Phosphorescent Organometallic Knots of Gold(I)-Bis(acetylide) Strands Directed by Copper(I) π -Coordination

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Abstract

Through elaborate ligand design to create knotted structures with specific topologies is a major challenge for chemists. In this work, the self-assembly between U-shape 3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole (H_2L) and Au^+ through gold(I)-bis(acetylide) linkages under π -bonded Cu^+ template gives rise to complex 1 with two interlocked metallostrands as well as complexes 3 ($n = 3$) and 4 ($n = 4$) with $[(AuL)_n]^{n-}$ metallostrands showing trefoil knot topology. Upon incorporating two $[Au(dppb)Au]^{2+}$ (dppb = $Ph_2P(CH_2)_4PPh_2$) moieties through bis(Au-acetylide) coordination bonds, the interlocked structure (1) is fully closed to form a figure-eight knotted structure in complex 2. The folding and threading of metallocyclic strings are directed by Cu^+ , which are π -ligated to two or three acetylides to generate double-folding or triple-folding cross points. Complexes 1-4 show intense phosphorescence in both solutions and solid states at ambient temperature, originating from admixture of metal centered $^3[d\sigma p/s]$, 3IL (intraligand), and $^3[p(L) \otimes s/p(Au/Cu)]$ 3LMCT triplet states.

Background

As an important member of non-trivial topological family, knots are not only basic moieties of structures, but also ubiquitous in nature.¹⁻⁴ However, achieving artificially knotted molecules still remains a great challenge for synthetic chemists.⁵⁻²⁸ The most intensively studied strategy is a stepwise metal template approach, in which nitrogenous ligands are firstly pre-organized to fold, intersect, and interpenetrate under the coordination template effect of metal ions, followed by the end-connection of coordination strands through organic coupling reactions.^{1-4,10-13,15,16} By comparison, direct synthesis of molecular knots in one-step reactions^{9,14,17,19,22,27} through self-assembly of metal coordination is more elusive in most cases. Other weak interactions such as hydrogen bond,^{5,6} hydrophobic effect,^{7,8} p-p stacking,⁹ etc are also exploited as driven forces to attain knotted molecules. After decades of development, prime knots with different topological structures have been artificially realized.¹⁰⁻²⁸ But to date, only a limited number of building blocks are available for constructing molecular strands that allow to twist, fold and interpenetrate, which is one of the main factors that cause quite limited types and quantities of synthetic knot structures. Thus, developing new synthons or modulars that allow the strands or strings to twist, fold and interpenetrate before closure are highly significant for achieving artificially knotted molecules with specific topologies.

It is known that d^{10} metal-acetylide complexes attract great attentions owing to their structural diversities and intriguing luminescent and optoelectronic properties.²⁹⁻³⁵ Remarkably, some coinage metal acetylide complexes show peculiar catenane^{36,37} or rotaxane³⁸ structures, but nontrivial knot topologies based on metal acetylide complexes have not been reported to date. As a rigid U-shape bis(acetylide) ligand,^{39,40} the s-coordination of 3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole (H_2L) to Au(I) through quasi-linear $-C^{\circ}C-Au-C^{\circ}C-$ linkages gives rise to metallocyclic strands. Under the template of d^{10} metal ion such as Ag^+ or $Cu(I)$ through p-coordination to acetylides, the Au-acetylide metallocyclic strands are likely to twist,

fold, thread or interpenetrate to achieve catenane or knot structures with various topologies, which can be further stabilized by substantial d^{10} - d^{10} metallophilic interactions comparable to hydrogen bonds. Furthermore, the strong spin-orbital coupling by multi-metal atoms significantly facilitates intersystem crossing from singlet to triplet state, rendering them excellent phosphorescent properties.

In this work, by manipulating the reactant ratios, the self-assembly reactions (Scheme 1) of H_2L , Au^+ and Cu^+ lead to the synthesis of complex **1** with two interlocked metallostrands $[Au_3L_2(HL)_2]^{3-}$, as well as complexes **3** and **4** with 3_1 trefoil knotted metallocyclic strands $[Au_nL_n]^{n-}$ ($n = 6$ for complex **3** and 8 for complex **4**). Since there are four free $-C^{\circ}CH$ groups in complex **1**, it is an excellent modular for further molecular fabrication to attain more intriguing topologies with folding and interpenetrating structures as depicted in Scheme 2. To this end, upon connecting the four free $-C^{\circ}CH$ groups of two interlocked metallostrands $[Au_3L_2(HL)_2]^{3-}$ with two $[Au(dppb)Au]^{2+}$ ($dppb = Ph_2P(CH_2)_4PPh_2$) moieties through Au-acetylide σ -coordination, complex **2** with 4_1 figure-eight knotted $[Au_{10}L_8(dppb)_2]^{6-}$ metallocyclic strand is successfully attained as designed.

Results

Synthesis and characterization of complexes 1-4. As shown in Scheme 1, complex **1** was prepared in 78% yield by the reaction of $Au(tht)_2ClO_4$, $Cu(MeCN)_4ClO_4$ and H_2L in 3 : 2 : 4 molar ratio in the presence of NEt_3 as a base. Treatment of complex **1** with 2 equiv. $dppb$ and 4 equiv. $Au(tht)_2ClO_4$ followed by the addition of NEt_3 gave complex **2** in 58% yield. Alternatively, complex **2** was accessible in 63% yield by one-pot reaction of $Au(tht)_2ClO_4$, $Cu(MeCN)_4ClO_4$, H_2L and $dppb$ in 5 : 2 : 4 : 1 molar ratio in the presence of NEt_3 . As indicated in Scheme 2, when two of the four free ethynyl groups in complex **1** with interlocking structure are linked in three different modes, it is likely to obtain ring-closed [2]catenane, 4_1 figure-eight knot or 5_2 knot topology. So far, we have not yet obtained [2]catenane or 5_2 molecular knot topology based on interlocking complex **1** as a precursor.

When the reaction of $Au(tht)_2ClO_4$, $Cu(MeCN)_4ClO_4$ and H_2L was performed in 3 : 1 : 4 molar ratio under the aid of NEt_3 , complex **3** was crystallized from the solution as yellow flat bar-like crystals in 45% yield. Furthermore, the same reaction in 4 : 3 : 5 molar ratio gave complex **1** as yellow precipitate in 52% yield together with complex **4** as a minor product, which was crystallized from the filtrate as red block crystals in 10% yield. Attempt to attain complex **4** in higher yield proved fruitless by modifying reaction conditions such as reactant ratio, concentration, solvent and temperature. This is likely due to the close composition ratio between complex **4** ($Au : Cu : L$ in 4 : 3 : 4 ratio) and complex **1** ($Au : Cu : L/HL$ in 3 : 2 : 4 ratio), so that complex **1** with poor solubility is more easier to precipitate from the reaction solution.

In the high-resolution mass spectrometry (HRMS), dianionic complexes $[Au_6Cu_4L_4(HL)_4]^{2-}$, $[Au_{10}Cu_4L_8(dppb)_2]^{2-}$ and $[Au_8Cu_6L_8]^{2-}$ were detected as the base peaks of complex **1** (Fig. S1), complex **2** (Fig. S3) and complex **4** (Fig. S8), respectively. For complex **3** (Fig. S6), the fragments $[(HNEt_3)$

$\{\text{Au}_6\text{Cu}_2\text{L}_6\}^{3-}$, $[(\text{HNEt}_3)_2\{\text{Au}_6\text{Cu}_2\text{L}_6\}]^{2-}$ and $[(\text{HNEt}_3)_3\{\text{Au}_6\text{Cu}_2\text{L}_6\}]^{-}$ occurred as the peaks in high abundant. In the ^1H NMR spectrum of complex **1** (Fig. S2), the proton signals of L^{2-} and HL^- together with those of HNEt^{3+} are unequivocally defined. For complex **2** (Fig. S5), the proton signals of L^{2-} and cationic HNEt^{3+} are clearly assigned although those of phenyl groups in dppb show severe overlapping. Likewise, the ^1H NMR spectrum of complex **3** (Fig. S7) is well resolved to make a clear assignment on the proton signals of L^{2-} and HNEt^{3+} . By comparison, the ^1H NMR spectrum of complex **4** (Fig. S9) is much more complicated owing to the structural asymmetry of coordination molecule as well as the bonding difference among four sets of L^{2-} ligands. The DOSY NMR spectra of complex **1-4** (Figs. S10-S13) further confirm that they are stable compounds in solutions without dynamic or fluxional structures.

All in all, the HRMS and ^1H NMR spectroscopic characterization demonstrate that complexes **1-4** show robust structures in solutions and keep the intact topologies as those in crystals, which are also independent of solution concentrations. The Thermogravimetric analysis indicates that complexes **1-4** (Fig. S16, Supplementary Information) are thermally stable below 160 °C without degradation.

Crystal structure of complex 1. The structures of complexes **1-4** were determined by single crystal X-ray diffraction. As shown in Fig. 1a, complex **1** shows an interlocked structure formed by two $[\text{Au}_3\text{L}_2(\text{HL})_2]^{3-}$ metallocyclic strands folding and interlocking under the guidance of Cu(I) template. Each Cu(I) is bound to three acetylides through p-coordination to generate triply-folding cross $-\text{C}^\circ\text{C}-\text{Au}-\text{C}^\circ\text{C}-$ linkages. The interlocked structure arises from two $[\text{Au}_3\text{L}_2(\text{HL})_2]^{3-}$ metallocycles linked by four Cu(I) ions through p-coordination to twelve acetylides, which is highly stabilized by substantial Au(I)-Cu(I) ($d_{\text{Au}-\text{Cu}} = 2.760(4)\text{-}2.990(2)$ Å) contact. Interestingly, the interlocked topology is further stabilized through Au(I)-Au(I) ($d_{\text{Au}-\text{Au}} = 3.0883(14)$ Å) interaction between two $[\text{Au}_3\text{L}_2(\text{HL})_2]^{3-}$ metallocycles (Fig. 1c). To date, only a limited number of d^{10} metal cluster complexes have been found to exhibit interlocked (pseudo-catenane) or [2]catenane structures driven by $d^{10}\text{-}d^{10}$ intermetallic interactions.^{36,37}

The Au_6Cu_4 kernel is composed of two Au_3Cu_2 clusters, which are linked together through Au(I)-Au(I) interaction. Each Au_3Cu_2 cluster (Fig. 1a) formed through Au-Cu interaction gives rise to a trigonal bipyramidal geometry with two Cu atoms at the apexes and three Au atoms at the trigonal plane. Ligand H_2L is deprotonated at one or two ethynyl groups, which are bound to Au(I) through σ -coordination to make U-shape metallocyclic strands through quasi-linear $-\text{C}^\circ\text{C}-\text{Au}-\text{C}^\circ\text{C}-$ linkages with the C-Au-C angles of $174.7(8)\text{-}176.5(10)^\circ$. The Au-C distances are $1.958(17)\text{-}2.04(2)$ Å. Four dicationic L^{2-} ligands are situated on the front whereas other four monocationic HL^- ligands on the side. The L^{2-} adopt $\mu_4\text{-}\eta^1(\text{Au})$, $\eta^1(\text{Cu})$: $\eta^1(\text{Au})$, $\eta^2(\text{Cu})$ bonding fashion while the HL^- exhibit $\mu_2\text{-}\eta^1(\text{Au})$, $\eta^2(\text{Cu})$ coordination mode.

Crystal structure of complex 2. Complex **2** (Fig. 1b) results from incorporating complex **1** to two $[\text{Au}(\text{dppb})\text{Au}]^{2+}$ moieties through four Au-acetylide σ -coordination bonds. Owing to one free ethynyl group of HL^- in interlocked complex **1**, the two $[\text{Au}_3\text{L}_2(\text{HL})_2]^{3-}$ metallostrands are not fully closed (Fig. 1c). Considering that the free ethynyl groups are likely ligated by $[\text{AuPPh}_2(\text{CH}_2)_n\text{Ph}_2\text{PAu}]^{2+}$ ($n = 3, 4, 5$ etc) metallostrands through Au-acetylide σ -coordination, diphosphine ligand dppb ($n = 4$) was chosen as a bridging ligand to make a fully closed strip. As depicted in Scheme 2, the four endpoints of two interlocked threads can be theoretically linked into a ring-closed $[2]$ catenane, 4_1 figure-eight knot or 5_2 knot depending on the linking modes. When each $[\text{Au}(\text{dppb})\text{Au}]^{2+}$ moiety is bound to two free ethynyl groups of two interlocked $[\text{Au}_3\text{L}_2(\text{HL})_2]^{3-}$ strands in the same side, a closed $[\text{Au}_{10}\text{L}_8(\text{dppb})_2]^{6-}$ strand with figure-eight knot topology is attained as depicted in Fig. 2d. The $[\text{Au}_{10}\text{L}_8(\text{dppb})_2]^{6-}$ metallacyclic strand is topologically equivalent to D_2 -symmetric representation with four crossings of figure-eight knot. To the best of our knowledge, such a deformation of figure-eight knot in complex **2** have not been observed before in artificial molecules.^{9,14b,19-21}

The trigonal bipyramidal Au_3Cu_2 clusters in complex **2** (Fig. 1b) are similar to those in complex **1** (Fig.1a), as reflected by the comparable Au-Cu distances (average 2.90 Å vs 2.90 Å). As depicted in Fig. 1b, two $[\text{Au}(\text{dppb})\text{Au}]^{2+}$ units are σ -bonded to four acetylides through two quasi-linear linkages - $\text{C}^\circ\text{CAu}(\text{dppb})\text{AuC}^\circ\text{C}$ - with the four Au centers further contacting to two Au_3Cu_2 clusters via aurophilic interactions ($d_{\text{Au-Au}} = 3.0377(9)$ - $3.3417(9)$ Å).

Crystal structure of complex 3. As depicted in Fig. 2, the closed $[(\text{AuL})_6]^{6-}$ metallocyclic strand in complex **3** exhibits typical trefoil knot topology (Fig. 2b), driven by Cu(I) template effect and further stabilized by significant Au-Cu interactions. Each Au(I) is ligated by two acetylides through σ -coordination to give quasi-linear $\text{C}^\circ\text{C-Au-C}^\circ\text{C}$ whereas each Cu(I) is p -bonded to three acetylides to form a triply-folding cross point. Complex **3** can be viewed as a combination of two Cu(I) centers encapsulated by $[(\text{AuL})_6]^{6-}$ hexamer, where the metallocyclic strand is folded and interpenetrated under the template effect of two Cu(I) ions bound to six acetylides through p -coordination. It may be also regarded as three $(\text{AuL}_2)^{3-}$ moieties disposed around a Au_3Cu_2 cluster with trigonal bipyramidal geometry. The L^{2-} adopts $\mu_3\text{-}\eta^1(\text{Au})$, $\eta^2(\text{Cu}) : \eta^1(\text{Au})$ coordination mode. The kernel of **3** consists of a Au_3Cu_2 cluster with trigonal bipyramidal geometry linked to three surrounding Au centers through aurophilic interaction. Based on the shorter Au-Cu distances, the Au_3Cu_2 core of complex **3** (average $d_{\text{Au-Cu}} = 2.86$ Å) is more compact than that of complexes **1** (average $d_{\text{Au-Cu}} = 2.90$ Å) and **2** (average $d_{\text{Au-Cu}} = 2.90$ Å). The Au-Au distances are in the range of 3.1490(12)-3.1804(8) Å.

Crystal structure of complex 4. As shown in Fig. 3a, the six Cu(I) centers in complex **4** are encapsulated by a $[(\text{AuL})_8]^{8-}$ octamer, where the metallocyclic strand is folded and interpenetrated around six Cu(I) ions

bound to sixteen acetylides through p-coordination. The closed [(AuL)₈]⁸⁻ (Fig. 3b) metallocyclic strand in complex **4** topologically resembles to an overhand knot with two ends connected, which is a *D*₂-symmetric form of trefoil knot. The six template Cu(I) ions fall into two categories, four of them are respectively p-bound to three acetylides to form four triply-folding cross points, while the rest two are respectively p-ligated to two acetylides to give two doubly-folding cross points. Noticeably, the eight negative charge of [(AuL)₈]⁸⁻ octamer is well compensated by six Cu(I) ions that are p-bound to acetylides so that the Au₈Cu₆ heterometallic structure is further stabilized by substantial Au(I)-Cu(I) interaction. The bonding modes of L²⁻ are rather complicated, which were categorized into four groups such as $\mu_3\text{-}\eta^1(\text{Au}) : \eta^1(\text{Au}), \eta^1(\text{Cu}), \mu_3\text{-}\eta^1(\text{Au}) : \eta^1(\text{Au}), \eta^2(\text{Cu}), \mu_4\text{-}\eta^1(\text{Au}), \eta^2(\text{Cu}) : \eta^1(\text{Au}), \eta^2(\text{Cu})$ and $\mu_5\text{-}\eta^1(\text{Au}), \eta^2(\text{Cu}) : \eta^1(\text{Au}), \eta^2(\text{Cu}), \eta^2(\text{Cu})$. The kernel Au₈Cu₆ of consists of one trigonal bipyramid arranged Au₃Cu₂ cluster and four Au-Cu pairs through Au-Cu interaction together with one isolated Au(I) center without involving intermetallic contact. The Au-Cu distances of Au₃Cu₂ cluster with trigonal bipyramidal geometry are in the range of 2.7253(13)-2.9516(12) Å with the average value of 2.84 Å, which is the shortest one among Au-Cu complexes **1-4**.

Table 1. The UV-Vis Absorption and Luminescent Data of Complexes **1-4** at Ambient Temperature.

complex	$\lambda_{\text{abs}}^a / \text{nm} (\epsilon / \text{M}^{-1} \text{cm}^{-1})$	$\lambda_{\text{em}} (\text{nm}) / t_{\text{em}} (\mu\text{s}) / \phi_{\text{em}} (\%)^b$	
		CH ₂ Cl ₂ ^c	solid
1	303 (131024), 312(127772), 375 (65627), 395 (58650)	530/2.5/15	525/2.7/4.4
2	285 (197835), 315 (166640), 382 (104520), 432 (38800)	545/2.3/44	530/3.9/20
3	313 (39574), 381 (24966)	550/2.4/16	515/5.2/8.0
4	313 (165796), 391 (99944)	600/3.4/27	582/3.7/2.7

^a Measured in 5´10⁻⁵ M CH₂Cl₂ solutions. ^b Excitation at 370-400 nm. ^c Measured in degassed CH₂Cl₂ solutions at a concentration of 5 ´ 10⁻⁵ M.

Photophysical properties of complexes 1-4. The absorption spectral data together with luminescent data are listed in Table 1. The UV-Vis absorption and emission spectra of complexes **1-4** in CH₂Cl₂ solution are shown in Fig. 4. The low-energy absorption bands with initial point around 350 nm ascend rapidly to the peaks within 375-395 nm and then slowly tail to 520 nm. They mainly derive from the admixture of metal cluster-centered (¹MC), intraligand (¹IL) and ligand-to-metal charge transfer (¹LMCT) transitions as demonstrated by theoretically computational studies. The high-energy absorption bands with spectral

maxima within 300-315 nm are ascribed to the $[\pi \rightarrow \pi^*]$ transitions of carbazole-1,8-bis(acetylide) ligands. The absorption band peaked at 285 nm for complex **2** originates likely from dppb intraligand transition.

Upon irradiation at $\lambda_{\text{ex}} > 260$ nm, complexes **1-4** displayed brilliant luminescence in both CH_2Cl_2 solutions or solid states at ambient temperature. The large Stokes shifts and long-lived emission with microsecond lifetimes (Table 1) indicate triplet state character. On the basis of computational studies below, the phosphorescence of complexes **1-4** originates mostly from admixture of $^3[d \rightarrow s/p]$ (^3MC), $^3[p \rightarrow p^*]$ (^3IL) and $^3[p(\text{L}) \rightarrow s/p(\text{Au/Cu})]$ ($^3\text{LMCT}$) triplet excited states.

The luminescent quantum yields of complexes **1-4** are 15%-44% in degassed CH_2Cl_2 solutions at ambient temperature. The lower phosphorescent quantum yields of **1-4** in solid states ($\phi_{\text{em}} = 2.7\%-20\%$) than those in solutions ($\phi_{\text{em}} = 15\%-44\%$) arise likely from substantial intermolecular interactions between Cu-Au clusters, which aggravate deactivation in triplet excited states through thermally non-radiative process. The obvious hypsochromic shifts of the emission bands (Table 1) in solid state compared with those in solution are attributed to the rigidity effect in constrained state.

Since complex **1** is the precursor of complex **2**, the comparison of their emission properties is helpful for the insight of structure-luminescence correlation. As depicted in Fig. 4, the emission peak of complex **2** ($\lambda_{\text{em}} = 545$ nm) in degassed CH_2Cl_2 solution shows a distinct red-shift compared with that of complex **1** ($\lambda_{\text{em}} = 530$ nm). Such a red-shift of the emission can be rationalized by the higher nuclearity as well as the stronger Au-Cu interaction of complex **2** (average $d_{\text{Au-Cu}} = 2.897$ Å) than that of complex **1** ($d_{\text{Au-Cu}} = 2.906$ Å). Moreover, the phosphorescent quantum yield of complex **2** ($\phi_{\text{em}} = 44\%$) is nearly triple as high as that of complex **1** ($\phi_{\text{em}} = 15\%$). Undoubtedly, the thermal deactivation caused by free $-\text{C}^\circ\text{CH}$ groups in complex **1** through C-H vibrational process is dramatically inhibited upon ligation to the two $[\text{Au}(\text{dppb})\text{Au}]^{2+}$ moieties in complex **2**. Also, the better molecular rigidity of complex **2** with figure-eight knotted structure results likely in less thermally non-radiative process in triplet state than that of complex **1**.

Compared with that of complex **3** ($\lambda_{\text{em}} = 550$ nm), complex **4** ($\lambda_{\text{em}} = 600$ nm) shows a drastic red-shift of the emission in CH_2Cl_2 solution at ambient temperature. Indeed, the HOMO-LUMO gap of complex **4** (3.07 eV) is distinctly narrower than that of complex **3** (3.39 eV) as disclosed by theoretical studies. Since both complexes **3** and **4** adopt trefoil knot topology with the comparable structural characteristics, the red-shifted emission is most likely ascribed to the higher nuclearity together with the stronger Au-Cu interaction in complex **4** (average $d_{\text{Au-Cu}} = 2.839$ Å) than that in complex **3** (average $d_{\text{Au-Cu}} = 2.863$ Å).

TD-DFT studies of complexes 1-4. To get insight to photophysical properties of Au(I)-Cu(I) complexes **1-4**, time-dependent density functional theory (TD-DFT) calculations were performed in ground and triplet excited states. As depicted in Fig. 5, the HOMO focuses mainly on Au-Cu centers and L^{2-} ligands, while the

LUMO is distributed over Cu(I) and Au(I) centers as well as L^{2-} ligands. In any cases, the population of metal centers is mostly concentrated at Au_3Cu_2 clusters with trigonal bipyramidal geometry. Thus, the lowest-energy singlet (S_1) and triplet (T_1) excited states with electronic migration mainly from HOMO to LUMO is featured with $[d \rightarrow s/p]$ MC, $[p \rightarrow p^*]$ IL and $[p(L) \rightarrow s/p(Au/Cu)]$ LMCT transitions.^[39] Both the UV-Vis absorption and emission data are reproduced by theoretical computational studies (Tables S6-S13, Supplementary Information).

Discussion

Taking advantage of bis(s-acetylide)gold(I) modular as a new synthon, this work establishes a viable synthetic approach to achieve artificially knotted structures under the template effect of copper(I) p-bonded to acetylides, which are further stabilized by substantial intramolecular d^{10} - d^{10} interaction. The Cu(I) ion plays at least two aspects of roles in the formation of knotted structures. First, the metallocyclic strand is twisted, folded and interpenetrated around Cu(I) ions bound to acetylides through p-coordination. Second, the negative charge of $[(AuL)_n]^{n-}$ oligomer is well compensated by Cu(I) ions p-bound to acetylides so that the Au(I)-Cu(I) heterometallic structures are highly reinforced by Au(I)-Cu(I) interaction.

By manipulating the amount of Cu(I) ion, the coordination of H_2L to Au(I) under the aid of NEt_3 gives rise to whether two interlocked Au(I)-bis(acetylide) metallostrands $[Au_3L_2(HL)_2]^{3-}$ in complex **1** or trefoil knotted metallocyclic strands $[(AuL)_n]^{n-}$ ($n = 6$ in complex **3** and $n = 8$ in complex **4**). The concurrent formation of interlocked complex **1** as a major product and trefoil knotted complex **4** as a minor product is due to their similar composition ratio but the former precipitating more readily from the solution. Since there are four free ethynyl groups in complex **1** with two interlocked metallostrands $[Au_3L_2(HL)_2]^{3-}$, introducing two $[Au(dppb)Au]^{2+}$ moieties to it through bis(Au-acetylide) s-bonding brings successfully about complex **2** with figure-eight knotted structure. The closed metallocyclic strand $[Au_{10}L_8(dppb)_2]^{6-}$ in complex **2** topologically resembles the D_2 -symmetric representation of figure-eight knot, which is observed for the first time in artificially knotted molecules.

The d^{10} - d^{10} heterometallic complexes are brilliantly phosphorescent at ambient temperature, arising from admixture of 3MC , 3IL and 3LMCT triplet excited states. The intense phosphorescent properties are most likely associated with the knotted structures that lead to excellent molecular rigidity, which endows the least thermally non-radiative deactivation in triplet state. All in all, this research paves an avenue for achieving knotted organometallic molecules with folding and interpenetrating topologies by the use of specifically shaped diethynyl ligand as a modular through quasi-linear gold(I)-bis(s-acetylide) coordination.

Methods

Materials. All reactions were carried out under a dry argon atmosphere using Schlenk techniques and vacuum-line systems. The solvents were dried, distilled, and degassed prior to use. Spectroscopic grade reagents for spectroscopic measurements were purchased from commercial sources. 3,6-Di-*tert*-butyl-1,8-diethynyl-9H-carbazole (H_2L) was prepared by similar procedure described in literature.⁴¹

Synthesis of $(HNEt_3)_2[Au_6Cu_4L_4(HL)_4]$ (1**).** To a freshly prepared CH_2Cl_2 (10 mL) solution of $Au(tht)_2ClO_4$ (0.06 mmol, 28.4 mg) were added $Cu(CH_3CN)_4ClO_4$ (0.04 mmol, 13.1 mg) and H_3decz (0.08 mmol, 26.2 mg), followed by the dropwise addition of NEt_3 (20 μ L) under vigorous stirring. The stirring was kept for three minutes to blend thoroughly all reagents. The reaction flask was then sealed and put aside with exclusion of light for one week to give the product as yellow plate-like crystals. Yield: 78%. Anal. Calcd for $Au_6Cu_4C_{204}H_{220}N_{10}$: C, 57.68; H, 5.22; N, 3.30. Found: C, 57.54; H, 5.44; N, 3.26 (after desolvation). HRMS m/z (%): 2021.5012 (100) $[M-(HNEt_3)_2]^{2-}$ (Calcd 2021.5083). 1H NMR (400 MHz, $DMSO-d_6$, δ): 10.35 (s, 4H), 9.87 (s, 4H), 8.37 (s, 4H), 8.29 (s, 4H), 7.73 (s, 4H), 7.61 (s, 4H), 7.38 (s, 4H), 7.20 (s, 4H), 6.94 (s, 4H), 6.31 (s, 4H), 4.66 (s, 4H), 3.36–3.31 (m, 12H), 1.48 (s, 36H), 1.37 (s, 36H), 1.24–1.22 (m, 18H), 0.66 (s, 36H), 0.14 (s, 36H). IR (KBr, cm^{-1}): 3362m (N–H), 3310m ($C^{\circ}C-H$), 2102w ($C^{\circ}C$).

Synthesis of $(HNEt_3)_2[Au_{10}Cu_4L_8(dppb)_2]$ (2**).** To a freshly prepared CH_2Cl_2 (10 mL) solution of $Au(tht)_2ClO_4$ (0.1 mmol, 47.3 mg) were added $Cu(CH_3CN)_4ClO_4$ (0.04 mmol, 13.1 mg), dppb (0.02 mmol, 8.5 mg) and H_3decz (0.08 mmol, 26.2 mg), followed by the addition of NEt_3 (20 μ L) under vigorous stirring. The reaction mixture was continuously stirred overnight in the absent of light. Upon removal of the solvent by rotatory evaporation, the yellow solid was dissolved in 3 mL dimethylacetamide (DMAc) to give a clear yellow solution. Layering Et_2O onto the solution through slow diffusion gave yellow block crystals within one week. Yield: 63%.

Alternatively, complex **2** was prepared by mixing a CH_2Cl_2 solution of complex **1** with 4 equiv. $Au(tht)_2ClO_4$ and 2 equiv. dppb in the presence of NEt_3 . The solution was evaporated through rotary evaporator to dryness to give yellow solid. Yellow crystals were obtained by layering Et_2O onto a DMAc solution in one week. Yield: 58%. Anal. Calcd for $C_{260}H_{272}Au_{10}Cu_4N_{10}P_4$: C, 53.07; H, 4.66; N, 2.38. Found: C, 53.26; H, 4.79; N, 2.36 (after desolvation). HRMS m/z (%): 2840.0980 (100) $[M-(HNEt_3)_2]^{2-}$ (Calcd 2840.0936). 1H NMR (400 MHz, CD_2Cl_2 , δ): 11.06 (s, 4H), 10.21 (s, 4H), 8.02 (s, 4H), 7.67 (s, 4H), 7.44 (s, 4H), 7.34 (dd, $J = 12.1, 7.8$ Hz, 8H), 7.21 (s, 4H), 7.17–6.86 (m, 32H), 6.70 (t, $J = 7.2$ Hz, 8H), 6.59 (s, 4H), 6.05 (s, 4H), 4.10–3.94 (m, 5H), 3.03–2.87 (m, 18H), 2.40–2.23 (m, 5H), 1.49 (s, 36H), 1.34 (s, 36H), 1.01–0.91 (m, 18H), 0.67 (s, 36H), 0.52 (s, 36H). ^{31}P NMR (162 MHz, CD_2Cl_2 , δ): 34.46 (s, 4P). IR (KBr, cm^{-1}): 3360m (N–H), 2105w ($C^{\circ}C$).

Synthesis of (HNEt₃)₄[Au₆Cu₂L₆] (3). To a freshly prepared CH₂Cl₂ (10 mL) solution of Au(tht)₂ClO₄ (0.06 mmol, 28.4 mg) were added Cu(CH₃CN)₄ClO₄ (0.02 mmol, 6.5 mg) and H₃decz (0.08 mmol, 26.2 mg), followed by the dropwise addition of NEt₃ (20 uL). The reaction mixture was continuously stirred overnight in the absent of light. The solvent was then removed through rotatory evaporation to give a yellow solid. The crude product was washed by Et₂O for three times and then redissolved in CH₂Cl₂ (3 mL). To the resulting yellowish solution was slowly added n-hexane to form a layer between two solvents. Yellow flat bar-like crystals were obtained within one week. Yield: 45%. Anal. Calcd for Au₆Cu₂C₁₆₈H₂₀₂N₁₀: C, 54.98; H, 5.55; N, 3.82. Found: C, 54.91; H, 5.69; N, 3.77 (after desolvation). HRMS *m/z* (%): 3568.1442 (57) [M-(HNEt₃)₃]⁻ (Calcd 3568.1458); 1733.0136 (100) [M-(HNEt₃)₂]²⁻ (Calcd 1733.0084); 1120.9637 (86) [M-(HNEt₃)₃]³⁻ (Calcd 1120.9623). ¹H NMR (400 MHz, CD₂Cl₂, δ): 10.34 (s, 6H), 7.81 (d, *J* = 1.4 Hz, 6H), 7.65 (d, *J* = 1.4 Hz, 6H), 7.54 (d, *J* = 1.6 Hz, 6H), 6.46 (d, *J* = 1.6 Hz, 6H), 3.21 (q, *J* = 7.1 Hz, 24H), 1.42 (s, 54H), 1.27 (t, *J* = 7.3 Hz, 36H), 0.69 (s, 54H). IR (KBr, cm⁻¹): 3359m (N-H), 2097w (C°C).

Synthesis of (HNEt₃)₂[Au₈Cu₆L₈] (4). To a freshly prepared CH₂Cl₂ (10 mL) solution of Au(tht)₂ClO₄ (0.08 mmol, 37.8 mg) were added Cu(CH₃CN)₄ClO₄ (0.06 mmol, 19.6 mg) and H₃decz (0.1 mmol, 32.7 mg), followed by the dropwise addition of NEt₃ (20 uL) under vigorous stirring. The stirring was kept to proceed overnight in the absent of light. A large amount of yellow precipitate appeared, which was identified as Au₆Cu₄ complex **1** in 52% yield. After taken by filtration, the clear solution was evaporated to dryness, which was then redissolved in CH₂Cl₂ (3 mL). Slow diffusion of n-hexane into the solution gave red block crystals in one week. Yield: 10%. Anal. Calcd for C₂₀₄H₂₁₆Au₈Cu₆N₁₀: C, 51.42; H, 4.57; N, 2.94. Found: C, 51.30; H, 4.63; N, 2.82 (after desolvation). HRMS *m/z* (%): 2279.8914 (100) [M-(HNEt₃)₂]²⁻ (Calcd 2279.8884). ¹H NMR (400 MHz, CD₂Cl₂, δ): 10.74 (s, 2H), 9.99–9.93 (m, 4H), 9.58 (s, 2H), 8.57 (s, 4H), 8.09 (s, 2H), 8.05 (s, 2H), 7.89 (s, 2H), 7.85 (s, 2H), 7.55 (s, 4H), 7.31 (s, 2H), 7.26 (s, 2H), 7.09 (s, 4H), 6.65 (s, 4H), 5.83 (s, 2H), 5.78 (s, 2H), 3.40–3.30 (m, 12H), 1.60 (s, 72H), 1.47 (s, 36H), 1.43–1.41 (m, 18H), 0.12 (s, 36H). IR (KBr, cm⁻¹): 3411m (N-H), 2104w (C°C).

Data availability

The data that support the findings of this study are available within the article and its Supplementary Information files. Other relevant data are available from the corresponding author upon reasonable request. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2088667-2088670 for complexes **1-4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Declarations

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Author Contributions

Y.-Z.H. and Z.-N.C. conceived the experiments and wrote the manuscript. Y.-Z.H. carried out the major experiments. J.-Y.W. performed theoretical calculations. Z.J. and P.X. helped with preparation. The project was planned, directed, and supervised by Z.-N.C. All the authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Figures

Figure 1

(a) A perspective view of complex 1 from X-ray crystallography. (b) A perspective view of complex 2 from X-ray crystallography. (c) A view showing two interlocked $[\text{Au}_3\text{L}_2(\text{HL})_2]^{3-}$ metallostrands in complex 1. (d) A view showing a closed $[\text{Au}_{10}\text{L}_8(\text{dppb})_2]^{6-}$ strand with figure-eight knot topology in complex 2. The hydrogen atoms and tert-butyl groups together with the phenyl rings on phosphorous atoms were omitted for clarity.

Figure 2

(a) A perspective view of complex 3 from X-ray crystallography. (b) A view showing a closed $[(\text{AuL})_6]^{6-}$ metalocyclic strand with trefoil knot topology. The hydrogen and tert-butyl groups were omitted for clarity.

Figure 3

(a) A perspective view of complex 4 from X-ray crystallography. (b) A view showing a closed $[(AuL)_8]^{8-}$ metallocyclic strand with trefoil knot topology. The hydrogen and tert-butyl groups were omitted for clarity.

Figure 4

UV-Vis absorption (solid) and emission (dash) spectra of complexes 1-4 in CH_2Cl_2 solutions at ambient temperature. Inset: the luminescent images of complexes 1-1-4 upon irradiation under UV light at 365 nm.

Figure 5

Plots of HOMO and LUMO in the lowest-energy triplet state for complexes 1-4.

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