

Sulfide-capped wire-like metallaynes as connectors for Au nanoparticle assemblies†

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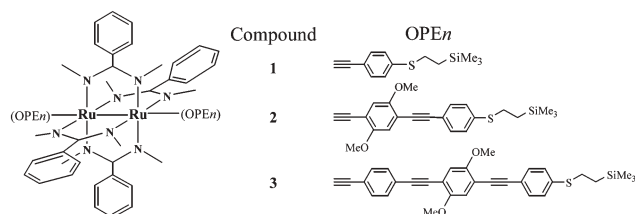
Received (in Cambridge, UK) 10th August 2004, Accepted 15th October 2004

First published as an Advance Article on the web 30th November 2004

DOI: 10.1039/b412336k

A new series of $\text{Ru}_2(\text{DMBA})_4(\text{oligo}(\text{phenyleneethyne}))_2$ compounds bearing sulfide termini was synthesized; structural characterization revealed both the rigid rod nature and extended π -conjugation in these metallaynes; in the presence of these metallaynes, Au nanoparticles readily assembled into dimers and chains with well-defined inter-dimer distances.

Molecular electronics and functional nanoparticles represent two of the most active research areas at the interface of chemistry, physics and material science.^{1,2} While there is considerable interest on nanoparticles as novel catalysts,^{3–6} the integration of nanoparticles with molecular bridges, especially conjugated rigid rod molecules, has emerged as an exciting new frontier during the recent years. Organization of nanoparticles using molecular linkers can be traced to the pioneering work of Alivisatos and others.^{7,8} Recent results with the emphasis towards electronic materials applications include hierarchical assemblies of Ag and Au nanoparticles with sulfide-capped linear and branched oligo(phenyleneethyne)s (OPE),^{9–11} conductance enhancement between two Au nanowires using sulfide-capped oligo(phenylenevinylene) (OPV) bridges,¹² transfer of spin coherence between CdSe nanoparticles mediated by 1,4-benzenedimethanethiol,¹³ magnetic flux closure in Co nanoparticles ring templated with resorcinarene^{14,15} and nano-cells constructed from *disordered* metallic Au islands and sulfide-capped OPEs.¹⁶ We are interested in achieving active materials for molecular electronic devices based on conjugated diruthenium metallaynes and reported high degree of electronic mobility across both the carbon backbone and diruthenium units recently.^{17,18} Here, we wish to report the synthesis of a new family of sulfide-capped diruthenium-bis(OPE) compounds (Scheme 1) and their utility for the preparation of dimers and linear chains of Au nanoparticles.



Scheme 1 Wire-like Ru_2 -(OPE) $_n$ metallaynes 1–3.

† Electronic supplementary information (ESI) available: Synthesis and characterization of 1–3, X-ray crystallographic details for 1 and 2, and experimental details for nanoparticle preparation and assembly experiments. See <http://www.rsc.org/suppdata/cc/b4/b412336k/> *akaifer@miami.edu (Angel E. Kaifer)

The sulfide capped OPE $_n$ ligands were prepared following literature procedures.^{19,20} Trimethylsilylethylene (TMSE) was chosen as the thiol protection group because of its superior chemical stability over acetyl protection group, and methoxy phenyl substituents were introduced in both OPE2 and OPE3 to improve the solubility of metallaynes. Using the weak base protocol,^{21–23} reactions between $[\text{Ru}_2(\text{DMBA})_4](\text{NO}_3)_2$ (DMBA = *N,N'*-dimethylbenzamidinate) and the appropriate OPE $_n$ ligand resulted in *trans*-(OPE $_n$) $_2\text{Ru}_2(\text{DMBA})_4$ compounds 1–3 as red, diamagnetic crystalline materials. Cyclic voltammetric measurements with compounds 1–3 revealed nearly identical voltammograms (Fig. 1) consisting of an oxidation (A) and a reduction (B), from which the HOMO–LUMO gap of the solvated metallaynes was estimated to be *ca.* 1.57 V. In comparison, the optical HOMO–LUMO gap of compounds 1–3 estimated from the lowest λ_{max} is *ca.* 1.42 eV.

The molecular structures of compounds 1 and 2,† shown in Fig. 2, provide structural insights of these conjugated metallaynes. The coordination geometry around the Ru_2 core in both cases is similar to that observed for other $\text{Ru}_2(\text{DMBA})_4(\text{C}_2\text{R})_2$ type compounds,²¹ indicating a very minimal structural perturbation by the OPE $_n$ ligand. In addition to the apparent rigid rod nature, the near co-planarity among phenyleneethyne units is noteworthy and reflects the extended π -conjugation across the entire metallayne, which is consistent with both the early structural analysis^{24–26} and more recent computational studies of pure organic OPEs.²⁷

The presence of terminal sulfide functional groups at both ends of these rod shaped molecules opens the possibility of using them as organometallic tethers between noble metal nanostructures. In order to test this possibility, we prepared 12-nm gold nanoparticles using a well-established method relying on the citrate reduction of aqueous solutions of AuCl_4^- .²⁸ Colloidal solutions of these Au nanoparticles were treated with aliquots of solutions containing compounds 1 to 3 (see ESI† for experimental details) until the corresponding surface plasmon resonance band shifted from a λ_{max} of 518 to 525 nm. At that point, the presence of discrete nanoparticle aggregates was presumed and substantiated by TEM analysis. Numerous well-defined nanoparticle dimers were

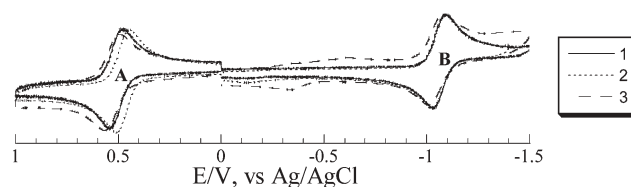


Fig. 1 Cyclic voltammograms of compounds 1–3 recorded in THF at a scan rate of 0.10 V s^{−1}.

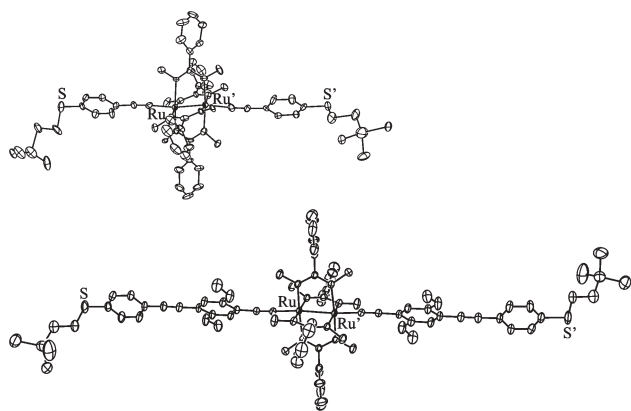


Fig. 2 ORTEP plots of compound **1** (top) and **2** (bottom) at 30% probability level.

observed in the TEM images of these preparations, confirming that compounds **1–3** serve as effective linkers between the Au nanoparticles (see Fig. 3). From the TEM images we measured 1.7 ± 0.2 , 2.6 ± 0.4 and 3.7 ± 0.9 nm as the averaged distances between nanoparticles prepared with tethers **1**, **2** and **3**, respectively. The corresponding S–S distances estimated based on the crystal structures of **1** and **2** and a molecular model of **3** are 2.08, 3.44 and 4.80 nm. Therefore, the measured distances separating adjacent nanoparticles in the observed dimer and chain aggregates correlate well with the S–S distances in the organometallic linkers (see plot in ESI†), providing additional support to the proposed structures. Notice that the average interparticle distances measured by TEM are shorter than the linker S–S distances, which may be due to dimer orientation effects and positioning away from the plane perpendicular to the direction of observation. Energy dispersive spectroscopy verified the presence of Ru in Au nanoparticle aggregates that were observed when excess linker was utilized in the nanoparticle assembly experiments. This finding further confirms the tethering activity of the Ru₂ metallocene disulfides **1–3** as nanoparticle connectors. We also verified in control experiments that any excess citrate that might be present in the Au nanoparticle sols does not react with compounds **1–3**.

From our TEM data we estimate that the yield of nanoparticle dimers under the experimental conditions utilized in this work is $32 \pm 3\%$ in all cases. Other well-defined aggregates were readily observed in the TEM images recorded after deposition on copper grids of drops of Au nanoparticle sols treated with linkers **1–3**. Specifically, linear chains of Au nanoparticles were easily detected

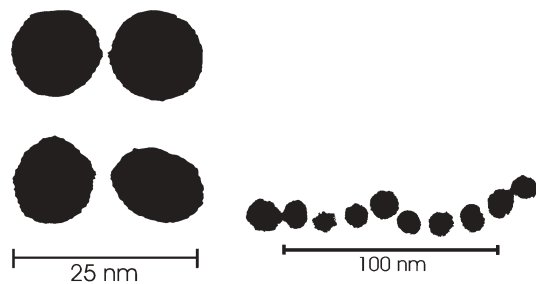


Fig. 3 TEM images of representative dimers (left) linked by compound **1** (top) and **3** (bottom) and a representative nanoparticle chain (right) obtained by tethering with compound **3**.

(Fig. 3) with all linkers and the corresponding inter-particle distances included in the statistical calculations of the values reported above.

In summary, we have prepared a series of three new conjugated Ru₂ metallaynes with two terminal trimethylsilylethylene sulfide groups. These compounds offer interesting and rare examples of extended conjugation over rather long molecular distances, with integral Ru₂ metallaynes, which are known to facilitate the electronic communication between the two molecular ends.^{17,18} We have also used these rigid organometallic disulfides as connectors of variable length for the preparation of Au nanoparticle dimers and chains. To the best of our knowledge, these are the first examples of variable-length nanoparticle tethers containing transition metal compounds in their backbones. Further investigation of these systems continues in our laboratories.

Financial support from the Office of Naval Research (N00014-03-1-0531) is gratefully acknowledged.

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Notes and references

† *Crystal data.* **1**-C₆H₁₄: C₆₈H₉₂N₈Ru₂S₂Si₂, monoclinic, space group *C2*, *a* = 11.2193(17), *b* = 18.897(3), *c* = 16.872(3) Å, β = 106.173(3)°, *V* = 3435.6(9) Å³, *Z* = 2, *D*_c = 1.299 g cm⁻³, λ(Mo-Kα) = 0.71074 Å, μ = 0.580 mm⁻¹. A total of 5540 independent reflections were collected on a SMART1000 CCD diffractometer at 300 K with the 2θ range of 4.8–50°. The structure was solved with direct method and refined with full-matrix least squares on *F*² to *R*1 = 0.041 and *wR*2 = 0.095. **2**-C₆H₁₄: C₈₈H₁₀₈N₈O₄Ru₂S₂Si₂, triclinic, space group *P1̄*, *a* = 12.9758(12), *b* = 13.8400(12), *c* = 14.2445(13) Å, α = 106.950(2), β = 104.661(2), γ = 107.477(2)°, *V* = 2165.2(3) Å³, *Z* = 1, *D*_c = 1.276 g cm⁻³, λ(Mo-Kα) = 0.71074 Å, μ = 0.477 mm⁻¹. A total of 7536 independent reflections were collected on a SMART1000 CCD diffractometer at 300 K with the 2θ range of 4.8–50°. The structure was solved and refined as above to *R*1 = 0.060 and *wR*2 = 0.105. CCDC 246907 and 246908. See <http://www.rsc.org/suppdata/cc/b4/b412336k/> for crystallographic data in .cif or other electronic format.

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