

Inverted Aggregates of Luminescent Ruthenium Metallosurfactants

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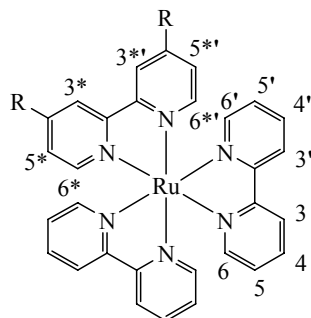
Dynamic Light Scattering and Atomic Force Microscopy. DLS is a standard tool to determine particle sizes in transparent solutions quickly. The size of any diffusing particle with a radius of a few nm up to microns is based on measuring the time-averaged auto correlation function of the “speckle” pattern produced by the scattering particles in solution. This auto-correlation function $g^{(1)}(q, \tau)$ related directly to the diffusion coefficient of the scattering object. Hence, by measuring the translational Diffusion coefficient we obtain the size of the particles through the Stokes-Einstein relation $D = kBT/(6\pi\eta R)$; η is simply the viscosity of the pure solvent. In general, nano-sized particles will feel a hydrodynamic friction due to the surrounding solvent thus dragging along some solvent molecules along. This is why the particles radius can appear larger, but still it gives a good estimate. The AFM images helped us to verify, whether the inverted vesicles are indeed hollow, or whether they are formed by multivesicular (onion-like) structures or are pure, unresolved Ru-complexes.

4,4'-di(3-ethyheptyl)-2,2'-bipyridine (3). A fresh solution of lithium diisopropylamine was prepared by dropwise addition of a 1.6 M solution of n-butyllithium in hexane (5.16 ml, 8.24 mmol) to a solution of diisopropylamine (1.12 ml, 8 mmol) in THF (10 ml) at -78°C . After stirring for 30 min, a suspension of 4,4'-dimethyl-2,2'-bipyridine (0.73 g, 4 mmol) in THF (30 ml) was slowly (30 min) added and stirred for additional 2 h at -78°C . 2-ethylhexylbromide (2.32 g, 12 mmol) in THF (15 ml) was slowly added maintaining the temperature at -78°C . The solution was then placed on an ice-bath (0°C) and stirred for 2 h, after which the ice-bath was removed and allowed stirring for 16 h. The solution was poured in brine (50 ml), the organic phase separated and the aqueous phase extracted additionally with ethylacetate (2 x 25 ml). The combined organic phases were dried with MgSO_4 , solvents evaporated and the crude yellowish oil chromatographed in silica with a hexane/diethyl ether (7:3) mixture as eluent. The pure compound was obtained as a colourless oil. Yield: 0.99 g (61%). ^1H NMR: δ 0.87 (m, 12H, CH_3), 1.20–1.70 (br m, 22H, $(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2)\text{CH}_2)$), 2.67 (t, 4H, $^2J_{\text{HH}} = 9.0$ Hz, CH_2Ar), 7.15 (d, 2H, $^2J_{\text{HH}} = 4.8$ Hz, $\text{H}^*-5,5'$), 8.25 (br s, 2H, $\text{H}^*-3,3'$), 8.56 (d, 2H, $^2J_{\text{HH}} = 4.8$ Hz, $\text{H}^*-6,6'$). $^{13}\text{C}\{^1\text{H}\}$: δ 10.9 ($\text{CH}_3\text{CH}_2\text{CH}$), 14.3 (CH_3), 23.3 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 25.9 ($\text{CH}_3\text{CH}_2\text{CH}$), 29.0 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 32.8 (CH_2CH), 33.02 ($\text{CH}_2\text{CH}_2\text{Ar}$), 34.4 (CH_2Ar), 38.9 (CH) 121.5 (C5), 124.1 (C3), 149.1 (C6), 153.6 (C4), 156.3 (C2). MS (FAB⁺): $m/z = 409.4$ [MH]⁺. Anal. Calcd for $\text{C}_{28}\text{H}_{44}\text{N}_2$: C, 82.29; H, 10.85; N, 6.85. Found: C, 82.42; H, 10.81; N, 6.78.

4,4'-di(17-tritriacontanyl)-2,2'-bipyridine (4). This synthesis is based on a previous similar recipe [1]. A fresh solution of lithium diisopropylamine (36.2 mmol) was prepared as described for compound 3. To this solution, a suspension of 4,4'-dimethyl-2,2'-bipyridine (1.5 g, 8.2 mmol) in THF (60 ml) was slowly (1 h.) added at -78°C and stirred for additional 2 h. 1-hexadecylbromide (15 g, 49 mmol) in THF (60 ml) was added dropwise and stirred for one hour. The solution was allowed to reach room temperature while stirring for 16 hours. The reaction was stopped, poured in brine (150 ml) and washed two additional times. The suspension was evaporated to dryness on the rotavapor. The yellow residue

obtained was dissolved in a methanol/ethanol (1:1) solution (200 ml) and filtered. The solid was recrystallised from heptane to obtain a fine off-white powder. Yield: 7.1 g (80%). ^1H NMR: δ 0.86 (t, 12H, $^2J_{\text{HH}} = 6.6$ Hz, $\text{CH}_3(\text{CH}_2)_{15}$), 1.05–1.45 (br m, 152H, $\text{CH}_3(\text{CH}_2)_{14}$), 1.63 (br s, 8H, $(\text{CH}_2)_{14}\text{CH}_2\text{CH}$), 2.59 (m, 2H $(\text{CH}_2)_{15}\text{CH}$), 7.09 (d, 2H, $^2J_{\text{HH}} = 1.8$ Hz, $\text{H}^*-5,5'$), 8.24 (s, 2H, $\text{H}^*-3,3'$), 8.56 (d, 2H, $^2J_{\text{HH}} = 2.1$ Hz, $\text{H}^*-6,6'$). ^{13}C { ^1H }: δ 14.3 (CH_3), 22.9 (CH_3CH_2), 27.8 ($\text{CH}_2\text{CH}_2\text{CHAr}$), 29.9 ($\text{CH}_3(\text{CH}_2)_2(\text{CH})_{11}$), 32.2 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 36.6 (CH_2CHAr), 46.4 (CHAr), 121.1 (C5), 123.4 (C3), 149.2 (C6), 156.6 (C4), 157.0 (C2). MS (FAB $^+$): $m/z = 1082.21$ [MH] $^+$. Anal. Calcd for $\text{C}_{76}\text{H}_{140}\text{N}_2$: C, 84.37; H, 13.04; N, 2.59. Found: C, 83.96; H, 13.01; N, 2.48.

4,4'-bis[3,4,5-tri(dodecyloxy)phenylmethoxy] 2,2'-bipyridine (5). A mixture of 4,4'-dihydroxy-2,2'-bipyridine (1.13 g, 6 mmol) and K_2CO_3 (4.98 g, 36 mmol), in DMF (20 ml) was warmed at 80°C for 30 min. Upon addition of 3,4,5-tri(dodecyloxy)phenylmethyl bromide (9.04 g, 12.5 mmol) dissolved in dioxane (30 ml), the reaction was allowed to stir at 75°C for 40 h. TLC was performed to check that all the bromide had reacted away and the solution was cooled down and filtered. Evaporation of DMF gave a yellow oil that was chromatographed on silica with a hexane/ethanol/triethylamine mixture (17:2:1) to obtain **5** as a light yellow oil that solidified upon standing. Yield: 5.84 g (66%). ^1H NMR: δ 0.90 (m, 18H, $\text{CH}_3(\text{CH}_2)_{11}$), 1.30–1.84 (br m, 120H, $\text{CH}_3(\text{CH}_2)_{10}$), 3.99 (m, 12H, CH_2OAr), 5.13 (s, 4H, CH_2Obpy), 6.68 (s, 2H, ortho to CH_2Obpy), 6.93 (dd, 2H, $^2J_{\text{HH}} = 5.4$ Hz, $^4J_{\text{HH}} = 2.4$ Hz, $\text{H}^*-5,5'$), 8.13 (d, 2H, $^2J_{\text{HH}} = 2.4$ Hz, $\text{H}^*-3,3'$), 8.47 (d, 2H, $^2J_{\text{HH}} = 6.0$ Hz, $\text{H}^*-6,6'$). ^{13}C { ^1H } NMR (CD_2Cl_2): δ 16.0 (CH_3), 24.8 (CH_3CH_2), 28.3 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{OAr}$), 31.8 ($\text{CH}_3(\text{CH}_2)_3(\text{CH})_5$), 32.5 ($\text{CH}_2\text{CH}_2\text{OAr}$), 34.1 ($\text{CH}_3\text{CH}_2\text{CH}_2$), 71.1 (CH_2OAr , 3,5 positions), 72.4 (CH_2Obpy), 75.5 (CH_2OAr , 4 position), 108.0 (C8), 109.1 (C5), 113.3 (C3), 133.0 (C10), 139.9 (C7), 152.3 (C6), 155.4 (C9), 159.8 (C4), 167.8 (C2). MS (FAB $^+$): $m/z = 1474.27$ [MH] $^+$. Anal. Calcd for $\text{C}_{96}\text{H}_{164}\text{N}_2\text{O}_8$: C, 78.21; H, 11.21; N, 1.90. Found: C, 78.39; H, 11.32; N, 1.89.



[Ru(4,4'-ditridecyl-2,2'-bipyridine)₂Cl₂] (6). A mixture of RuCl₃·3H₂O (83.7 mg, 0.32 mmol), 4,4'-di(tridecyl)-2,2'-bipyridine (0.333 g, 0.64 mmol) and LiCl (80.5 mg, 1.9 mmol) in DMF (10 ml) was heated to 110°C during 6 h. The reaction was cooled down, acetone (30 ml) added and the solution was further cooled to -20°C. The precipitate formed was filtered off and washed with water (3 x 20 ml). The residue was purified twice on Sephadex LH20 with a acetonitrile/isopropanol (1:9) mixture to obtain 6 as a purple solid. Yield 0.32 g (82%). ¹H NMR gave broad signals. ¹H NMR: δ 0.88 (m, 12H, CH₃(CH₂)₁₂), 1.18–1.80 (br m, 88H, CH₃(CH₂)₁₁), 2.89 (br s, 8H, CH₂Ar), 7.20-7.30 (br m, 4H, H-5,5'), 7.54-7.61 (br m, 4H, H-3,3'), 8.33 (br s, 4H H-6,6'). (FAB⁺): m/z = 1141.93 [M-2Cl]⁺. Anal. Calcd for C₇₂H₁₂₀Cl₂N₄Ru: C, 71.25; H, 9.97; N, 4.62. Found: C, 70.78; H, 9.66; N, 4.88.

[Ru(4,4'-ditridecyl-2,2'-bipyridine)₂(2,2'-bipyridine)]Cl₂ (9). A suspension of Ru(4,4'-ditridecyl-2,2'-bipyridine)₂Cl₂ (0.242 g, 0.2 mmol) and silver triflate (0.103 g, 0.4 mmol) in THF (15 ml) was stirred in the absence of light for 1 h. at room temperature, after which, still in the absence of light, was filtered through celite. 2,2'-bipyridine (31.2 mg, 0.2 mmol) is added to the filtered solution and the reaction refluxed in the absence of light for 14 h after which the suspension was cooled to room temperature, excess NaCl added and stirred for additional 1 h. The solvent was evaporated and the crude mixture chromatographed on Sephadex LH20 with isopropanol as eluent and subsequently on silica with methanol/acetonitrile/water/NaCl mixture (10:2.5:1:0.1). In both cases the red-intense band is collected and dried under vacuum to obtain 9 as a dark red solid. Yield: 0.202 g (74%). ¹H NMR: δ

0.89 (m, 12H, CH₃(CH₂)₁₁), 1.20–1.70 (br m, 120H, CH₃(CH₂)₁₀), 2.84 (t, 8H, ²J_{HH} = 8.1 Hz, CH₂Ar), 7.26 (d, 4H, ²J_{HH} = 6.6 Hz, H*-5,5'), 7.45–7.60 (m, 6H, H*-6,6' and H-5,5'), 7.72 (d, 2H, ²J_{HH} = 5.1 Hz, H-6,6'), 8.14 (br s, 2H, H-4,4'), 8.68 (s, 4H H*-3,3'), 9.21 (d, 2H, ²J_{HH} = 7.5 Hz, H-3,3'). MS (FAB⁺): m/z = 1291.37 [MH-2Cl]⁺. Anal. Calcd for C₈₂H₁₂₈Cl₂N₆Ru: C, 71.89; H, 9.42; N, 6.13. Found: C, 72.09; H, 9.86; N, 6.19.

[Ru(4,4'-di(3-ethyheptyl)-2,2'-bipyridine)₂(2,2'-bipyridine)]Cl₂ (11). A schlenk vessel was charged with RuCl₃·3H₂O (66.9 mg, 0.24 mmol), 3 (0.196 g, 0.48 mmol), LiCl (60.3 mg, 1.4 mmol) and DMF (8 ml). The suspension was heated to 110°C during 6 h, after which it was cooled down to room temperature and volatiles evaporated. The residue was dissolved in CH₂Cl₂ and filtered through a celite plug. The purple residue obtained was put in a schlenk, silver triflate (0.123 g, 0.48 mmol) added and in the absence of light, THF was added and allowed to react for 1 h. The mixture was filtered through celite, 2,2'-bipyridine (37.4 mg, 0.24 mmol) added and refluxed for 14 h in the absence of light. The reaction was then cooled down; NaCl (excess) added, stirred for 1 h and filtered. Volatiles were evaporated and the crude product chromatographed on silica with methanol/acetonitrile/water/NaCl mixture (10:2.5:1:0.1) collecting the bright red band. Yield: 0.202 g (74%). ¹H NMR (CD₂Cl₂): δ 0.88 (m, 24H, CH₃), 1.20–1.60 (br m, 44H, CH₃(CH₂)₃CH(CH₂)CH₂), 2.82 (br m, 8H, CH₂Ar), 7.27 (d, 4H, ²J_{HH} = 6.3 Hz, H*-5,5'), 7.40–7.55 (m, 6H, H*-6,6' and H-5,5'), 7.81 (br s, 2H, H-6,6'), 8.22 (br s, 2H, H-4,4'), 8.68 (s, 4H H*-3,3'), 9.17 (d, 2H, ²J_{HH} = 7.5 Hz, H-3,3'). MS (FAB⁺): m/z = 1073.34 [MH-2Cl]⁺. Anal. Calcd for C₆₆H₉₆Cl₂N₆Ru: C, 69.20; H, 8.45; N, 7.34. Found: C, 68.89; H, 8.74; N, 7.49.

[Ru(4,4'-di(17-tritriacontyl)-2,2'-bipyridine)(2,2'-bipyridine)₂]Cl₂ (12). [Ru(p-cymene)Cl₂]₂ (38 mg, 0.62 mmol) and 4,4'-di(17-tritriacontanyl)-2,2'-bipyridine (0.134 g, 0.124 mmol) were dissolved in DMF (10 ml) and the mixture warmed at 70°C. After 6 h., 2,2'-bipyridine (39 mg, 0.248 mmol) was added and the reaction allowed stirring at 140°C for 36 h. The reaction was cooled to room temperature

and volatiles evaporated. The crude product was dissolved in hexane, filtered and chromatographed on Sephadex LH20 with isopropanol and subsequently on silica with methanol/acetonitrile/water/NaCl mixture (10:2.5:1:0.1). In both cases the bright red band was collected and dried under vacuum to obtain **12** as a bright red solid. Yield: 0.153 g (79%). $^1\text{H NMR}$ (CD_2Cl_2): δ 0.89 (m, 12H, $\text{CH}_3(\text{CH}_2)_{16}$), 1.15–1.70 (br m, 120H, $\text{CH}_3(\text{CH}_2)_{15}$), 2.77 (m, 2H, CH_2Ar), 7.25 (d, 2H, $^2J_{\text{HH}} = 5.7$ Hz, H*-5,5'), 7.44-7.50 (m, 4H, H-5,5'), 7.61 (d, 4H, $^2J_{\text{HH}} = 5.7$ Hz, H-6,6'), 7.69 (m, 2H, $^2J_{\text{HH}} = 5.4$ Hz, H-6,6'), 8.15 (m, 4H, H-4,4'), 8.23 (s, 2H H*-3,3'), 9.19 (d, 2H, $^2J_{\text{HH}} = 7.8$ Hz, H-3,3'). MS (FAB⁺): $m/z = 1530.31$ $[\text{M}-\text{Cl}]^+$. Anal. Calcd for $\text{C}_{82}\text{H}_{128}\text{Cl}_2\text{N}_6\text{Ru}$: C, 71.89; H, 9.42; N, 6.13. Found: C, 72.09; H, 9.86; N, 6.19.

[Ru (4,4'-bis[3,4,5-tri(dodecyloxy)phenylmethoxy] 2,2'-bipyridine) (2,2'-bipyridine)₂Cl₂ (13). A suspension of $[\text{Ru}(\text{p-cymene})\text{Cl}_2]_2$ (59 mg, 0.96 mmol) and **5** (0.28 g, 0.192 mmol) dissolved in DMF (10 ml) was stirred for 6 h at 70°C. 2-2'-bipyridine (60 mg, 0.384 mmol) was then added and the reaction allowed stirring at 140°C for 36 h after which the reaction was cooled down and volatiles evaporated. The red residue was chromatographed first on Sephadex LH20 with isopropanol and then on silica with methanol/acetonitrile/water/NaCl mixture (10:2.5:1:0.1). In both cases the bright red band was collected and dried under vacuum to obtain **13** as a red solid. Yield: 0.153 g (79%).

$^1\text{H NMR}$ (CD_2Cl_2): δ 0.89 (m, 12H, $\text{CH}_3(\text{CH}_2)_{16}$), 1.15–1.70 (br m, 120H, $\text{CH}_3(\text{CH}_2)_{15}$), 2.77 (m, 2H, CH_2Ar), 7.25 (d, 2H, $^2J_{\text{HH}} = 5.7$ Hz, H*-5,5'), 7.44-7.50 (m, 4H, H-5,5'), 7.61 (d, 4H, $^2J_{\text{HH}} = 5.7$ Hz, H-6,6'), 7.69 (m, 2H, $^2J_{\text{HH}} = 5.4$ Hz, H-6,6'), 8.15 (m, 4H, H-4,4'), 8.23 (s, 2H H*-3,3'), 9.19 (d, 2H, $^2J_{\text{HH}} = 7.8$ Hz, H-3,3'). MS (FAB⁺): $m/z = 1922.70$ $[\text{MH}-\text{Cl}]^+$, 1877.25 $[\text{MH}-2\text{Cl}]^+$. Anal. Calcd for $\text{C}_{116}\text{H}_{180}\text{Cl}_2\text{N}_6\text{O}_8\text{Ru}$: C, 71.13; H, 9.26; N, 4.29. Found: C, 71.59; H, 9.34; N, 4.24.

[1] T. B. Hadda and H. L. Bozec, *Polyhedron* **1988**, 7, 575-577