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Construction of molecular wires based on a gold(I) bis-σ-acetylide building block incorporated into ruthenium(II) polypyridyl complexes†

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An Ru(II)–Au(I)–Ru(II) triad has been synthesized from [Ru(bpy)$_2$(3-ethynylphenanthroline)]$^{2+}$ with Au(tht)Cl and characterized by spectroscopic means such as NMR and ESI-MS; the Ru(II)–Au(I)–Ru(II) triad shows an intense emission at 620 nm upon excitation at 360 nm, which suggests an efficient energy transfer from the Au site to Ru sites *via* extended π-conjugation through the ethynyl units.

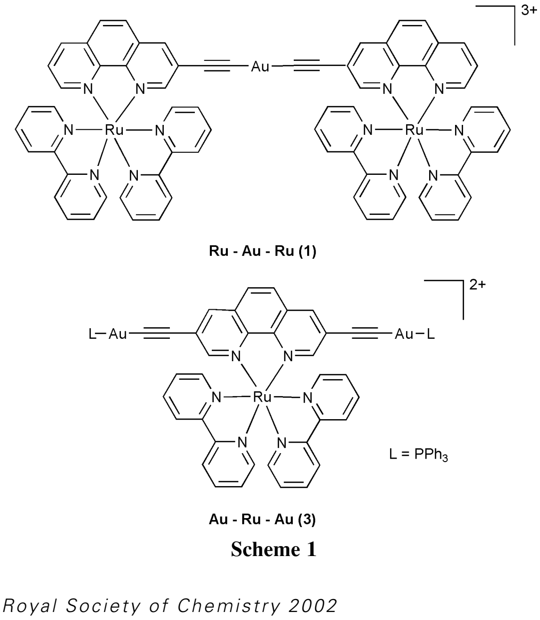
The development of molecular wires and rods has gained importance in view of their potential applications in the burgeoning field of nano-scale molecular electronic devices. An attractive pursuit in this area is the design of supra-architectures by use of rigid building blocks with readily tunable electronic, structural and photophysical characteristics.[1] Photoactive molecular-scale wires based on alkynylene-bridged ruthenium(II) polypyridyl complexes have been extensively studied by Ziessel and coworkers.[1,2] However, to the best of our knowledge, only one example of a multinuclear ruthenium(II) polypyridyl complex which possess bis-σ-acetylide platinum(II) units bonded to bipyridine ligands, has so far been reported. It has been further described that this bis-σ-acetylide platinum(II) system does not operate as a molecular wire in the previous research,[3] because the function as a molecular wire is interfered with by the supposed charge injection from the ruthenium center to the unsubstituted bipyridine ligand for this system. The design of a photoactive molecular wire requires efficient electron transfer in the excited state from the ruthenium center to the wire skeleton which contains a substituted diimine ligand. In this study, we became interested in the gold(I)–acetylide unit as a component to link to ruthenium(II) polypyridyl moieties, since gold(I) acetylide complexes L–Au(I)–C≡CR[4] and polynuclear gold(I) acetylide[5,6] have been shown to exhibit rich photophysics with long-lived emission, and are well known to form linear two-coordinate species which are suitable for designing rigid molecular wires. Herein, we report the synthesis, photophysical properties, and electrochemistry of novel trinuclear Ru(II)–Au(I)–Ru(II), Au(I)–Ru(II)–Au(I), and dinuclear Ru(II)–Au(I) complexes in which ethynyl substituents are σ-bonded to phenanthroline ligands.

These heteronuclear complexes were prepared according to a one-pot procedure without requirement for a catalyst. The Ru(II)–Au(I)–Ru(II) triad (**1**) (Scheme 1) was synthesized from Au(tht)Cl (tht = tetrahydrothiophene) and [(bpy)$_2$Ru(3-ethynylphenanthroline)](PF$_6$)$_2$ (**2**) (1 : 2 mol ratio, with an excess of diisopropylamine as a base), while the Au(I)–Ru(II)–Au(I) triad (**3**) and the Ru(II)–Au(I) dyad (**4**) were prepared by reacting Au(PPh$_3$)Cl with [(bpy)$_2$Ru(3,8-bis(ethynyl)phenanthroline)](PF$_6$)$_2$ (**5**) and **2**, respectively (2 : 1 and 1 : 1 ratio, respectively). These complexes were characterized by ESI-MS, ^{1}H NMR, IR, UV–Vis, emission–excitation (Em–Ex) spectroscopies and elemental analysis. Full details regarding the synthesis and characterization of these complexes are presented in the electronic supplementary information.†

In the ^{1}H NMR spectra, the proton signals assigned to the phenanthroline ligand are shifted up-field for the new complexes **1**, **3** and **4** compared with those of the precursor complexes **2** and **5**, while the signals of the bipyridine ligand are almost intact.[2] This up-field shift is construed in terms of π back-donation (dπ–pπ interaction) from the gold(I) center to the σ-ethynyl triple bond in the substituted phenanthroline ligand. Further evidence in support of this π back-donation and the extensive electron delocalization promoted by the bridging gold(I) ion is provided by the CV data described below.

Redox potentials for the new and precursor complexes were determined in MeCN by cyclic voltammetry. A reversible oxidation wave due to oxidation of the ruthenium(II) center is observed in addition to two or three reduction waves assignable to substituted phenanthroline and bipyridine ligands. The first reduction wave in these complexes possibly originates from the gold(I)–ethynyl unit bonded to the phenanthroline, because the extended π conjugate system over ethynylphenanthroline acts as a better π electron acceptor than the unsubstituted bipyridine ligands. The variation of the first reduction potential for these complexes shown in Table 1 (**1**, **4** < **2** and **3** < **5**) is consistent with the interpretation of the ^{1}H NMR data for these five complexes. Resulting π back-donation upon the formation of the linkage to Au(I)–ethynyl units should be responsible for the negative shift of the reduction potential of the phenanthroline ligand in these new supra-molecules.

The absorption spectrum of triad **1** in MeCN is displayed in Fig. 1. The gold–ethynyl chromophore is primarily responsible for the near-visible π–π* absorption band at 362 nm[6] and the



Ru - Au - Ru (1)

Au - Ru - Au (3)

Scheme 1

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† Electronic supplementary information (ESI) available: preparation and characterization data for **1**, **3** and **4** and Fig. S1. See http://www.rsc.org/suppdata/cc/b1/b111248c/

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Table 1 Relevant spectroscopic and electrochemical data

	Absorption[a]	Emission[a]		CV data[b]		
Complex	λ/nm ($10^{-4}\varepsilon$/dm^{3}mol^{-1}cm^{-1})	λ_{max}/nm	Em$_{max}$[c]/eV	E_{ox}/V	E_{red1}/V	ΔE[d]/V
1	452 (2.63), 424 (2.28), 362 (5.65)	620	2.00	0.998	−1.596	2.594
3	452 (1.38), 428 (1.28), 369 (5.86), 359 (5.73)	627	1.98	1.043	−1.499	2.542
4	452 (1.11), 423 (0.96), 343 (2.76)	619	2.00	1.000	−1.616	2.616
Ru(bpy)$_3$	451 (1.38), 423 (1.09)	622	1.99	0.983	−1.655	2.638
2	450 (1.44), 423 (1.31)	641	1.93	1.011	−1.466	2.477
5	486 (0.94), 438 (1.58), 330 (3.00)	666	1.86	1.040	−1.357	2.397

[a] UV–Vis and emission spectra were taken in CH_3CN. [b] Cyclic voltammograms were measured in 1 mM acetonitrile solutions containing 0.1 M Bu_4NPF_6, using a $Ag/AgNO_3/CH_3CN$ reference electrode and Pt, working at 100 mV s^{-1} scan rate. Under these conditions, $E_{1/2} = 0.084$ V for Fc/Fc$^+$. [c] Wavelengths of emission maxima are converted to eV ($Em_{max} = 1240/\lambda_{max}$). [d] $\Delta E = E_{ox} - E_{red1}$

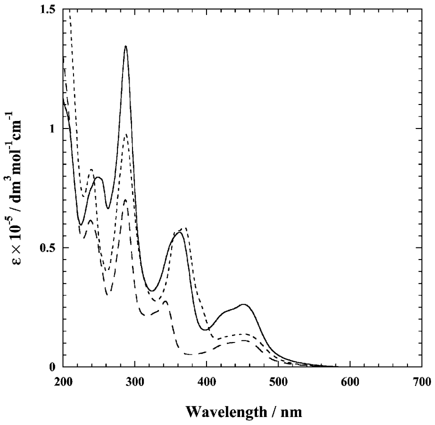

Fig. 1 UV–Vis absorption spectra of **1** (—), **3** (- - -), and **4** (— —) in acetonitrile at room temperature.

absorptions (400–500 nm) in the visible region are due to the dπ(Ru) ⟶ π*(ligand) MLCT transition in **1**. Similar absorption spectra are observed for triad **3** and dyad **4**. Molecular absorption coefficients for the π–π* absorptions (359 and 369 nm) in **3** are close to those of **1** but twice the intensity as those (342 nm) of **4** (Fig. 1). As the absorption coefficient is proportional to the number of the Au(I)–ethynyl units, this finding supports the interpretation that the near-visible absorption bands are assignable to π–π* (C≡C–phen) transitions. The red shift of the π–π* absorptions in **1** relative to those in **4** is attributed to more electron delocalization between two ethynylphenanthroline ligands through the bridging gold(I) ion as described above. Visible absorption bands and absorption coefficients per Ru(II)–polypyridyl unit of these three complexes are almost in accord with the data of the related $[Ru(bpy)_3](PF_6)_2$ complex (Table 1). Thus the lowest energy absorption band is assignable to the MLCT on the Ru(II) unit, not on the Au(I) unit.

Triad **1** displays only one visible emission band centered at 620 nm in deoxygenated acetonitrile at room temperature upon excitation at 360 nm as shown in Fig. S1 (ESI†). This emission is characteristic of the MLCT-based luminescence typically observed in Ru(II)–diimine complexes and no luminescent and/or phosphorescent emission originating from the gold(I)–ethynyl unit is exhibited.[7] The corrected excitation spectrum of **1** between 300 and 500 nm is approximately compatible with the absorption spectrum in this region, which suggests that the efficiency of the energy transfer is about 95%. The hybrid architecture in **1** constructed from Ru(II)–polypyridyl and Au(I)–ethynyl units harvests near-visible light, and converts the blue and/or green gold(I)–acetylide luminescence[6] to an orange MLCT-based emission. Triad **3** and dyad **4** exhibit similar photophysical characteristics. The present triads and dyad, to the best of our knowledge, are the first ruthenium–gold systems which display the aforementioned photophysical behaviors although similar luminescent systems have been reported for Ru(II)–polypyridyl complexes which incorporate organic chromophores.[8] Another interesting finding is that there is a good correlation between the wavelength of luminescence maxima (λ_{em}) and the separation between the oxidation and the first reduction potential (ΔE) (Table 1). Emission maxima λ_{em} for these complexes decrease with an increase of the separation ΔE; the ΔE value is strongly influenced by the reduction potential of the ligand rather than by the oxidation potential for Ru(II/III). The correlation indicates that this emission in the excited triplet state is based on the charge transfer from the ruthenium center to the ethynylphenanthroline.[1a,3] The present Ru(II)–Au(I) system is useful not only for the construction of molecular wire but also for antenna systems which efficiently harvests near-visible light; the platinum(II)–ethynylbipyridyl system did not exhibit such characteristics as mentioned above.

We are currently investigating the photophysical and electrochemical properties of other metal polypyridyl complexes linked with gold(I) bis-σ-acetylide organometallic units.

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