Supporting Information

Photochemistry of Ruthenium tris-bipyridine Functionalized on Gold Nanoparticles

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Experimental details

Synthesis of 4-(3-bromopropyl)-4'-methyl-2,2'-bipyridine, 2a. To a degassed solution of lithium diisopropyl amine (1 equiv., prepared by mixing 2 mL of butyl lithium and 1mL of diisopropyl amine in dry THF) was added 4,4'dimethyl 2,2'bipyridine (500 mg, 2.71 mmol) at -15 ^{o}C. The resulting solution was stirred at this temperature for 1 h to stabilize the monoanion produced. To the above stirring solution 1,2-dibromoethane (2.4 mL, 27.1 mmol) was added at -15 ^{o}C and stirred at room temperature for 12 h. The reaction mixture was quenched with ice to remove excess LDA and then concentrated to remove the THF. Crude product was dissolved in dichloromethane and extracted with water to remove the inorganic salts. The organic washings were concentrated and column chromatographed over silica gel (100-200 mesh) using 20% ethyl acetate/hexane mixture to give 400 mg of **2a** (53 %) having a melting point 85-87 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.12-2.55 (m, 7H, aliphatic), 3.30-3.33 (t, 2H, CH_2Br), 7.02- 7.08 (d, 2H, aromatic), 8.40 (s, 2H, aromatic), 8.61-8.65 (d, 2H, aromatic) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.62, 28.85, 33.33, 34.71, 124.56, 125.31, 148.52, 149.76, 155.85 ppm; Mass-FAB: [M^+] 290.11 (calculated 290.04), [M+2] 292.12 (calculated 292.04).

Synthesis of 3-(4'-methyl-2,2'-bipyridin-4-yl)propane-1-thiol, 3a. A mixture of tetrabutylammonium fluoride (98 mg, 0.38 mmol) and hexamethyldisilathiane (73 mg, 0.4 mmol) in THF (10 mL) was added to compound **2a** (100 mg, 0.35 mmol) in THF (10 mL) kept at -10 ^{o}C. The mixture was allowed to warm to room temperature, while being stirred and was further stirred at room temperature for 12 h. The reaction mixture was concentrated to remove THF and diluted with dichloromethane and then washed with

saturated ammonium chloride solution. The organic layer was concentrated and column chromatographed over alumina using 10 % ethyl acetate/hexane as eluent to give 50 mg of **3a** (62%) having melting point 65-67 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.51-1.56 (t, 1H, thiol), 1.92-2.56 (m, 9H, aliphatic), 7.02- 7.09 (d, 2H, aromatic), 8.43 (s, 2H, aromatic), 8.65-8.69 (d, 2H, aromatic) ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 24.62, 28.85, 33.33, 34.71, 124.56, 125.31, 148.52, 149.76, and 155.85 ppm; Mass-FAB: [M^+] 244.11 (calculated 244.10).

Synthesis of Ru-C_3-SH. To a stirring solution of the **3a** (50 mg, 0.2 mmol) in 1:1 mixture of ethanol: water (4 mL), same equivalents of $Ru(bpy)_2Cl_2$ (100 mg, 0.2 mmol) in 1:1 mixture of ethanol: water (4 mL) was added and the reaction mixture was allowed to stir at reflux at 80 ^{o}C for 8 h. The reaction mixture is concentrated to remove the solvent and an aqueous solution of ammonium hexafluorophosphate is added which results in the precipitation of the product in dark red color. Crude product was filtered, dissolved in acetonitrile and column chromatographed over silica gel (100-200 mesh) using 50 % acetonitrile/dichloromethane as eluent to give 150 mg (90 %) of the product. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.51-1.56 (t, 1H, thiol), 1.92-2.56 (m, 9H, aliphatic), 7.02- 7.09 (m, 12H, aromatic), 8.43-8.52 (t, 6H, aromatic), 8.65-8.69 (m, 4H, aromatic) ppm; Exact mass calcd. for $C_{34}H_{32}N_6RuSPF_6$ [M-PF_6]+ 803.1094, found 803.1090 (FAB, high-resolution mass spectroscopy).

Synthesis of 4-(7-bromoheptyl)-4'-methyl-2,2'-bipyridine, 2b. To a degassed solution of lithium diisopropyl amine (1 equiv; prepared by mixing 2 mL of butyl lithium and diisopropyl amine in dry THF) was added 4,4' dimethyl 2,2' bipyridine (500 mg, 2.71 mmol) at -15 ^{o}C. The resulting solution was stirred at this temperature for 1 h to

stabilize the monoanion produced. To the above stirring solution 1,2 dibromohexane was added at -15 ^{o}C and stirred at room temperature for 12 h. The reaction mixture was quenched with ice to remove excess LDA and concentrated to remove the solvent. Crude product was dissolved in dichloromethane and extracted with water to remove the inorganic salts. The organic washings were concentrated and column chromatographed over silica gel (100-200 mesh) using 20 % ethyl acetate/hexane mixture to give 700 mg of **2b** (75 %) having a melting point 100-102 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.29-2.56 (m, 13H, aliphatic), 3.30-3.34 (t, 2H, CH_2Br), 7.02- 7.09 (d, 2H, aromatic), 8.44 (s, 2H, aromatic), 8.61-8.69 (d, 2H, aromatic)ppm; ^{13}C NMR ($CDCl_3$, 75MHz) δ 24.62, 27.85, 29.21, 30.33, 31.52, 32.71, 33.71, 36.31, 124.56, 125.31, 148.52, 149.76, 155.85 ppm; Mass-FAB: [M^+] 346.07 (calculated 346.10), [M+2]348.05 (calculated 348.10).

Synthesis of 7-(4'-methyl-2,2'-bipyridin-4-yl)heptane-1-thiol, 3b. A mixture of tetrabutylammonium fluoride (415 mg, 1.58 mmol) and hexamethyldisilathiane (308 mg, 1.7 mmol) in THF (10 mL) was added to compound **2b** (500 mg, 1.4 mmol) in THF (10 ml) kept at -10 ^{o}C. The mixture was allowed to warm to room temperature, while being stirred and was further stirred at room temperature for 12 h. The reaction mixture was concentrated to remove THF, diluted with dichloromethane and then washed with saturated ammonium chloride solution. The organic layer was concentrated and column chromatographed over alumina using 10 % ethyl acetate/hexane as eluent to give 220 mg of **3b** (60 %) having melting point 75-78 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.51-1.55 (t, 1H, thiol), 1.92-2.56 (m, 17H, aliphatic), 7.02- 7.08 (d, 2H, aromatic), 8.42 (s, 2H, aromatic), 8.63-8.69 (d, 2H, aromatic); ^{13}CNMR ($CDCl_3$, 75MHz) δ 24.62, 28.85,

33.33, 34.71, 30.52, 124.56, 125.31, 148.52, 149.76, 155.12, 155.85 ppm; Mass-FAB: [M^+] 300.12 (calculated 300.17).

Synthesis of Ru-C_7-SH. To a stirring solution of the **3b** (150 mg, 0.5 mmol) in 1:1 mixture of ethanol:water (4 mL), same equivalents of $Ru(bpy)_2Cl_2$ (240 mg, 0.5 mmol) in 1:1 mixture of ethanol:water (4 mL) was added and the reaction mixture was allowed to stir at reflux at 80 ^oC for 8 h. The reaction mixture was concentrated to remove the solvent and an aqueous solution of ammonium hexafluorophosphate was added to the concentrated reaction mixture which resulted in the precipitation of the crude product in dark red color. The crude product was filtered, dissolved in acetonitrile and column chromatographed over silica gel (100-200 mesh) using 50 % acetonitrile/dichloromethane as eluent to give 350 mg (85 %) of the product. ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.92-2.56 (m, 17H, aliphatic), 7.02- 7.09 (m, 12H, aromatic), 8.43-8.52 (t, 6H, aromatic), 8.65-8.69 (m, 4H, aromatic)ppm; Mass-FAB: [M-PF_6] 858.13 (calculated 858.21), [M-$2PF_6$] 714.21 (calculated 714.23).

Synthesis of $Au(S\text{-}EG_3)_x$

In a typical preparation of $Au(S\text{-}EG_3)_x$ protected gold nanoparticles, 30 mL of MeOH (HPLC grade) and 5.0 mL of acetic acid were mixed in a 250 mL Erlenmeyer flask by stirring for 2-5 min. Then, 78.0 mg (0.2 mmol) of tetrachloroauric acid ($HAuCl_4$ XH_2O) (99.99%) and 13.6 mg (0.1 mmol) of monothiol of triethylene glycol (EG_3SH) were added to the above mixed solvents and dissolved by stirring for 5 min, which gave a clear, yellow solution. Subsequently, a solution of sodium borohydride (75.0 mg (2.0 mmol) dissolved in 5.0 mL of distilled water was added drop wise into the above solution with rapid stirring. On addition of the first drop of $NaBH_4$, the $HAuCl_4$ solution

immediately turned to dark brown from yellow and rapid stirring was continued for 2 h. The reaction mixture was transferred into a 10 mL plastic centrifuging tube and centrifuged at 2500 rpm for 30 s to remove large particles, if there were any. The supernatant liquid was then filtered through a filter paper, concentrated under vacuum to remove methanol and acetic acid, washed several times with ether to remove the excess thiol. The product was dissolved in dichloromethane and extracted with water to remove excess sodium borohydride. The organic washings are dried over anhydrous Na_2SO_4, concentrated and redissolved in 10 mL of dichloromethane.

Estimation of the number of ruthenium molecules on Ru-C_7-SH and Au(S-C_7-SH)$_L$

Gold ions used = 0.024 mmol

Size of cluster = 4.5 nm

No. of gold atoms per cluster (tight packed spherical model) = 2769

No. of gold atoms in 0.024 mmol = $0.024 \times 10^{-3} \times 6.023 \times 10^{23} = 1.45 \times 10^{19}$ atoms

No. of gold clusters = $1.45 \times 10^{19}/2769 = 5.23 \times 10^{15}$

For Au(S-C_7-SH)

[Ru-C_7-SH] on Au nanoparticles (after correction for unbound Ru-C_7-SH) = 1.26 μmol

No. of Ru-C_7-SH molecules = $1.26 \times 10^{-6} \times 6.023 \times 10^{23} = 7.6 \times 10^{17}$ molecules

No. of Ru-C_7-SH per cluster = $7.6 \times 10^{17}/5.23 \times 10^{15}$ = **145 molecules**

For Au(S-C_7-SH)$_L$

Ru-C_7-SH on gold nanoparticles = 0.44 μmol

No. of Ru-C_7-SH molecules = $0.44 \times 10^{-6} \times 6.023 \times 10^{23} = 2.65 \times 10^{17}$ molecules

No. of Ru-C_7-SH per cluster = $2.65 \times 10^{17}/5.23 \times 10^{15}$ = **50 molecules**

Calculation of the percentage volume of the chromophores in the shell

(i) Au(S-C_7-Ru)

The volume of nanoparticle core (*radius = 2.25 nm*) = 4.77×10^{-20} cm^3

The volume of Au(S-C_7-Ru) core-shell structure (*radius = 3.65 nm*) = 20.40×10^{-20} cm^3

Space occupied by the shell of monolayer = 20.40×10^{-20} cm^3 - 4.77×10^{-20} cm^3
= **15.63×10^{-20} cm^3**

Molecular volume of a single molecule of Ru-C_7-SH in the shell = 716.93×10^{-24} cm^3

Volume of 145 molecules of Ru-C_7-SH = $145 \times 716.93 \times 10^{-24}$ cm^3
= 10.39×10^{-20} cm^3

Space occupied by 145 molecules of Ru-C_7-SH in the shell of monolayer
= $10.39 \times 10^{-20} / 15.63 \times 10^{-20}$ = **65 %**

(ii) Au(S-C_7-Ru)$_L$

Volume of 50 molecules of Ru-C_7-SH = $50 \times 716.93 \times 10^{-24}$ cm^3
= 3.58×10^{-20} cm^3

Space occupied by 50 molecules of Ru-C_7-SH in the shell of monolayer
= $3.58 \times 10^{-20} / 15.63 \times 10^{-20}$ = **23 %**

Table 1. Absorption and emission properties of Ru-C_3-SH and Ru-C_7-SH in Acetonitrile.

Compounds	ε (x 10^4 $M^{-1}cm^{-1}$)		λ_{max} em/nm	Φ_{em}	τ (ns)
	π,π* bpy (288 nm)	MLCT (453 nm)			
Ru-C_3-SH	8.12	1.41	617	0.070	960
Ru-C_7-SH	8.94	1.55	617	0.071	961

Table 2. Fluorescence lifetimes[a-c] and Fractional Contributions[d] of Ruthenium Thiols and Gold Nanoparticles Functionalized with Ruthenium Chromophores.

		fluorescence lifetimes		
system	solvent (dielectric constant)	τ_1, ns (χ_1 %)	τ_2, ns (χ_2 %)	χ^2
Ru-C_7-SH	Acetonitrile (39.8)	961 (100%)	-	1.01
Au(S-C_7-Ru)	Acetonitrile (39.8)	960 (30%)	4.2 (70%)	1.05
Au(S-C_7-Ru)	Dichloromethane (9.8)	1100 (80%)	4.3 (20%)	1.10
Au(S-C_7-Ru)$_L$	Acetonitrile (39.8)	960 (100%)	-	1.02

[a] τ_1 and τ_2. [b] Error limit ±5%. [c] Excited at 440 nm. [d] χ_1 and χ_2.

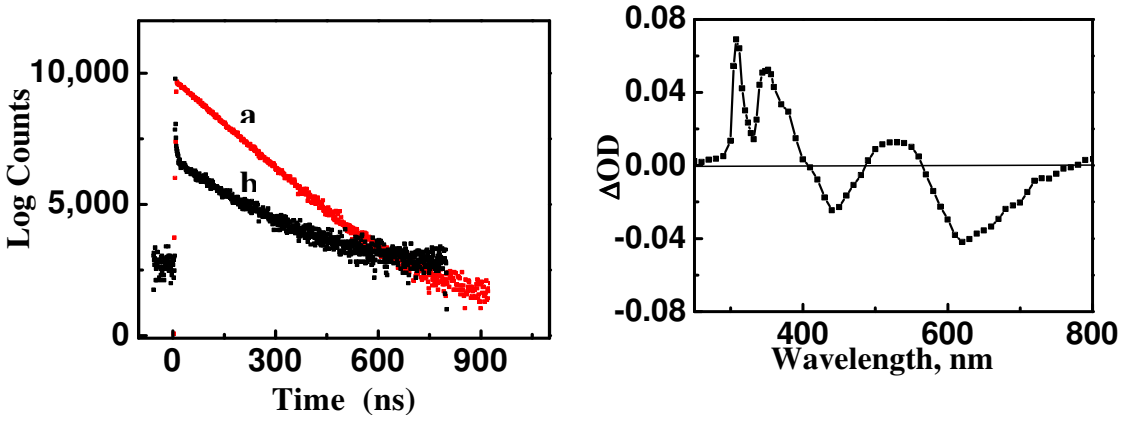

Figure S1. (A) Luminescence lifetime spectra of (a) Ru-C_3-SH and (b) Au(S-C_3-Ru) in acetonitrile; **(B)** Nanosecond transient absorption spectra of degassed acetonitrile solution of Au(S-C_3-Ru)

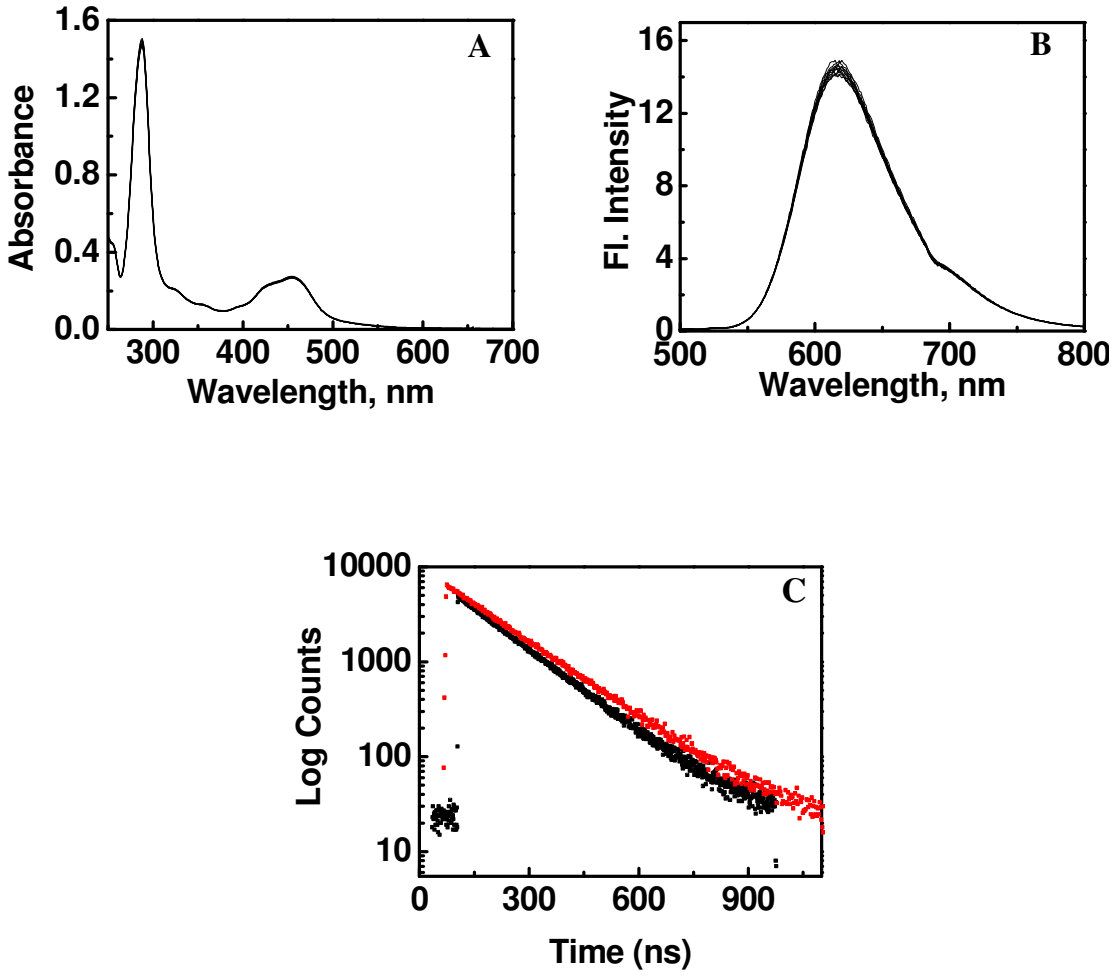

Figure S2. (A) Absorption (B) emission and (C) luminescence lifetime spectra of Ru-C_7-SH on addition of EG_3SH in acetonitrile.