the dissociation of **2** due to overlapping resonances and peak broadening. However, the greater stability of **2** versus **1** is consistent with the steric argument that PPhMe_2 is smaller than PEt_3 (the cone angle⁵⁹ of PPhMe_2 is 122° and that of PEt_3 is 132°), and thus creates a more tightly bound Au_4 cluster.

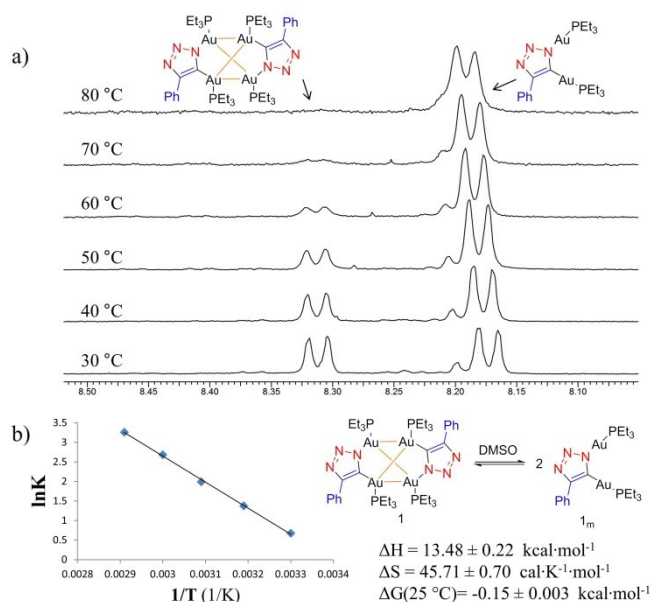
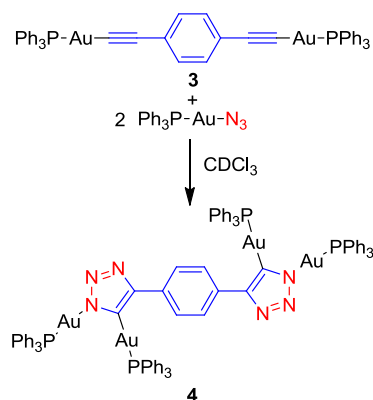


Figure 2. a) Variable temperature ^1H NMR spectra (8.10-8.30 ppm region) of the dissociation of complex **1** in $\text{DMSO-}d_6$ from 30-80 °C. b) Van't Hoff plot ($\ln K$ vs $1/T$).

Considering the tetranuclear cluster remains intact in chloroform, it seemed reasonable that the multiple auriphilic interactions within the cluster would collectively be strong enough to generate polymeric or oligomeric compounds. Employing a single alkyne unit in the preparation of **1** and **2** by default terminates the complex in a tetranuclear cluster. However, employing a diacetylide unit provides the means to propagate the interaction. The first step was to determine if two iClick reactions could occur within a single unit. To stop the reaction at the initial iClick stage and purposely prevent formation of the tetranuclear cluster, the larger PPh_3 (cone angle = 145°) ligands were incorporated. Thus, treating the diacetylide complex **3**⁶⁰ with two equiv of PPh_3AuN_3 ¹⁴ in CDCl_3 at room temperature for 2 days provides complex **4** as colorless crystals in 68% yield (Scheme 3). Complex **4** precipitates during the course of the reaction and is insoluble in all standard solvents. Fortunately, complex **4** grows as analytically pure (validated by combustion analysis) single crystals suitable for X-ray crystallographic interrogation.

Scheme 3. iClick synthesis of tetragold complex **4**.



In the solid state (Figure 3), complex **4** is pseudo- C_{2h} symmetric and crystallizes in the $P1$ space group with two chloroform lattice molecules. The coordination geometries of the gold atoms are nearly linear; $N1-Au1-P1 = 173.81(10)^\circ$ and $C1-Au2-P2 = 174.50(12)^\circ$. One of the most important structural features is the $-C_6H_4-$ ring links two 1,5-*bis*-triphenylphosphine gold-1,2,3-triazolates formed during the iClick reaction. Interestingly, the bridging $-C_6H_4-$ linker lies coplanar to the two triazolates with dihedral angles of only $\sim 2.5^\circ$ and $\sim 3.0^\circ$, indicative of electron delocalization across the ring system.

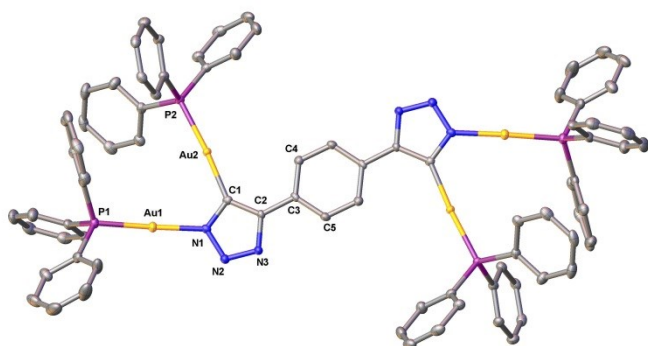
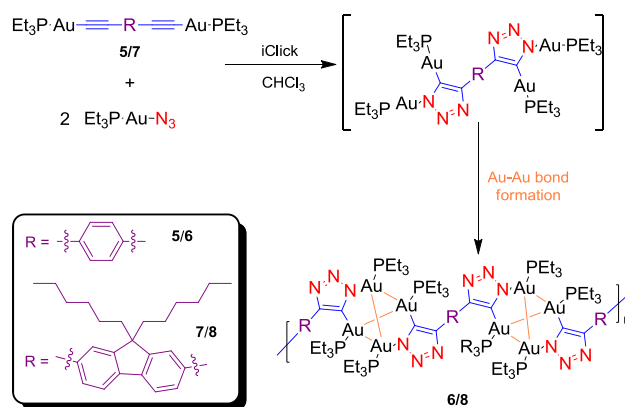


Figure 3. The crystal structure of tetragold complex **4**. H atoms and lattice chloroform molecules are removed for clarity.

Characterization of complex **4** provides ample evidence that two iClick reactions can occur across a diacetylide unit. The large PPh_3 ligands serve to prevent tetranuclear cluster formation. Thus, reducing the size of the PR_3 ligands should activate Au_4 cluster formation and promote oligomerization. Scheme 4 depicts the general concept for inducing higher order materials. In the first step two iClick reactions provide the bridged tetragold unit (analogous to **4**). In the second step, as long as the R_3P group is small enough, step growth polymerization via Au^I-Au^I bond formation provides oligomers. PEt_3 derivatives of the complexes in Scheme 4 were prepared as a proof of concept. Treating $[PEt_3Au]_2(C\equiv CC_6H_4C\equiv C)$ (**5**) with two equiv of PEt_3AuN_3 in $CDCl_3$ at $40^\circ C$ for two days provides reddish-brown **6** that precipitates from the reaction medium as a powder during the course of the reaction. The material is insoluble in all common solvents, and unlike complex **4**, the material does not deposit as single crystals. An

IR spectrum of **6** indicates both the azide (2053 cm^{-1}) and the acetylide stretches (2110 cm^{-1}) are absent and a new stretch assigned to the triazolate ring appears at 1610 cm^{-1} (see ESI). The IR data is conclusive evidence that the iClick reaction is complete. Complex **6** is tentatively assigned as an oligomer. Unfortunately, poor solubility thwarted attempts to ascertain if multiple units are bound within a chain. Moreover, a powder X-ray diffraction experiment confirmed the material is amorphous (see ESI). Some evidence points toward complex **6** being higher ordered. For example, complex **4** is colorless yet complex **6** is highly colored (red-brown). If **6** is simply a tetranuclear species analogous to **4**, it too would presumably be colorless. Confirmation of a higher order species however, requires the material to be soluble, and thus a soluble version of **6** was sought.

Scheme 4. Construction of organogold oligomers via iClick and aurophilic interactions.



Switching the organic linking R-group to 9,9-dihexyl-9H-fluorene provides first the diacetylide **7** in good yield (63%) as a light yellow solid. Next, treating **7** with Et_3PAuN_3 in C_6D_6 at $37^\circ C$ for 48 h provides *soluble* oligomeric **8**. Upon removal of all volatiles, the solid does not redissolve in hydrocarbon solvents, however it readily dissolves in chlorinated solvents. Attempts to grow single crystals of **8** were unsuccessful. Instead, 1H DOSY NMR experiments provide conclusive evidence that **8** is oligomeric. The first evidence that **8** is at least larger than a single Au_4 unit comes from a comparison of its diffusion coefficient with **1** and **2** (Table 1). Compared to **1** ($6.96 \pm 0.03 \times 10^{-10}\text{ m}^2\text{s}^{-1}$) and **2** ($6.25 \pm 0.03 \times 10^{-10}\text{ m}^2\text{s}^{-1}$), the diffusion coefficient for complex **8** is dramatically smaller ($0.35 \pm 0.03 \times 10^{-10}\text{ m}^2\text{s}^{-1}$) and corresponds to a hydrodynamic radius of 89.9 \AA . In addition, conclusive evidence for oligomer formation comes from a variable concentration study. The magnitude of the diffusion coefficient decreases as the concentration of **8** increases indicating a growth in the degree of oligomerization. To calibrate, the TMS signal was monitored, and its diffusion coefficient does not change (Table 2). Therefore, the change in D observed is compelling evidence that the degree of oligomerization increase with concentration. Finally, the degree of oligomerization was reduced purposefully. Complex **8** was dissolved in C_6D_6 and cluster **1**,

acting as a terminating/capping group, was titrated into the solution. As the concentration of **1** increases, multiple species appear in solution, as determined by ^{31}P NMR spectroscopy (see ESI). The new species are due to the complex **8** being broken apart, and confirming this, the new species exhibit larger diffusion coefficients, i.e. they are smaller than **8** (ESI). Finally, as a testament to the strength of the aurophilic interaction within the Au_4 linkage, the normalized diffusion coefficient for complex **8** (see ESI) does not change significantly as a function of temperature. Thus, the linkages remain intact not only in solution, but even at elevated temperatures (50°C). Only after heating above 55°C does the diffusion coefficient increase, signaling the dissociation of oligomeric **8**.

Table 2. Concentration dependent diffusion coefficients for **8**.^a

[8]	10 μM	20 μM	30 μM
Region	\mathbf{D} ($10^{-10} \text{ m}^2\text{s}^{-1}$)	\mathbf{D} ($10^{-10} \text{ m}^2\text{s}^{-1}$)	\mathbf{D} ($10^{-10} \text{ m}^2\text{s}^{-1}$)
9 ppm	1.05 ± 0.03	0.89 ± 0.03	0.52 ± 0.02
8 ppm	1.05 ± 0.04	0.97 ± 0.03	0.53 ± 0.03
2 ppm	1.07 ± 0.03	0.92 ± 0.03	0.56 ± 0.02
average	1.06 ± 0.06	0.93 ± 0.05	0.54 ± 0.04
TMS	21.25 ± 0.32	n/a	20.78 ± 0.64

^a Diffusion coefficients for $5 \mu\text{M}$ ($1.39 \pm 0.10 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) and $50 \mu\text{M}$ ($0.35 \pm 0.10 \times 10^{-10} \text{ m}^2\text{s}^{-1}$) were determined from one region.

Additional proof complex **8** has an extended structure in solution comes from emission data. Figure 4a depicts the emission spectra of the previously synthesized⁹ digold complex **9** and the Au_4 cluster **1**. It is clear that no emission occurs upon excitation at 285 nm for the digold complex **9**; however, complex **1** exhibits an emission band at 324 nm, and is attributable to the Au-Au bond. These data offer strong support that the Au_4 cluster remains intact in solution. Figure 4b depicts emission data for oligomer **8** when dissolved in DCM and DMSO-DMAC (1/1 v/v) and excited again 285 nm. The emission band at 324 nm is identical to the emission band for the cluster complex **1** indicating the oligomer retains the Au_4 linkage in

solution. In contrast, in the more polar solvent mixture of DMSO-DMAC no emission occurs indicating the Au_4 linking unit must dissociate. Dissociation in DMSO-DMAC is consistent with NMR studies of cluster **1** in DMSO- d_6 (see Figure 2 above). Previously reported, the degree of oligomerization of $\text{K}[\text{AuCN}]$ through aurophilic interactions greatly influences the emission spectra. Specifically, as the degree of oligomerization increases, the emission band shifts to lower energy.⁴⁴⁻⁴⁵ Oligomer **8** exhibits the same phenomenon. Excitation at 353 nm results in emission from the fluorene moiety in oligomer **8**. Comparing the emission band of the $50 \mu\text{M}$ sample with that of the $5 \mu\text{M}$ sample, there is a significant red shift (18 nm). The red shift at higher concentration is indicative of an increase in the degree of oligomerization, which is also consistent with the variable concentration DOSY NMR data already discussed above (Table 2).

Conclusions

Materials that incorporate gold-gold bonds are important from the standpoint of their unique luminescent properties⁶¹⁻⁶³ and crystal engineering.²⁹⁻³⁰ However, the majority of these materials only retain their aurophilic interactions within the solid state, and therefore solution processing is not possible. The paucity of solution stable oligomeric/polymeric materials that feature gold-gold bonds as the linking repeat unit is well understood from the inadequate gold-gold bond strength. In this work, the inadequacy is overcome by incorporating *four* aurophilic interactions into each repeating linkage in the form of a self-assembling organo- Au_4 cluster. The iClick reaction that first forms the intermediate digold subunit plays an important role, in that access to such a species would be challenging in the absence of the newly discovered metal-azide/metal-acetylide cycloaddition.⁹⁻¹⁰ This work opens new opportunities for exploiting aurophilic interactions to build complex structures, not only in the solid state, but in solution too.

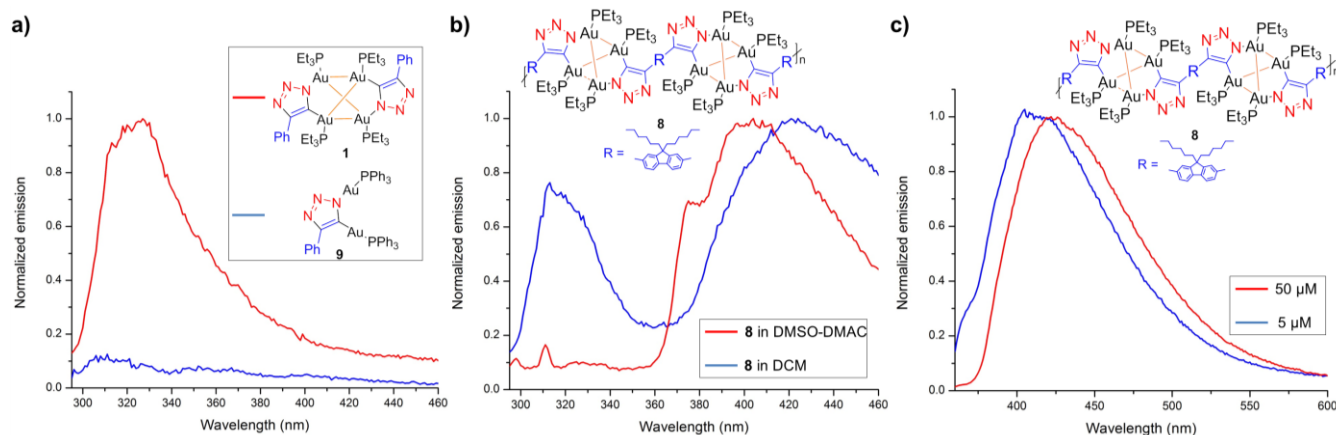


Figure 4. a) Normalized emission spectra of complex **1** and **9** in CH_2Cl_2 at 298 K (excited at 285 nm). b) Normalized emission spectra of complex **8** in different solvents: DCM and DMSO-DMAC (1/1, v/v) at 298 K with concentrations as $20 \mu\text{M}$ for both (excited at 285 nm). c) Normalized emission spectra of complex **8** at 5 and $50 \mu\text{M}$ in DCM (excited at 353 nm).

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Notes and references

University of Florida, Department of Chemistry, Center for Catalysis, P.O. Box 117200, Gainesville, Florida, 32611. Electronic Supplementary Information (ESI) available: ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, 2-D NMR spectra, IR, UV-vis absorption and emission and crystallographic data. This material is available free of charge via the Internet at <http://pubs.rsc.org/>.

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