Solvent-dependent Aggregation Behavior of a New Ru(II)polypyridyl Based Metallosurfactant

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1. Experimental Section:

1.1. Materials and Reagents:

Analytical reagent grade solvents and compounds were used for preparations. 4,4'-Dimethyl-2,2'-bipyridyl, 4-methoxybenzaldehyde, 1-bromooctadecane, butyllithium, diisopropylamine, ruthenium trichloride were purchased from Sigma-Aldrich, all other chemicals were purchased from S. D. Fine chemicals (India). Solvents used for reactions and various other studies were of A.R. grade (Merck, India) and were used as received.

1.2. Instrumentation:

¹HNMR spectra were recorded on Bruker 500 MHz FT NMR (model: Advance-DPX 500) spectrometer at room temperature (25°C). The chemical shifts (δ) and coupling constant (*J*) values are given in ppm and Hz, respectively, throughout this manuscript unless mentioned otherwise. Tetramethylsilane (TMS) was used as an internal standard for all ¹HNMR studies. ESI-MS measurements were carried out on Waters QTof-Micro instrument. Microanalyses (C, H, N) were performed using a Perkin-Elmer 4100 elemental analyzer. Infrared spectra were recorded as a KBr pellets using Perkin Elmer Spectra GX 2000 spectrometer. UV-Vis spectra of the compounds in solution were obtained by using Cary 500 Scan UV-Vis-NIR spectrometer. AFM studies were carried out under ambient conditions using Scanning probe microscope NT-MDT (Model: Ntegra Aura; Moscow) in semi-contact mode using rectangular cantilever of Si₃N₄. The HRTEM images were recorded using Jeol JEM-2100 Transmission Electron Microscope. DLS was performed on Malvern Zetasizer ZS90 (UK). Ten repeat measurements were performed for each sample and the average data was considered for analysis. Data evaluation of the DLS measurements was performed using the CONTIN algorithm. SLS studies were performed using NABITEC spectrosize TM 300 (Germany) Intensity of the scattered light was measured at varying angle from 30-150°. For

TEM study lacey carbon formvar coated copper grid was used and for some experiment the sample was stained with 1% uranyl nitrate solution. For AFM measurement freshly cleaved mica was used.

1.3. Preparation of sample solution:

The vesicle solution was prepared by dissolving 2 mg of complex **1** in 200 μ L of methanol, to that solution 1.8 ml was added dropwise and the solution was stirred for 24 hrs. The suspension was then centrifuged at 3500 rpm for 10 minutes. The clear solution was then filtered through 0.45 μ m pore sized micron filter and used for several studies.

The reverse vesicle solutions were prepared by sonicating complex 1 in toluene and cyclohexane and then centrifuged at 3500 rpm for 10 minutes. The clear solution was then filtered through 0.45 µm pore sized micron filter and used for several studies.

1.3. Synthesis:

1.3.1. ESI Scheme 1: Synthetic methodology for the synthesis of complex 1.



a) (i) BuLi, Di-isopropyl amine, 4-Methoxybenzaldehyde, Dry THF, 0°C; (ii) POCl₃ and Pyridine; b) Pyridine, HCl, 200°C; c) 1-Bromo-octadecane; DMF, K_2CO_3 , KI; d) RuCl₃, Ethanol:Dioxan = 1:1, 90°C.

1.3.2. Synthesis of ligand L₁ and L₂:

Ligand L_1 and L_2 were synthesized following the reported procedure. (Ref: M. D. Ward et. al., *J. Chem. Soc. Dalton. Trans.*, 1992, 703)

1.3.3. Synthesis of ligand L₃:

350 mg (1.22 mmole) of ligand L_2 was dissolved in 60 ml dry DMF in a 100 ml 2 necked round bottomed flask under N₂ atmosphere. To this solution 251.9 mg (1.82 mmole, 1.5 mole equivalent) K₂CO₃ (hot and grinded) was added under vigorous stirring, colour of the solution immediately changed from pale yellow to dark yellow. To this solution 0.42 ml (1.22 mmole) of 1-bromooctadecane was added dropwise through a syringe. Then to this solution 302.1 mg (1.82 mmole, 1.5 mole equivalent) of KI (hot) was added. The whole mixture was heated around ~90°C for 48 hours. After that the reaction mixture was cooled to room-temperature (25°C) and filtered using Whatman-42 filter paper. The residue was washed several times with CH₂Cl₂ and the filtrate was evaporated to dryness through rotary evaporator to get the crude product (Crude yield was 500 mg). Then the crude product was purified by column chromatography using silica gel as stationary phase and CH₂Cl₂ as eluent. Isolated yield of the purified compound L_3 (yield was calculated based on the starting compounds) was 70%. ¹H NMR (500 MHz, CDCl₃, SiMe₄, J (Hz), δ (ppm)): 8.61 (1H, d, J = 5, H^{bpy}₆), 8.57 (1H, d, $J = 4.5, H^{bpy_{6'}}$, 8.48 (1H, s, $H^{bpy_{3'}}$), 8.25 (1H, s, $H^{bpy_{3}}$), 7.49 (2H, d, $J = 8, H^{phenyl_{3,5}}$), 7.40 $(1H, d, J = 16, H^{vinyl}), 7.34 (1H, d, J = 4, H^{bpy_5}), 7.15 (1H, d, J = 3.5, H^{bpy_{5'}}), 6.98 (1H, d, J = 1.5, H$ 16, H^{vinyl}), 6.91 (1H, d, J = 8, $H^{\text{phenyl}_{2,6}}$), 3.99-3.97 (2H, t, $H^{\text{O-CH}_2}$), 2.45 (3H, s, $H^{\text{bpy-CH}_3}$), 1.78 (2H, m, H^{longchain(-CH₂)}), 1.26 (30H, b, H^{(-CH₂)15}), 0.88-0.87 (3H, t, H^{longchain(-CH₃)}). ESI-MS (+ve mode): m/z 541.59 (100%) (M⁺ + H⁺) and Calcd. for C₃₇H₅₂N₂O is 540.82. Elemental Analysis Calcd: C: 82.2, H: 9.7, N: 5.2 and Found: C, 82.0; H, 9.5; N, 5.3.

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1.3.4. Synthesis of complex 1: Ligand L₃ (170 mg, 0.315 mmole), RuCl₃.xH₂O (21.77 mg, 0.105 mmole) were added to 60 ml 1:1 mixture (v/v) of ethanol and dioxan. The mixture was refluxed for 24 hours under N₂ atm with continuous stirring. The mixture was cooled to room temperature and evaporated to dryness. The crude product was chromatographed on alumina grade-III (eluent acetonitrile). Isolated yield of the compound 1 (yield was calculated based on the starting compounds) was found to be 25 %. ¹H NMR (500 MHz, CDCl₃, TMS, J (Hz), δ (ppm)): 9.13-9.09 (6H, m, H^{bpy6,6'}), 7.99 (3H, d, J = 17, H^{vinyl}), 7.65 (6H, d, J = 8, H^{phenyl3,5}), 7.59-7.5 (6H, m, H^{bpy3,3'}), 7.38-7.37 (3H, m, H^{bpy5}), 7.22-7.20 (3H, m, H^{bpy5'}), 7.09 (3H, d, J = 16.5, H^{vinyl}), 6.92 (6H, d, J = 8.5, H^{phenyl2,6}), 3.98 (6H, t, H^{O-CH2}), 2.66 (9H, s, H^{bpy-CH3}), 1.78 (6H, b, H^{longchain-CH2}), 1.46-1.44 (6H, m, H^{longchain-CH2}), 1.26 (84H, b, H^{longchain-CH2}), 0.88 (9H, t, H^{longchain-CH3}). ESI-MS (+ve mode): m/2z 862.16 (23%) (M²⁺) and Calcd. for C₁₁₁H₁₅₆N₆O₃Ru was 1723.53. Elemental Anal. Calcd: C, 77.2; H, 9.1; N, 4.9 and Found: C, 77.1; H, 9.0; N, 5.1.

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2.¹H NMR spectra

2.1. ¹H NMR spectra of L₃:



Figure S1:¹H NMR spectra of L₃ recorded in CDCl₃.

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2.2. ¹H NMR spectra of 1:



Figure S2: ¹H NMR spectra of **1** in CD_2Cl_2 .

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3. ESI-Mass spectra:

3.1. ESI-Mass spectra of L₃:



Figure S3: ESI-Mass spectra of L₃.

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3.2. ESI-Mass spectra of 1:



Figure S4: ESI-Mass spectra of 1.

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4. AFM images:



Figure S5: AFM height contrast image of **1** on mica upon evaporation of (A) methanol:water = 1:9 (v/v); (B) toluene; (C) cyclohexane solution. Cross section for the respective images is shown at the bottom of each individual image.

5. Emission spectra of absorption matched rhodamine B in absence and presence of vesicle/reverse vesicle:

We have investigated the dye encapsulation ability of these aggregates. We have recorded the emission spectra of rhodamine B and rhodamine B in presence of the vesicle in methanol:water (1:9, (v/v) medium, having same absorbance value. If a certain amount of rhodamine B is uniformly distributed in a solvent that it is soluble in, such as water, it could fluoresce without any self-quenching effects. However in presence of vesicle they got encapsulated in the vesicles and undergo self quenching due to the high local concentration inside the vesicles.



Figure S6: Emission spectra of absorption matched rhodamine B (A) in methanol:water = 1:9 (v/v) and in presence of vesicle, (B) in water and in presence of reverse vesicle in toluene solution, (C) in water and in presence of reverse vesicle in cyclohexane solution of complex 1.

Again rhodamine B is neither soluble in toluene nor in cyclohexane. However in presence of the reverse vesicle they became soluble in these non polar solvents and showed linear absorbance spectra. Rhodamine B, being polar, interacts with the polar head groups of the metalloamphiphiles in the reverse bilayer and got solubilized. This accounts for the self-quenching and hence the poor emission. In reverse vesicles the effect of quenching of the dye was much higher compared to the vesicles. This is possibly, in reverse vesicle the polar dye molecules are trapped in the reverse bilayer and more organised upon interaction with the polar head groups, whereas in vesicles the dye molecules are in the interior are less organized.



6. Absorbance and emission spectra of complex 1 in different solvents:

Figure S7: (A) Absorbance and (B) emission spectra of complex 1 in ethanol, toluene, cyclohexane and methanol:water = 1:9 (v/v).

7. TEM images:

7.1. Expanded TEM images of vesicles and reverse vesicles:



Figure S8: Expanded TEM images of (A) vesicle formed in methanol:water (1:9, v/v); reverse vesicles formed in (B) Toluene and (C) Cyclohexane.

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7.2. TEM images with and without staining:



Figure S9: TEM images of methanol:water (1:9, v/v) medium of **1** (A) after negative staining with $UO_2^{2^+}$, (B) without staining.

7.3. TEM images showing fusion and fission of vesicles:



Figure S10: TEM images of methanol: water (1:9, v/v) medium of **1** (A) fusion of two nearby vesicles, (B) fission of a small vesicle from a large one.

8. Determination of radius of gyration from Guinier law:

In static light scattering (SLS), the excess light scattering intensity of the aggregates in different solvents was measured as a function of the angle of scattering. SLS permits one to estimate the radius of gyration (R_g) of these aggregates. For low scattering vectors, i.e. $qR_g \le$ 1, the scattering intensity follows the well known Guinier law.

$$I(q) = I(0) \exp(-q^2 R_g^2/3)$$

Where $q = (4\pi n/\lambda) \sin(\theta/2)$, n = refractive index and λ = wavelength of the light.

ln(I) was plotted against q^2 at different scattering angle and from the slope of the plot R_g was calculated.

8.1. Guinier plots for calculation of R_g in different solvent system:



Figure S11: Static light scattering data in the form of Guinier plots in (A) methanol:water = 1:9(v/v), (B) toluene, (C) cyclohexane.

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9. DLS study:



Figure S12: Size distribution of **1** in (A) toluene, (B) toluene methanol mixture (25:1, v/v) and in (C) toluene:methanol mixture (25:4, v/v).