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Please cite this article as: S. Ibáñez, M. Poyatos, E. Peris, Preparation and self-aggregation properties of a series of pyrene-imidazolylidene complexes of gold (I), *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121284.

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Preparation and self-aggregation properties of a series of pyrene-imidazolylidene complexes of gold (I)

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ABSTRACT

This article describes the preparation of three different Au(I) complexes bearing a pyrene-imidazolylidene ligand, two of which are bound to phenyl-acetylene ligands. The supramolecular and photophysical properties of all three complexes are described. The supramolecular behavior of all three complexes is dominated by the presence of the pyrene moiety, which facilitates that all compounds show π-stacking interactions in solution and in the solid state. The molecular structures of all three complexes were determined by single crystal X-ray diffraction studies. The ^{1}H NMR studies performed in $CDCl_3$, show that the self-association constants are in the range of 11-44 M^{-1}.

INTRODUCTION

Gold(I) N-heterocyclic carbene (NHC) complexes have been recognized for years as a powerful synthetic tool for a large number of organic transformations, most usually those involving the use of alkenes or alkynes.[1-9] Together with their well-recognized properties in homogeneous catalysis,[10] Au-NHC complexes have recently experienced increased attention due to their extraordinary photoluminescence[11] and biological properties.[12] It is precisely the combination of the luminescence properties of Au-NHC complexes, together with their potential therapeutic properties, what makes this type of compounds especially useful in the development of optical theranostic agents.[13-14]

Gold (I) complexes are known to form linear compounds with aryl-acetylides.[15] This structural property has been extensively used for the preparation of oligomeric and polymeric materials with attractive photophysical properties.[16-20] Another interesting feature of gold-alkynyls is their tendency to form supramolecular architectures due to their ability to afford linear geometries and self-assembly structures through aurophilic interactions.[21-29] It is worth mentioning, that alkynyl-gold (I) complexes with NHC ligands have shown interesting industrial applications as electroluminescent materials.[30-33]

During the past three years we prepared a series of gold(I) metallotwezers[34-38] and metallocages[39-40] by combining the use of pyrene-functionalized NHCs and rigid bis-alkynyl linkers (Scheme 1). By doing so, we were able to obtain supramolecular systems that showed great ability to encapsulate polyaromatic aromatic hydrocarbons (PAHs).[38-40] Some other metallosupramolecules showed a large ability to self-associate in the presence of metal cations (Ag$^+$, Cu$^+$ and Tl$^+$) forming interesting self-associated structures[35, 37] and polymers,[36] due to a combination of $\pi-\pi$-stacking

and metallophilic interactions. These non-covalent interactions are known to play a very important role in the photophysical and catalytic[41-42] properties of metal complexes, as we recently observed for NHC complexes functionalized with rigid polyaromatic moieties.[43] With all these precedents in hand, herein we describe the preparation of a family of pyrene-functionalized NHC complexes of Au(I) containing aryl-alkynyl ligands. Their non-covalent self-assembly properties in solution, and their photophysical properties are also described.
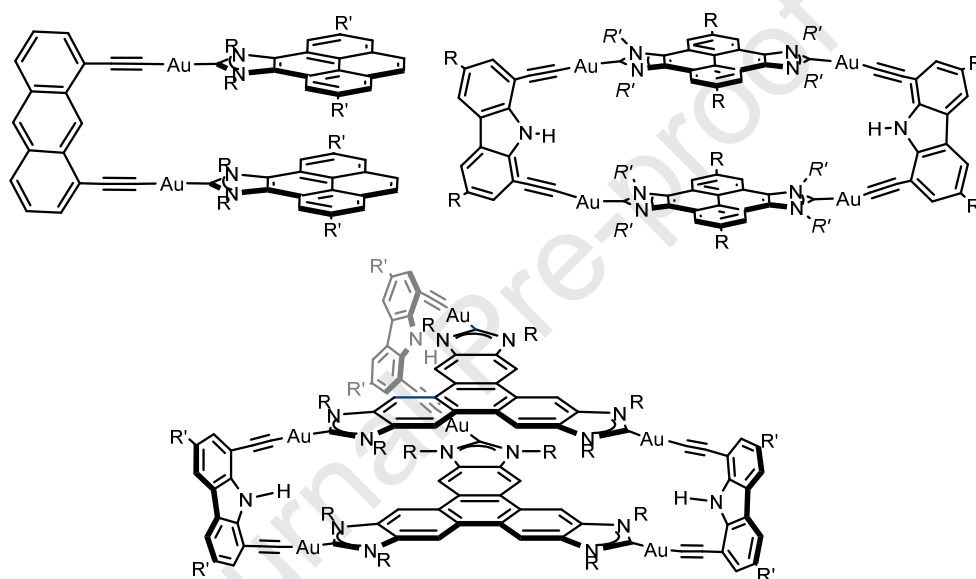

Scheme 1, Selected examples of Au(I)-based metallotweezers and metallocages recently described by our group.

RESULTS AND DISCUSSION

The Au(I) complexes that we obtained in this work were synthesized according to the procedure depicted in Scheme 2. The reaction of the pyrene-imidazolium iodide[44] with silver oxide in methylene chloride formed the corresponding silver-NHC complex, which reacted *in situ* with [AuCl(SMe$_2$)] yielding complex **1**, in 81% yield. Subsequent reaction of phenylacetylene or 1,4-diethynylbenzene with the NHC-Au(I) complex **1** in MeOH in the presence of NaOH, afforded complexes **2** and **3** as yellow solids, in 91%

and 73% yields, respectively. The NMR spectra of complexes **1**-**3** were in accordance

with the symmetry of their predicted structures. The ^{13}C NMR spectra shows the signals

due to the metallated carbene-carbons at 177.89, 193.27 and 193.28 ppm for **1**, **2** and **3**,

respectively.
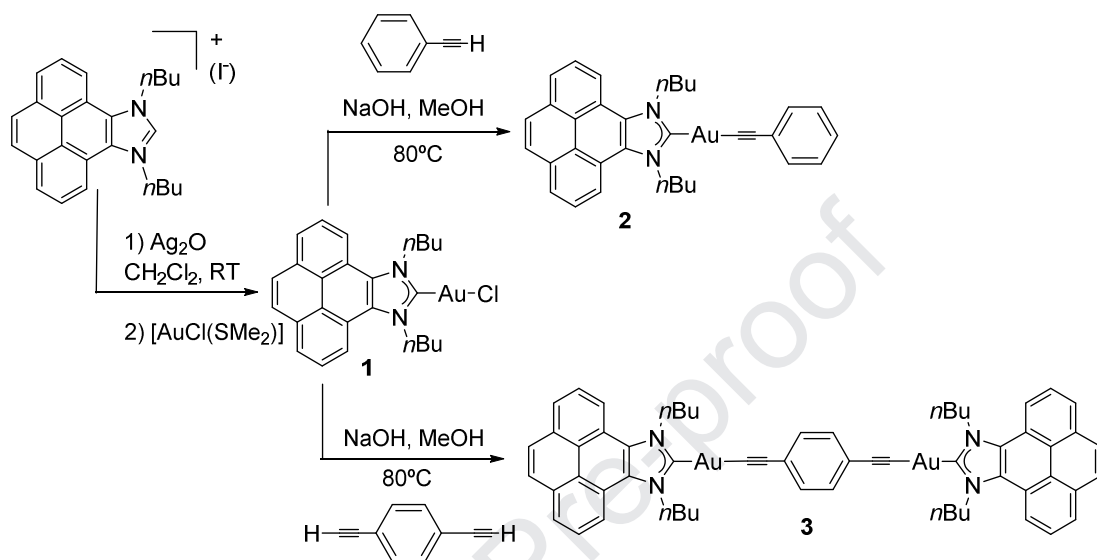
Scheme 2. Synthesis of complexes **1**-**3**.

The molecular structures of **1**, **2** and **3** were confirmed by single crystal X-ray

diffraction (Figure 1). The molecular structure of **1** (Figure 1a) contains a pyrene-

imidazolylidene ligand bound to an Au-Cl fragment. The Au-C$_{carbene}$ bond distance is

1.994(13) Å, therefore in the typical range for other Au-NHC complexes.[45] The Au

atom is slightly deviated from the plane formed by the extended polycyclic ligand, at a

distance of 0.6 Å. The molecular structure of **2** (Figure 1b) contains a pyrene-

imidazolylidene ligand bound to an Au-phenylacetylene fragment. The Au-C$_{carbene}$ bond

distance is 2.028(3) Å and the Au-C(2) bond distance is 1.987(3) Å. The coordination

about the metal center is quasi-linear, as reflected by the C(1)-Au-C(2) angle of

175.13(12)°.The Au atom is slightly deviated from the plane formed by the extended

polycyclic ligand by 0.8 Å, and the angle between the planes formed by the pyrene and

phenyl moieties is of 68.9°. Complex **3** (Figure 1c) contains a diethynylbenzene ligand

bridging two Au pyrene-imidazolylidene moieties, forming a nanosized sinuous-shaped molecule. The distance between the Au atoms and the carbene carbons are 2.040(5) or 2.029(5) Å. The two gold atoms are separated at a distance of 12.04 Å. The two pyrene moieties are disposed in a parallel fashion, and the angle established between the planes formed by the two pyrenes and the bridging phenylene ring is of 51.2º.
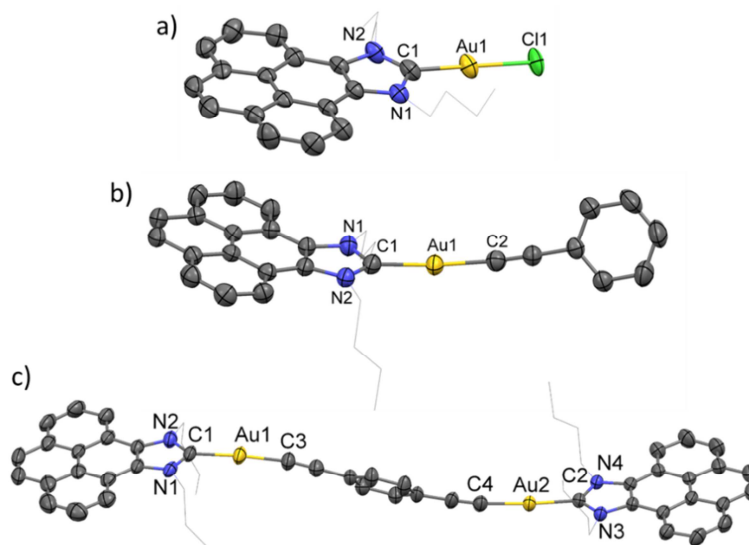

Figure 1. Molecular structures of complexes **1**(a), **2** (b) and **3** (c). Hydrogen atoms and solvent are omitted for clarity. N-butyl groups are represented in the wireframe form. Selected bond distances Å and angles (º). Complex **1**: Au(1)-Cl(1) 2.300(3), Au(1)-C(1) 1.994(13), C(1)-Au(1)-Cl(1) 179.4(4). Complex **2**: Au(1)-C(1) 2.028(3), Au(1)-C(2) 1.987(3), C(1)-Au(1)-C(2) 175.13(12). Complex **3**: Au(1)-C(1) 2.040(5), Au(1)-C(3) 1.997(6), C(1)-Au(1)-C(3) 174.8(3), Au(2)-C(2) 2.029(5), Au(2)-C(4) 2.009(6), C(2)-Au(1)-C(4) 176.2(2).
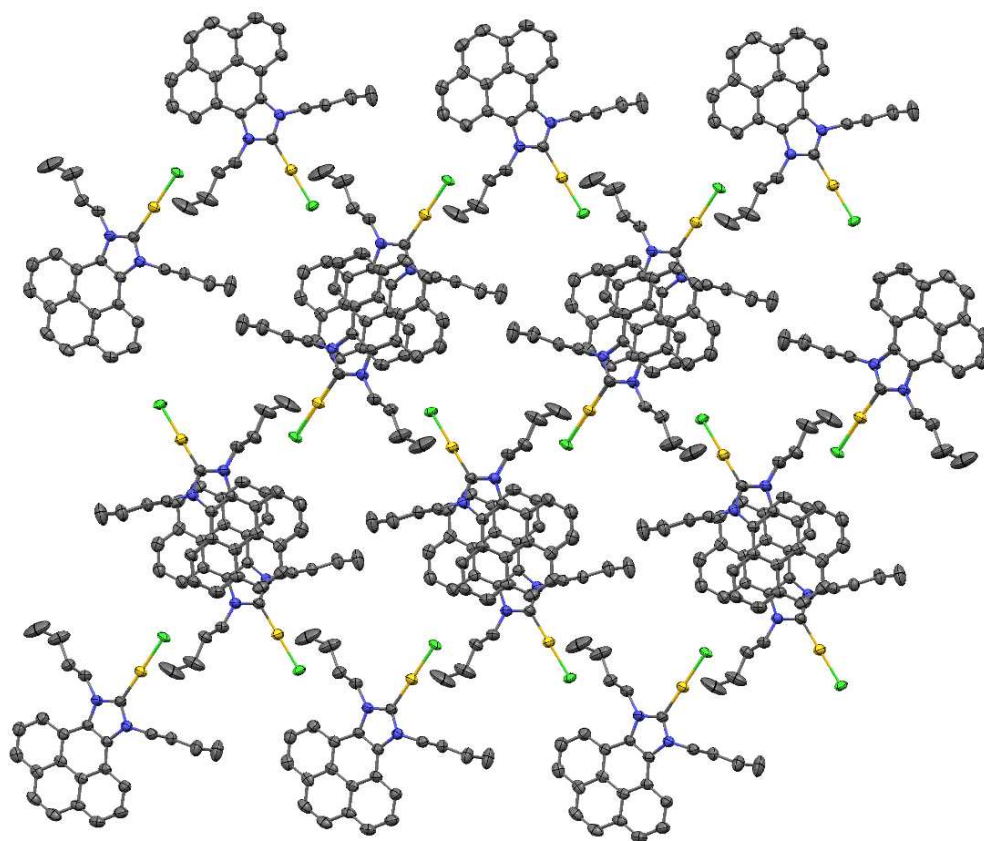
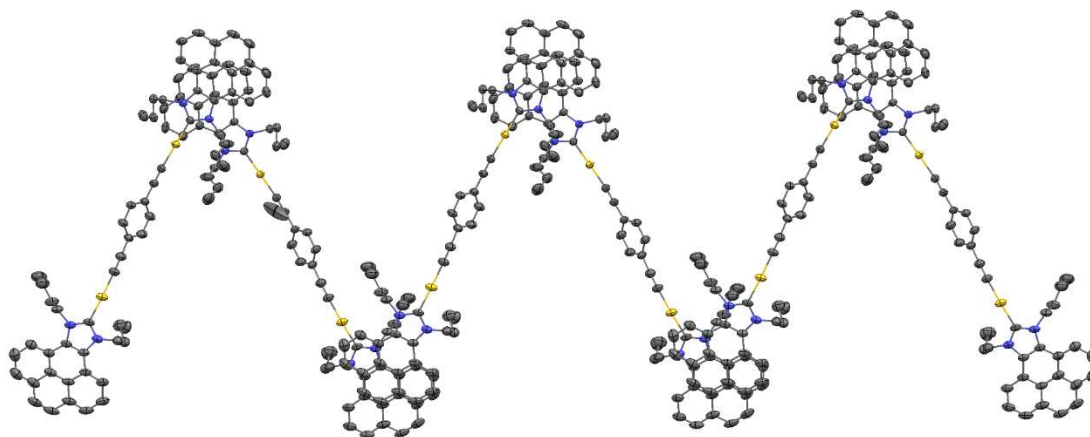**Figure 2.** Molecular arrangement observed in the crystal packing of **1**.

Figure 3. Molecular arrangement observed in the crystal packing of **3**.

The crystal packing of the compound is dominated by the π–π-stacking interactions established between the pyrene moieties of the molecules. For example, the crystal

packing of complex **1** shows a rhombohedral arrangements of π-stacks disposed in an antiparallel manner, as shown in Figure 2. The crystal structure of complex **3** (Figure 3) shows the formation of zig-zag chains formed by the π−π-stacking interaction of both pyrene moieties of the dimetallic molecule, so that the linear axis of each molecule is oriented at an angle of 59º with respect to the axis of the subsequent one. None of the crystal structures of complexes **1**-**3** showed aurophilic interactions, as all the shortest Au···Au intermolecular distance was of about 7.5 Å.

In order to learn if the non-covalent interactions were also taking place in solution, we performed a series of ^{1}H NMR spectra in CDCl$_3$ at different concentrations of all three complexes. As an illustrative example, Figure 4 shows a series of ^{1}H NMR spectra of complex **3** at concentrations ranging from 0.24-11.57 mM. The series of spectra show that one of the signals assigned to an aromatic proton of the pyrene moiety is upfield shifted by 0.11 ppm upon increasing the concentration of the complex. This observation strongly suggests that the complex self-aggregates through the π−π-stacking of the pyrene moiety. In addition, the signal due to the protons of the methylene group bound to the nitrogen atoms of the imidazolylidene ligand are also significantly shifted upfield ($\Delta\delta$ = 0.10 ppm). This observation is a clear indication that the complex shows significant self-association in the range of concentrations used. The global nonlinear regression analysis of the data[46-47] allowed determining a self-association constant of 44(1) M^{-1}, as shown in the binding isotherm depicted in Figure 5a. By doing the same type of NMR study, we obtained the related self-association constants for **1** and **2**, as 11(1) and 29(1) M^{-1}, respectively (see ESI for full details). The self-association constant for **1**, is identical to the one that we found for a similar complex but bearing a pyrene-imidazolylidene ligand functionalized with two *tert*-butyl groups, although in that case the constant was calculated in CD$_3$CN.[48] In any case, these self-association constants

are quite significant, and indicate that self-aggregated species exist in a significant percentage at the milimolar range. For example, at 5 mM of **3**, about 26% of the complex is self-aggregated at room temperature, as can be observed in the speciation plot shown in Figure 5b. As we pointed out in a previous study, this may have important implications in the properties of the complex as in, for example, its catalytic performance.[48]
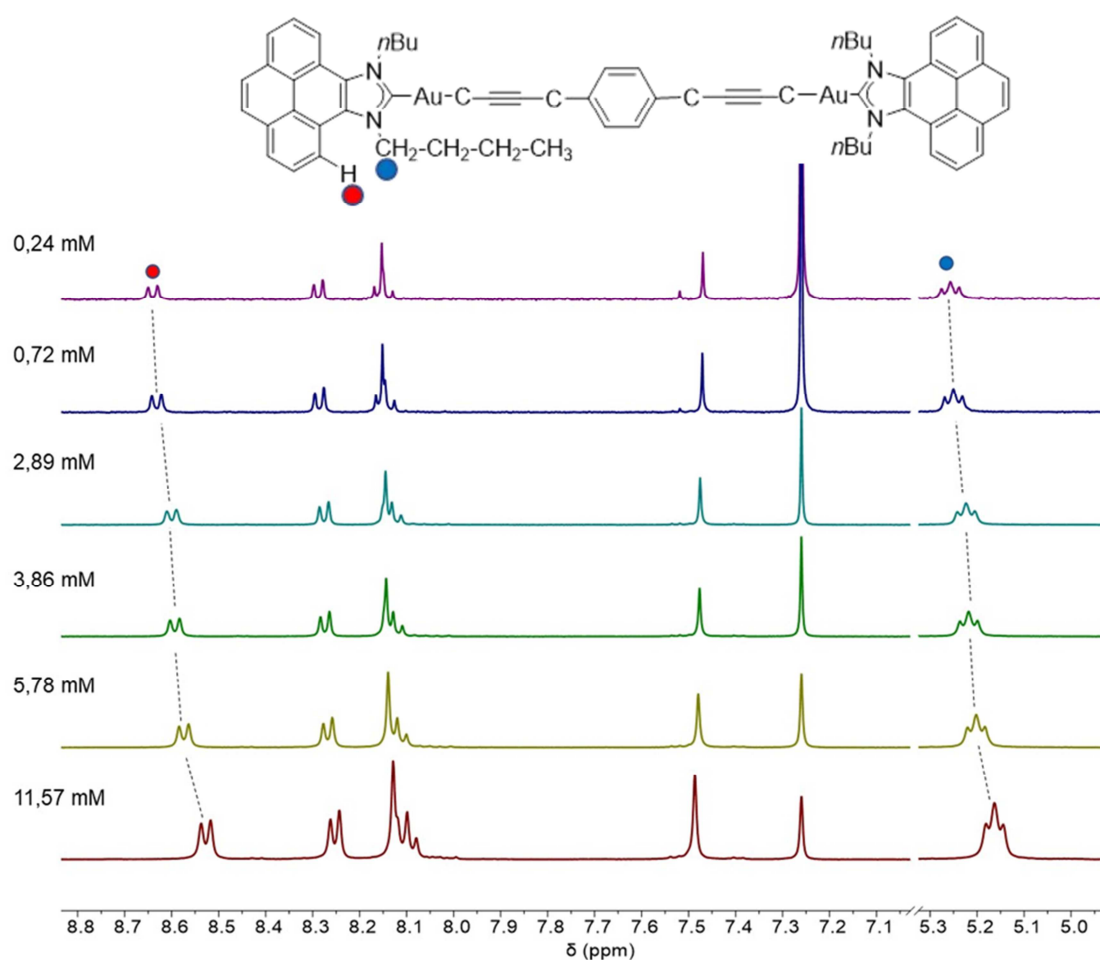

Figure 4. Selected region of a series of ^{1}H NMR spectra (400 MHz) of complex **3** in CDCl$_3$ at different concentrations (the complete set of spectra are shown in the Supplementary Information, Figure S5).
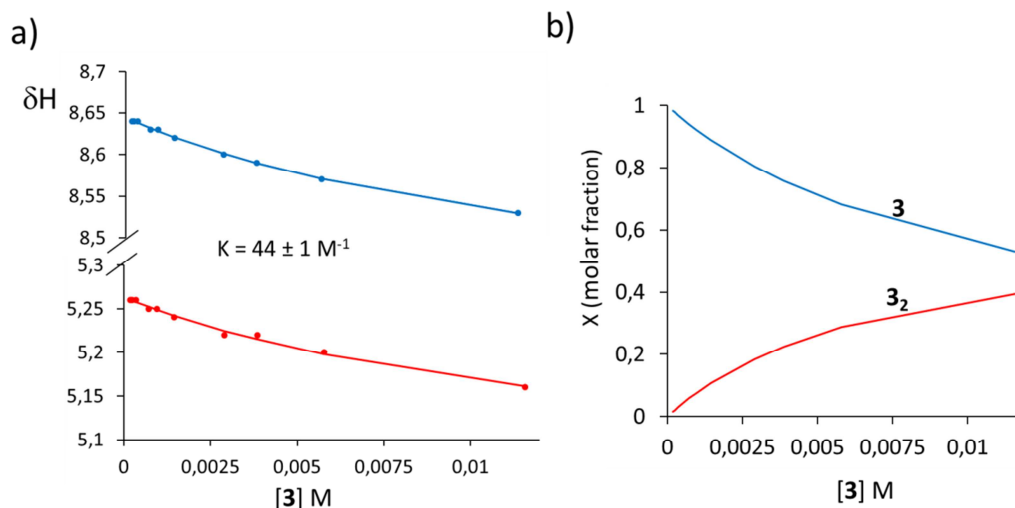
Figure 5. a) Binding isotherm with the resulting self-aggregation constant obtained from the non-linear regression. b) Speciation plot.

Once the self-aggregation properties of complexes **1**-**3** were studied, we turned out attention toward the electronic properties of these compounds. The Uv-vis. and emission spectra of all three complexes are shown in Figure 6. The electronic spectra of complexes **1**-**3** show similar absorption spectra with two sets of bands centered at 275 (high energy) and 325 (low energy) nm. The low energy band is assigned to the pyrene-centered singlet state, as in previously reported pyrene-imidazolylidene containing complexes.[37, 49-50] Complexes **2** and **3** also exhibit absorption bands between 274-325 nm, due to the intraligand (IL) $\pi-\pi^*$ transitions of the alkynyl ligands.[51-53] In the case of complex **3**, this band is more intense, and significantly red-shifted compared to that shown by **2**, due to the elongated conjugation promoted by the *para* substitution about the central benzene ring.[54] The emission spectra of all three complexes are superimposable, and exhibit a vibronically-resolved band with a peak maximum at 375 nm, which is coincident with the typical monomer emission band of pyrene, as shown in

other pyrene-based NHC ligands.[49-50] The quantum yields for complexes **1**, **2** and **3** were calculated to be 0.029, 0.011 and 0.012, respectively.
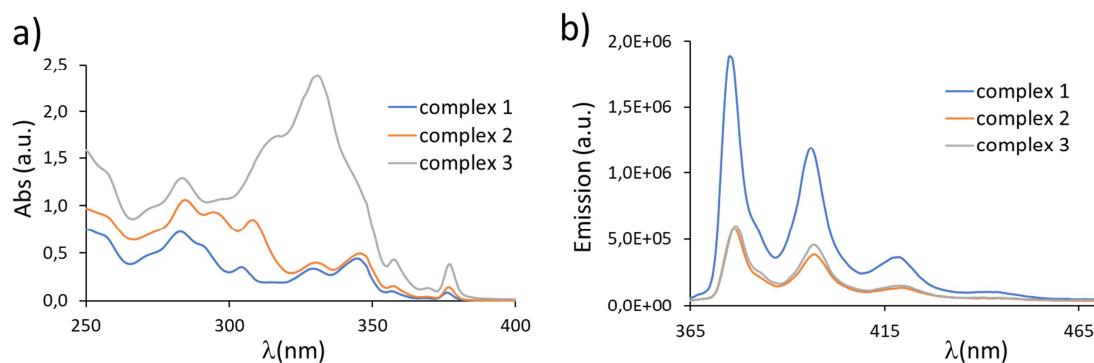

Figure 6. Uv-Vis (a) and emission (λ_{ex} = 345 nm) (b) spectra of complexes **1**-**3**. All spectra were recorded in CH_2Cl_2, using 10^{-5} M solutions of the complexes.

Finally, we studied the electrochemical properties of complexes **1**-**3** by cyclic voltammetry (Figure 7). All complexes **1**-**3** show one irreversible oxidation wave at 1.55, 1.55 and 1.60 V, respectively, which is assigned to the oxidation of the Au(I) centre. Additional irreversible waves at 1.32 and 1.19 V are observed for **2**, and **3**, respectively, which are attributed to the alkynyl ligand-centered oxidation. Similar oxidation waves have been found for related Au(I)-NHC complexes with phenyl-acetylene ligands.[55-56] The presence of a single oxidation wave for the two Au(I) centres in **3**, indicate that the electronic communication between the two metal centers in the complex through the phenyl-di-acetylene ligand is negligible.
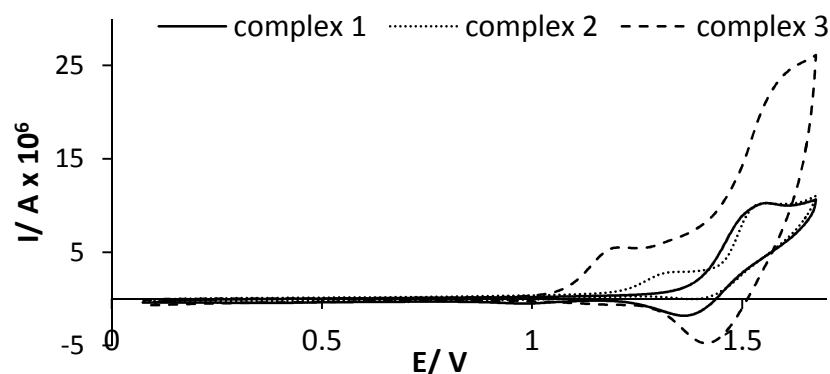
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Figure 7. Cyclic voltammetry (CV) plot of complexes **1**, **2** and **3**. Measurements were performed on a 1mM solution of the analyte in dry CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte, 100 mV/s scan rate, Fc/Fc$^+$ used as standard with $E_{1/2}$(Fc/Fc$^+$) = 0.46 V vs SCE.

Conclusions

In summary, in this work we reported the preparation and full characterization of three different gold(I) complexes bearing a pyrene-imidazolylidene ligand. Two of the complexes are bound to phenyl-acetylene ligands, and one of the compounds is a di-Au(I) complex with a diethynylbenzene ligand. The presence of the pyrene moiety in all three complexes determines their supramolecular behavior, which is illustrated by the π-stacking interactions shown by all three complexes in the solid state and in solution. The self-association constants of all three complexes in chloroform solution are very significant, thus indicating that this type of supramolecular behavior must be taken into account when considering the physicochemical properties of these complexes in solution.

Given the current interest for developing new Au(I)-NHC complexes with alkynyl ligands, we believe that our study contributes to understand the electronic and supramolecular properties of this interesting type of compounds.

Experimental Section

General considerations. The pyrene-based imidazolium salt was prepared according to literature methods.[44] All other reagents were used as received from commercial

suppliers. NMR spectra were recorded on a Bruker 300 MHz MHz or Bruker 400 MHz using $CDCl_3$ as solvents. Infrared spectra (FTIR) were performed on a FT/IR-6200 (Jasco) spectrometer equipped with a Pro One ATR with a spectral window of 4000-400 cm^{-1}. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas. Elemental analyses were carried out on a TruSpec Micro Series. UV-Visible absorption spectra were recorded on a Varian Cary 300 BIO spectrophotometer using dichloromethane under ambient conditions. Emission spectra were recorded on a modular Horiba FluoroLog-3 spectrofluorometer employing dichloromethane. Fluorescence quantum yields were determined using a Hamamatsu integrating sphere, exciting at 345 nm. Electrochemical studies were carried out by using an Autolab Potentiostat (Model PGSTAT101) using a three-electrode cell. The cell was equipped with platinum working and counter electrodes, as well as a silver wire reference electrode. In all experiments, $[NBu_4][PF_6]$ (0.1 M in dry CH_2Cl_2) was used as the supporting electrolyte with analyte concentration of approximately 1 mM. Measurements were performed at 100 mVs^{-1} scan rates. All redox potentials were referenced to the Fc$^+$/Fc couple as internal standard with $E_{1/2}$(Fc/Fc$^+$) *vs.* the saturated calomel electrode SCE = +0.46 V.

Synthesis of complex 1. A suspension of the pyrene-imidazolium salt (250 mg, 0.57 mmol) and Ag_2O (66.5 mg, 0.29 mmol) in dichloromethane (30 mL) was stirred at room temperature for 4 h under the exclusion of light. Then, $[AuCl(SMe_2)]$ (169.1 mg, 0.57 mmol) was added and the resulting mixture was stirred at room temperature overnight. The suspension was filtered through a pad of Celite and the solvent removed under vacuum. The desired solid was isolated as a bright yellow crystalline solid. Yield: 271.9 mg, 81 %. Electrospray MS (20 V, *m/z*): 592.2 [M-Cl+MeCN]$^+$. Anal. Calcd. for $C_{25}H_{26}N_2AuCl \cdot CH_2Cl_2$ (671.72): C, 46.48; H, 4.20; N, 4.17. Found: C, 46.79; H, 4.32;

N, 4.23. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (d, $^3J_{\text{H-H}}$ = 9 Hz, 2H, CH_{pyr}), 8.28 (d, $^3J_{\text{H-H}}$ = 9 Hz, 2H, CH_{pyr}), 8.15 (s, 2H, CH_{pyr}), 8.12 (t, $^3J_{\text{H-H}}$ = 9 Hz, 2H, CH_{pyr}), 5.17-5.05 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 2.16-2.03 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.73-1.57 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 1.04 (t, $^3J_{\text{H-H}}$ = 15 Hz, 6H, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 177.89 (Au-C_{carbene}), 132.35 ($C_{\text{q pyr}}$), 128.51 (CH_{pyr}), 127.53 ($C_{\text{q pyr}}$), 126.66 (CH_{pyr}), 126.39 (CH_{pyr}), 123.50 ($C_{\text{q pyr}}$), 120.93 ($C_{\text{q pyr}}$), 119.12 (CH_{pyr}), 52.28 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.36 (NCH$_2$CH$_2$CH$_2$CH$_3$), 20.14 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.01 (NCH$_2$CH$_2$CH$_2$CH$_3$).

Synthesis of complex 2. Phenylacetylene (9.54 µL, 0.085 mmol) and NaOH (8.52 mg, 0.213 mmol) were dissolved in methanol (20 mL). The solution was heated at reflux for 1 hour. Then, complex **1** (50.00 mg, 0.085 mmol) was added as a solid and the resulting suspension was heated at reflux for 4 h. The mixture was evaporated to dryness and the solid residue was extracted with dichloromethane, and the solution was filtered through a short pad of Celite. Complex **2** was isolated as a yellow solid. Yield: 50.80 mg, 91%. IR (ATR): ν(C≡C): 2115 cm^{-1}. HRMS ESI-TOF-MS (positive mode): 653.3 [M+H]$^+$. Anal. Calcd. for C$_{33}$H$_{31}$N$_2$Au (652.50): C, 60.73; H, 4.79; N, 4.29. Found: C, 60.74; H, 4.73; N, 4.26. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.53 (d, $^3J_{\text{H-H}}$ = 6 Hz, 2H, CH_{pyr}), 8.25 (d, $^3J_{\text{H-H}}$ = 6 Hz, 2H, CH_{pyr}), 8.12 (s, 2H, CH_{pyr}), 8.10 (t, $^3J_{\text{H-H}}$ = 9 Hz, 2H, CH_{pyr}), 7.58 (d, $^3J_{\text{H-H}}$ = 6 Hz, 2H, CH_{ben}), 7.31-7.19 (m, 3H, CH_{ben}), 5.26-5.09 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 2.22-2.02 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.79-1.57 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 1.03 (t, $^3J_{\text{H-H}}$ = 16 Hz, 6H, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 193.27 (Au-C_{carbene}), 132.57 (CH_{ben}), 132.30 ($C_{\text{q pyr}}$), 128.42 (CH_{pyr}), 128.00 (CH_{ben}), 127.68 ($C_{\text{q pyr}}$), 126.55 (CH_{pyr}), 126.50 ($C_{\text{q ben}}$), 126.14 (CH_{pyr}), 125.81 ($C_{\text{q pyr}}$), 123.45 ($C_{\text{q pyr}}$), 121.10 ($C_{\text{q acetylide}}$), 119.12 (CH_{pyr}), 105.60 ($C_{\text{q acetylide}}$), 51.92

(N$CH_2CH_2CH_2CH_3$), 32.51 (NCH$_2$$CH_2CH_2CH_3$), 20.19 (NCH$_2CH_2$$CH_2CH_3$), 14.07 (NCH$_2CH_2CH_2$$CH_3$).

Synthesis of complex 3. 1,4-Diethynylbenzene (10.74 mg, 0.085 mmol) and NaOH (17.04 mg, 0.426 mmol) were dissolved in methanol (20 mL). The solution was heated at reflux for 1 hour. Then, complex **1** (100.00 mg, 0.170 mmol) was added as a solid and the resulting suspension was heated at reflux for 4 h. The mixture was evaporated to dryness and the solid residue was extracted with dichloromethane, and the solution was filtered through a short pad of Celite. Complex **3** was isolated as a yellow solid. Yield: 76.00 mg, 73%. IR (ATR): ν(C≡C): 2112 cm^{-1}. HRMS ESI-TOF-MS (positive mode): 1227.4 [M+H]$^+$. Anal. Calcd. for $C_{60}H_{56}N_4Au_2 \cdot CH_2Cl_2$ (1311.79): C, 55.84; H, 4.46; N, 4.27. Found: C, 55.67; H, 4.86; N, 4.33. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.42 (d, $^3J_{\text{H-H}}$ = 6 Hz, 2H, CH_{pyr}), 8.22 (d, $^3J_{\text{H-H}}$ = 6 Hz, 2H, CH_{pyr}), 8.10 (s, 2H, CH_{pyr}), 8.05 (t, $^3J_{\text{H-H}}$ = 9 Hz, 2H, CH_{pyr}), 7.50 (s, 2H, CH_{ben}), 5.18-4.98 (m, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 2.19-1.95 (m, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.74-1.54 (m, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 1.02 (t, $^3J_{\text{H-H}}$ = 9 Hz, 6H, NCH$_2$CH$_2$CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 193.28 (Au-C_{carbene}), 132.18 ($C_{\text{q pyr}}$), 132.15 (CH$_{\text{ben}}$), 129.47 ($C_{\text{q pyr}}$), 128.38 (CH$_{\text{pyr}}$), 127.46 ($C_{\text{q pyr}}$), 126.46 (CH$_{\text{pyr}}$), 126.05 (CH$_{\text{pyr}}$), 123.74 ($C_{\text{q ben}}$), 121.27 ($C_{\text{q pyr}}$), 120.93 ($C_{\text{q acetylide}}$), 119.01 (CH$_{\text{pyr}}$), 105.94 ($C_{\text{q acetylide}}$), 51.82 (NCH$_2$CH$_2$CH$_2$CH$_3$), 32.46 (NCH$_2$$CH_2CH_2CH_3$), 20.16 (NCH$_2CH_2$$CH_2CH_3$), 14.06 (NCH$_2CH_2CH_2$$CH_3$).

Acknowledgements

Conflict of interests

The authors declare no conflict of interests.

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Highlights:

- Three pyrene-imidazolylidene complexes of gold(I) are described and fully characterized.

- The properties of these complexes are dominated by their tendency to self-aggregate, as shown by their solid state structures and by the ^{1}HNMR studies in solution.

- The photophysical properties of the complexes have been studied, including Uv-Vis and emission spectra, emission quantum yields and cyclic voltammetry

Conflict of interests

The authors declare no conflict of interests.