

Electronic Supplementary Information

“Sulfide-capped Wire-like Metallaynes As Connectors for Au Nanoparticle Assemblies”

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Experimental

n-BuLi and Pd(PPh₃)₂Cl₂ were purchased from Aldrich, 1-bromothiophenol, diisopropylamine, triethylamine, iodine, 1,4-dimethoxybenzene, vinyltrimethylsilane, tert-butyl peroxide and copper iodide from ACROS, trimethylsilylacetylene and trimethylsilyl ethynyl iodobenzene from GFS, and silica gel from Merck. Ru₂(DMBA)₄(NO₃)₂ was prepared according to the literature.¹ THF was distilled over Na/benzophenone under an N₂ atmosphere prior to use. ¹H NMR spectra were recorded on a Bruker AVANCE300 NMR spectrometer, with chemical shifts (δ) referenced to the residual CHCl₃. Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer using KBr disks. Vis-NIR spectra were obtained with a Perkin-Elmer Lambda-900 UV-Vis-NIR spectrophotometer. Cyclic voltammograms were recorded in 0.2 M (*n*-Bu)₄NPF₆ solution (THF, N₂-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. The concentration of diruthenium species is always 1.0 mM. The ferrocenium/ferrocene couple was observed at 0.586 V (vs. Ag/AgCl) under experimental conditions.

1. Synthesis of H-OPE1

H-OPE1 was prepared from literature procedure, and the sample was identified by comparison of NMR data with those reported in literature.²

2. Synthesis of TMS-OPE2

A solution of 0.500 g (1.4 mmol) of 2-iodo-5-(trimethylsilyl)ethynyl-1,4-dimethoxybenzene, which was prepared using literature procedure with slight modification,² and 0.325 g (1.39 mmol) of OPE1, 0.139 g (0.2 mmol) of Pd(PPh₃)₂Cl₂, 0.139 g (0.70 mmol) of CuI, 30 mL of diisopropylamine and 30 mL of THF was stirred under argon at 70 °C overnight. The solvents were removed and the residue was purified by column chromatography with CH₂Cl₂/hexanes (1/5, v/v) to yield 0.57 g (88%) of pure product. Data for OPE2: ¹H NMR: 7.47 (*d*, 2H, aromatic), 7.25 (*m*, 2H, aromatic), 6.98 (*d*, 2H, aromatic), 3.88 (*d*, 6H, CH₃O-), 3.02-2.98 (*m*, 2H, TMSCH₂CH₂S-), 0.98-0.95 (*m*, 2H, TMSCH₂CH₂S-), 0.29 (*s*, 9H, -Si(CH₃)₃), 0.09 (*s*, 9H, -Si(CH₃)₃).

3. Synthesis of TMS-OPE3

A mixture of 0.500 g (1.27 mmol) of *H*-OPE2, which was prepared by desilylation of TMS-OPE2 with excess of K₂CO₃ in THF/CH₃OH (1/1, v/v), and 0.38 g (1.27 mmol) of trimethylsilyl ethynyl iodobenzene, 0.150 g (0.21 mmol) of Pd(PPh₃)₂Cl₂, 0.150 g (0.8 mmol) of CuI, 40 mL of diisopropylamine and 40 mL of THF was stirred under argon at 70 °C overnight. Solvents were removed and the residue was purified by column chromatography with CH₂Cl₂/hexanes (1/5, v/v) to yield 0.550 g (76%) of pure product. Data for TMS-OPE3: ¹H NMR: 7.50–7.42 (*m*, 7H, aromatic), 7.25-7.22 (*m*, 1H, aromatic), 7.01 (*d*, 2H, aromatic), 3.89 (*d*,

6H, CH₃O-), 3.01-2.95 (*m*, 2H, TMSCH₂CH₂S-), 0.97-0.91 (*m*, 2H, TMSCH₂CH₂S-), 0.25 (*s*, 9H, -Si(CH₃)₃), 0.05 (*s*, 9H, -Si(CH₃)₃).

4. Synthesis of Ru₂(DMBA)₄(OPE1)₂

To a suspension of 0.200 g (0.22 mmol) of Ru₂(DMBA)₄(NO₃)₂ in 50mL THF was added 0.500 g (2.14mmol) of *H*-OPE1 and 20mL of Et₃N. The reaction mixture was stirred at room temperature for 2h. Upon the solvent removal, the residue was triturated with methanol and filtered to afford a red powder 0.180 g (73%). Data for Ru₂(DMBA)₄(OPE1)₂: ¹H NMR: 7.42-7.36 (*m*, 12H, aromatic), 7.14 (*d*, 4H, aromatic), 6.99 (*t*, 12H, aromatic), 3.26 (*s*, 24H, MeN-), 2.85 – 2.79 (*m*, 4H, TMSCH₂CH₂S-), 0.87 – 0.80 (*m*, 4H, TMSCH₂CH₂S-), 0.03 (*s*, 18H, -Si(CH₃)₃); MS-FAB (*m/e*, based on ¹⁰¹Ru): 1262 [M⁺H]; Vis-NIR, λ_{max}(nm, ε(M⁻¹cm⁻¹)): 890(1,660), 510(12,130), 340(37,130); IR (cm⁻¹): ν(≡CH) 2078.0 (*s*) ; Electrochemistry, E_{1/2}/V, ΔE_p/V, *i*_{backward}/*i*_{forward}: **A**, 0.517, 0.057, 0.960; **B**, -1.060, 0.057, 0.939. E_g: 1.58

5. Synthesis of Ru₂(DMBA)₄(OPE2)₂

To a suspension of 0.160 g (0.18 mmol) of Ru₂(DMBA)₄(NO₃)₂ in 50 mL THF was added 0.496 g (1.06 mmol) of *H*-OPE2 and 20mL Et₃N. The reaction mixture was stirred at room temperature for 2h. Upon the solvent removal, the residue was purified by column chromatography, and eluted with THF/hexanes (1/5, v/v) to afford 0.108 g (38%) title compound as red crystalline solid. Data for Ru₂(DMBA)₄(OPE2)₂: ¹H NMR: 7.48-7.41 (*m*, 16H, aromatic), 7.21 (*d*, 4H, aromatic), 7.05 (*d*, 8H, 6.90 aromatic), 6.89 (*s*, 2H, aromatic), 6.63 (*s*, 2H, aromatic), 3.80 (*s*, 6H, CH₃O-), 3.70 (*s*, 6H, CH₃O-), 3.35 (*s*, 24H, MeN-), 2.99 – 2.94 (*m*, 4H, TMSCH₂CH₂S-), 0.95 – 0.83 (*m*, 4H, TMSCH₂CH₂S-), 0.04 (*s*, 9H, -Si(CH₃)₃), 0.01 (*s*, 9H,

-Si(CH₃)₃); MS-FAB (m/e, based on ¹⁰¹Ru): 1581 [M⁺H]; Vis-NIR, λ_{max}(nm, ε(M⁻¹cm⁻¹)): 870(2,225), 500(18,120), 400(61,880); IR (cm⁻¹): ν(≡CH) 2068.5 (s) ; Electrochemistry, E_{1/2}/V, ΔE_p/V, i_{backward}/i_{forward}: **A**, 0.478, 0.061, 0.988; **B**, -1.056, 0.061, 0.885. E_g: 1.534

6. Synthesis of Ru₂(DMBA)₄(OPE3)₂

To a suspension of 0.200 g (0.22 mmol) of Ru₂(DMBA)₄(NO₃)₂ in 50 mL THF was added 0.680 g (1.38 mmol) of *H*-OPE3, prepared from desilylation of *TMS*-OPE3 with excess of K₂CO₃ in THF/CH₃OH (1/1, v/v), and 20 mL Et₃N. The reaction mixture was stirred at room temperature for 2h. Upon the solvent removal, the residue was purified by column chromatography, and eluted with THF/hexanes (1/5, v/v) to afford 0.130 g title compound (33%).

Data for Ru₂(DMBA)₄(OPE3)₂: ¹H NMR: 7.49-7.39 (*m*, 20H, aromatic), 7.28 - 7.26 (*m*, 4H, aromatic), 6.93 - 7.05 (*m*, 16H, 6.90 aromatic), 3.90 (*s*, 12H, CH₃O-), 3.32 (*s*, 24H, MeN-), 3.03 - 2.97 (*m*, 4H, TMSCH₂CH₂S-), 0.99 - 0.86 (*m*, 4H, TMSCH₂CH₂S-), 0.07 (*s*, 9H, -Si(CH₃)₃), 0.02 (*s*, 9H, -Si(CH₃)₃); MS-FAB (m/e, based on ¹⁰¹Ru): 1283 [M⁺ - OPE3]; Vis-NIR, λ_{max}(nm, ε(M⁻¹cm⁻¹)): 860(3,489), 510(sh), 380(99,020); IR (cm⁻¹): ν(≡CH) 2069.3 (s) ; Electrochemistry, E_{1/2}/V, ΔE_p/V, i_{backward}/i_{forward}: **A**, 0.530, 0.073, 0.987; **B**, -1.047, 0.075, 0.887. E_g: 1.577

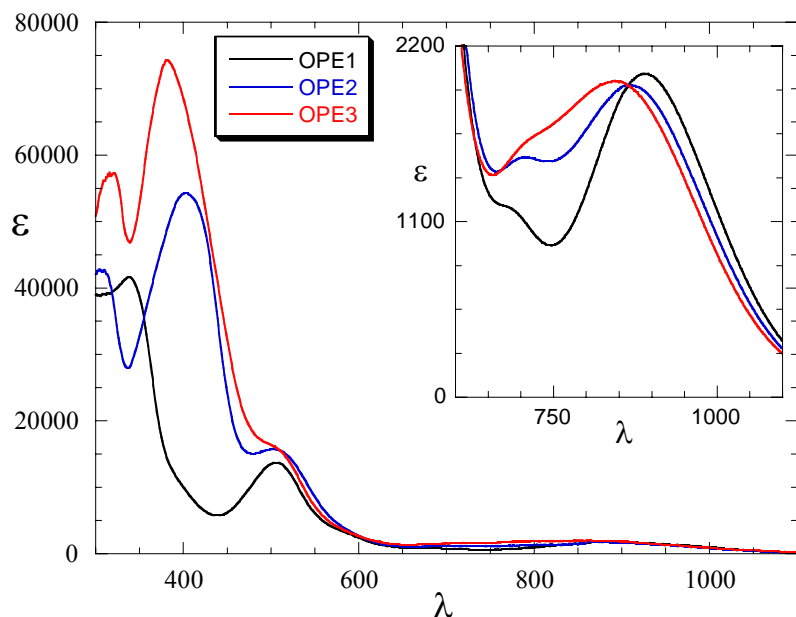


Figure ESI1. UV-Vis-NIR spectra of metallaynes $\text{Ru}_2(\text{DMBA})_4(\text{OPE1})_2$, $\text{Ru}_2(\text{DMBA})_4(\text{OPE2})_2$ and $\text{Ru}_2(\text{DMBA})_4(\text{OPE3})_2$, recorded in THF.

Preparation of Gold Nanoparticles.

A 1.0 mM solution of HAuCl_4 (250 mL) was brought to a rolling boil with vigorous stirring. A solution of 2% sodium citrate (25 mL) was added rapidly to the HAuCl_4 solution, giving rise to a dramatic color change from pale yellow to burgundy. Boiling and vigorous stirring was continued for 10 minutes. The gold nanoparticles in the final solution were characterized by UV-visible spectroscopy ($\lambda_{\text{max}} = 518 \text{ nm}$) and TEM (average particle size of $11.6 \pm 1.6 \text{ nm}$) in excellent agreement with the original report.³

Linker solution preparation.

Linker solutions were prepared by dissolving 0.5 mg of Ru_2 metallayne linker in 0.2 mL THF followed by the addition of ethanol (1 mL) and water (7 mL) in that order.

Nanoparticle assembly.

A 1.0-mL aliquot of colloidal gold solution was diluted to 10 mL and linker solution was added in 10- μ L aliquots, with continuous stirring over a period of about 30 minutes. The reaction was followed by UV-visible spectroscopy and the addition of the linker was stopped once the wavelength of maximum absorption for the surface plasmon resonance band of the gold nanoparticles shifted from 518 nm to 525 nm (Figure SI2). Excess linker leads to extensive aggregation of the gold nanoparticles. However, energy dispersive spectroscopic analysis reveals the presence of Ru in the aggregates (Figure SI3), providing additional support for the tethering action of the Ru₂ metallayne compounds. Furthermore, control experiments with similar compounds containing a single sulfide terminal group did not allow the observation of nanoparticle dimers or chains.

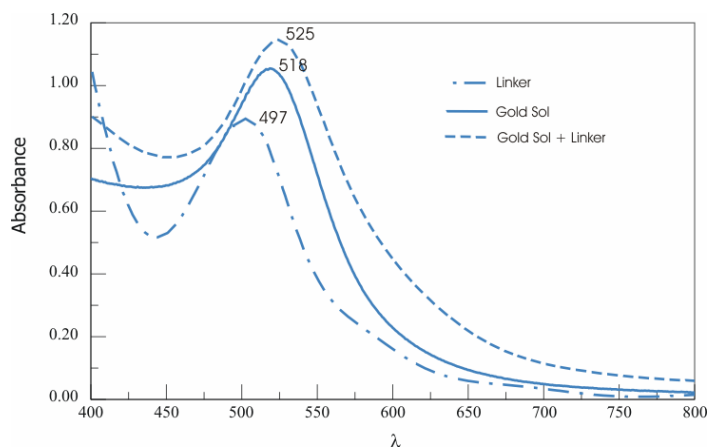


Figure ESI2. Typical visible spectra of the gold nanoparticle solution before and after controlled addition of the shortest linker. Similar spectra with obtained with all the linker compounds. The spectrum of the linker in the absence of nanoparticles is also shown.

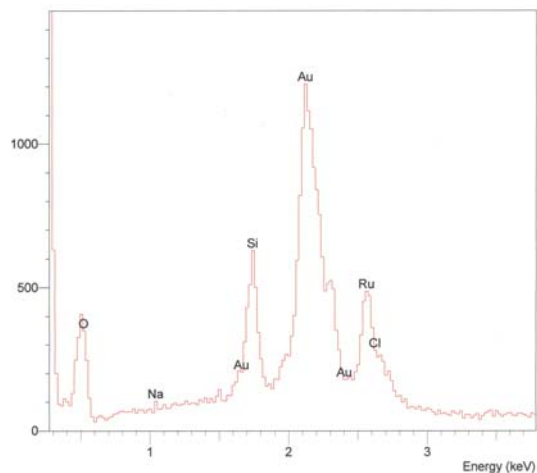


Figure ESI3. Energy dispersive spectrum of Au nanoparticle aggregates obtained by addition of excess **1**.

TEM

One or two drops of linked gold nanoparticle solution were placed on a formvar coated copper grid in contact with filter paper for imaging.

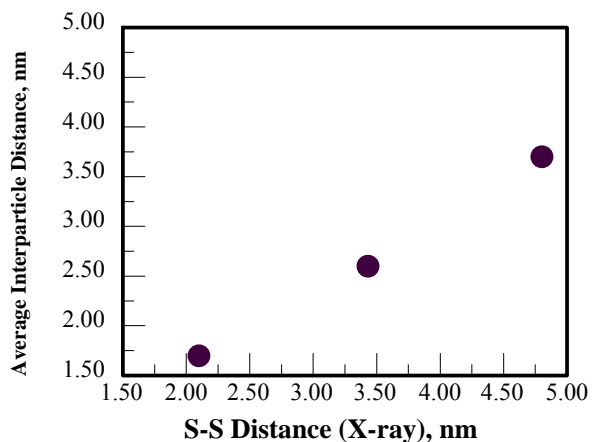


Figure ESI4. Dependence of the average interparticle distance (as measured in TEM experiments) on the S-S distance of the corresponding Ru₂ metallayne linker.

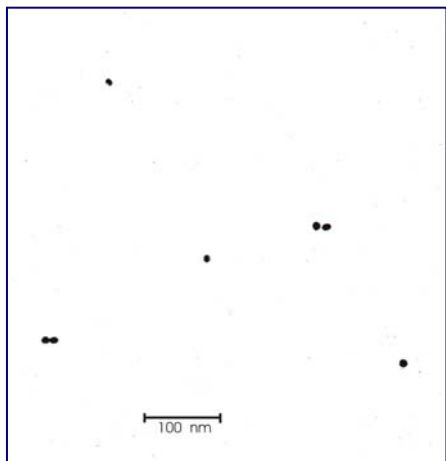


Figure ES15. TEM showing a larger field that captures two dimers and three single nanoparticles. This image was obtained with the longest linker.

Table S1. Crystallographic parameters for compounds **1**C₆H₁₄ and **2**:2C₆H₁₄

	1 C ₆ H ₁₄	2 :2C ₆ H ₁₄
Formula	C ₆₈ H ₉₂ N ₈ Ru ₂ S ₂ Si ₂	C ₈₈ H ₁₀₈ N ₈ O ₄ Ru ₂ S ₂ Si ₂
fw	1343.9	1664.3
Space group	<i>C</i> 2	<i>P</i> $\bar{1}$
<i>a</i> (Å)	11.219(2)	12.976(1)
<i>b</i> (Å)	18.897(3)	13.840(1)
<i>c</i> (Å)	16.872(3)	14.245(1)
α (°)	90	106.950(2)
β (°)	106.173(3)	104.661(2)
γ (°)	90	107.477(2)
Volume (Å ³)	3435.6(9)	2165.2(3)
<i>Z</i>	2	1
<i>d</i> _{calc.} (gcm ⁻³)	1.299	1.276
μ (mm ⁻¹)	0.580	0.477
Radiation	MoK α	MoK α
T (K)	300(2)	300(2)
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.041, 0.095	0.060, 0.12

Table S2. Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

	1	2
Ru-Ru'	2.4597(8)	2.4626(8)
Ru-C1	1.995(5)	1.968(5)
Ru-N1	1.907(14)	1.996(4)
Ru-N2	2.074(13)	1.977(4)
Ru-N3	2.181(12)	2.103(4)
Ru-N4	2.064(14)	2.101(4)
C1-C2	1.204(7)	1.207(7)
C1-Ru-Ru'	160.19(17)	161.38(17)
C2-C1-Ru	172.6(5)	174.6(5)
N1-Ru-Ru'	96.5(4)	95.73(11)
N2-Ru-Ru'	96.3(4)	97.08(12)
N3-Ru-Ru'	80.0(4)	80.09(11)
N4-Ru-Ru'	79.4(4)	78.86(11)

References:

- (1) Xu, G.-L.; Jablonski, C. G.; Ren, T. *Inorg. Chim. Acta* **2003**, *343*, 387.
- (2) Yu, C. J.; Chong, Y. C.; Kayyem, J. F.; Gozin, M. *J. Org. Chem.* **1999**, *64*, 2070.
- (3) Grabar, K. C.; Freeman, R. G.; Hommer, M. B.; Natan, M. J. *Anal. Chem.* **1995**, *67*, 735.