Asian Journal of Chemistry; Vol. 35, No. 8 (2023), 1850-1854

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2023.27860

# Spectroscopic and Electrochemical Investigation of Peripherally Diruthenated Complexes of *octakis*(benzylthio) and (methylthio)tetraazaporphyrinmagnesium(II)

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*Received*: 30 May 2023; *Accepted*: 14 June 2023; *Published online*: 31 July 2023; AJC-21316

Four new trinuclear complexes were successfully synthesized through the dative binding of one unit of $(bpy)_2Ru^{II}$ and one unit of $(phen)_2Ru^{II}$ to the periphery of *octakis*(benzylthio)tetraazaporphyrinmagnesium(II) [Mg(OBTTAP)] and *octakis*(methylthio)tetraazaporphyrinmagnesium(II) ([Mg(OMTTAP)]). Spectroscopic techniques were used to perform an extensive characterization of the complexes, including an analysis of their fluorescence excitation/emission spectra and redox behaviours. Effective electronic interaction between the peripheral $(bpy)_2Ru^{II}$/$(phen)_2Ru^{II}$ and [Mg(OBTTAP)] units is evidenced by the presence of these complexes. In cyclic voltammetry, the oxidation waves were slightly altered to a higher positive potential upon attaching a second Ru(II) unit in complexes **6**, **7**, **8** and **9**.

**Keywords: Tetraazaporphyrin, Magnesium, Fluorescence, Ruthenium, Bipyridyl, Phenanthroline.**

## INTRODUCTION

Porphyrazines, also known as tetraazaporphyrins, exhibit exceptional and distinct photophysical, photochemical and electrochemical properties [1]. Tetraazaporphrins are the fascinating class of macrocyclic compounds that have gained significant attention in the field of coordination chemistry and catalysis. The extensive delocalization of π-electrons within tetrapyrrole macrocycles makes them highly suitable for the optoelectronic applications [2-4]. Specifically, porphyrins and phthalocyanines, which are two significant subgroups within this family, are utilized as dyes in organic photovoltaics (OPV) and for the development of materials for non-linear optics (NLO) [5]. However, the closely related porphyrazine macrocycles have received less attention in this field, despite their intriguing structural and optical properties.

Porphyrazines offer the advantage of easy and versatile synthesis, a broader range of UV-visible absorption, thereby showing promise for the development of panchromatic photovoltaic materials. Additionally, under specific conditions, they can form columnar liquid crystal mesophases. Despite limited studies on their applications in NLO and OPV, porphyrazines hold untapped potential [6,7]. The tetraazaporphyrin framework provides a versatile platform for coordinating metal ions, leading to the development of metalloporphyrin complexes with intriguing properties and applications [8-12]. Peripherally substituted tetraazaporphyrins have been extensively investigated for their potential use in catalysis, sensing and energy conversion [13-15]. Polynuclear metalloporphyrin arrays with strong electronic and excitonic communication offer diverse applications in molecular photovoltaics, data storage devices, sensors and semiconductor materials [16-18].

Ruthenated porphyrin complexes serve as efficient photosensitizers in catalysis, photodynamic therapy and have a tendency to bind to DNA. Some reported polynuclear metalloporphyrin arrays consist of polypyridyl-Ru(II) units linked through *meso*-pyridyl groups or axial coordination, showing promise for optoelectronic applications [19-22]. In previous studies, Prasad *et al.* [23-27] reported the synthesis of several dinuclear and pentanuclear metallo-tetraazaporphyrin complexes possessing $(bpy)_2Ru^{II}$, $(phen)_2Ru^{II}$ or $Cp(PPh_3)Ru^{II}$ moieties. These complexes exhibited reversible redox behaviour, strong fluorescence and a high degree of interchromophore connectivity. In present work, a hybrid trinuclear *octakis*(benzylthio)-

tetraazaporphyrinmagnesium(II) and *octakis*(methylthio)-tetraazaporphyrinmagnesium(II) complexes with peripheral bonding to $(bpy)_2Ru^{II}$ and $(phen)_2Ru^{II}$ units in both *cis* and *trans* configurations are synthesized (**Scheme-I**). Several spectroscopic techniques, including UV-vis, fluorescence, mass and NMR spectroscopy, were employed for the characterization, while the cyclic voltammetry (CV) was utilized to investigate the electrochemical behaviour.

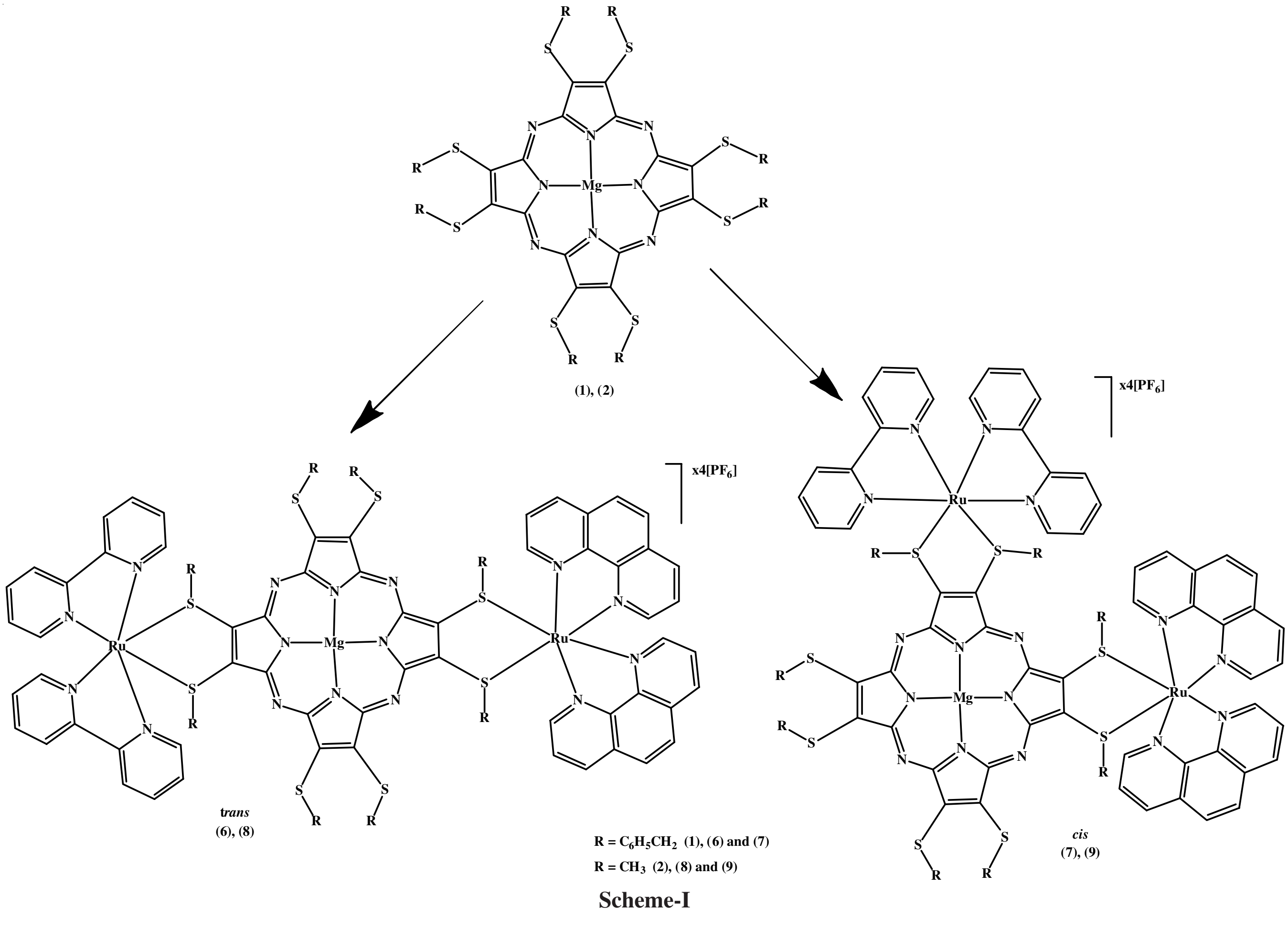
## EXPERIMENTAL

All chemicals used were of analytical reagent (AR) grade and used as received, unless otherwise specified. $RuCl_3 \cdot H_2O$, 2,2′-bipyridine and 1,10-phenanthroline were obtained from Loba Chemie, India. Tetraethylammonium perchlorate (TEAP) used in cyclic voltammetry (CV) studies was sourced from Fluka. Spectroscopic grade dichloromethane ($CH_2Cl_2$) was employed for the electronic spectral and fluorescence investigations. Dry benzene and acetonitrile were utilized for the cyclic voltammetry studies. Benzene was dried using sodium, while acetonitrile was dried by passing it through activated neutral alumina, preheated at 450 ºC for 24 h. All the synthesis processes were carried out under a nitrogen atmosphere. The precursors [Mg(OBTTAP)] (**1**), [Mg(OMTTAP)] (**2**), $[Ru(bpy)_2Cl_2] \cdot 2H_2O$ and $[Ru(phen)_2Cl_2] \cdot 2H_2O$ were synthesized following the procedures described in the literature [28-30].

A range of instrumental techniques was utilized for analysis purposes. The IR spectra were recorded using KBr pellets on a Thermo Nicolet-Nexus FTIR spectrophotometer, while electronic spectra were obtained in $CH_2Cl_2$ solutions using Shimadzu-1601 spectrophotometer. Fluorescence excitation and emission spectra were measured in deaerated $CH_2Cl_2$ solution using a Perkin Elmer LS 50B spectrofluorimeter. $^1H$ NMR spectra were recorded in acetone-$d_6$ solutions on a Bruker DRX-300 FTNMR spectrometer and MALDI TOF mass spectra were acquired using a Micromass TofSpec 3E instrument with 3,5-dihydroxybenzoic acid matrix. The cyclic voltammetry studies were conducted on a CHI 600A voltammetric analyzer with a three-electrode assembly, employing 0.1 M TEAP as supporting electrolyte. Elemental analyses, including C, H, N, as well as metal and sulfur determinations, were performed using an Elementar Vario EL III auto analyzer and wet ashing with standard methods, respectively.

### General procedure

**Synthesis of $[\{Mg(OBTTAP)\}\{Ru(bpy)_2\}\{Ru(phen)_2\}][PF_6]_4$; (6 and 7):** A mixture of $[Mg(OBTTAP)\{Ru(bpy)_2\}][PF_6]_2$ (**3**, 0.100 g, 0.05 mmol) and $[Ru(phen)_2Cl_2] \cdot 2H_2O$ (0.026 g, 0.05 mmol) was prepared in 30 mL of methanol. The reaction mixture was stirred continuously for 15 h at room temperature, followed by refluxing for 5 h under a nitrogen atmosphere. The volume of the reaction mixture was then reduced to approximately 1 mL through vacuum evaporation. Subsequently, 2-3 drops of conc. $NH_4PF_6$ in MeOH were added. The resulting mixture was filtered, dried under vacuum and subjected to



(1), (2)

*trans*
(6), (8)

*cis*
(7), (9)

$R = C_6H_5CH_2$ (1), (6) and (7)
$R = CH_3$ (2), (8) and (9)

Scheme-I

purification using a cellulose column (30 cm × 2.5 cm) with elution using a mixture of $CH_2Cl_2$ and petroleum ether (2:5 v/v).

**Compound 6:** Yield: 0.04 g (~ 40%); $^1$H NMR (acetone-*d*$_6$): 0.87, 1.29, 3.60 (3s, 16H, $CH_2$), 6.50-10.50 (br-m, Ph/phen/bpy-H); IR: (ν, cm$^{-1}$): 3543 m, 3478 m, 3415 s, 2921 m, 1634 s, 1617 s, 1443 w, 1384 s, 1256 w, 1111 b, 844 vs, 765 w, 622 m; UV/vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε): 660 (4.28), 472 (4.44), 369 (4.62), 294 (4.93), 257 (4.96), 233 nm (5.05); CV ($CH_3CN$): $E_{1/2}$ = +0.50, +1.09 V Ag/AgCl; Elemental analysis of calcd. (found) % $C_{68}H_{56}N_{16}F_{24}P_4S_8MgRu_2$: C, 37.68 (37.81); H, 2.61 (2.58); N, 10.37 (10.15); S, 11.88 (10.12).

**Compound 7:** Yield: 0.03 g (~ 30%); $^1$H NMR (acetone-*d*$_6$): 0.87, 1.29, 3.60 (3s, 16H, $CH_2$), 6.50-10.50 (br-m, Ph/phen/bpy-H); IR: (ν, cm$^{-1}$): 3432 b, 2952 w, 2918 s, 2849 m, 1965 w, 1713 w, 1626 w, 1601 s, 1425 w, 1383 s, 1096 m, 1021 b, 842 vs, 764 m, 721 w, 558 s; UV/vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε): 656 (4.26), 462 (4.38), 369 (4.59), 294 (4.87), 263 (4.87), 231 (5.02); CV ($CH_3CN$): $E_{1/2}$ = +0.49, +1.06 V Ag/AgCl; Elemental analysis of calcd. (found) % $C_{68}H_{56}N_{16}F_{24}P_4S_8MgRu_2$: C, 37.81 (37.56); H, 2.61 (2.46); N, 10.37 (10.21); S, 11.88 (11.04).

**Synthesis of $[\{Mg(OMTTAP)\}\{Ru(bpy)_2\}\{Ru(phen)_2\}][PF_6]_4$ (8 and 9):** A solution containing $[Mg(OMTTAP)\{Ru(bpy)_2\}][PF_6]_2$, (**5**, 0.070 g, 0.05 mmol) and $[Ru(phen)_2Cl_2]\cdot 2H_2O$ (0.026 g, 0.05 mmol) was prepared by dissolving them in a mixture of 30 mL of $CH_3OH$ and 15 mL of $CH_2Cl_2$. The resulting reaction mixture was stirred continuously for 15 h at room temperature, followed by refluxing for 5 h under a nitrogen atmosphere. Subsequently, the volume of the reaction mixture was reduced to approximately 1 mL using vacuum evaporation. A few drops (2-3 drops) of conc. $NH_4PF_6$ in MeOH were then added to the concentrated solution. The resulting mixture was filtered and subsequently dried under vacuum. To purify the obtained product, it was subjected to a purification process using a cellulose column (30 cm × 2.5 cm) with elution using a mixture of $CH_2Cl_2$ and petroleum ether (4:1 v/v).

**Compound 8:** Yield: 0.045 g, ~45%; $^1$H NMR (acetonitrile-*d*$_3$) δ ppm: 2.51-4.10 (br, 24H, $CH_3$), 6.50-10.50 (br m, phen/bpy-H); IR: (ν, cm$^{-1}$): 3445 b, 1635 s, 1465 w, 1426 w, 1384 s, 1321 m, 1265 b, 1024 b, 968 s, 844 vs, 794 s, 557 m; UV/vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε): 667.5 (4.65), 481.0 (4.49), 375 (4.82), 291.0 (4.98), 267.5 (5.08), 230.5 (5.07); CV ($CH_3CN$): $E_{1/2}$ = +0.50, +1.09 V Ag/AgCl; Elemental analysis of calcd. (found) % $C_{116}H_{88}N_{16}F_{24}P_4S_8MgRu_2$: C, 5032 (50.22); H, 3.20 (3.05); N, 8.09 (7.86); S, 9.26 (8.97).

**Compound 9:** Yield: 0.035 g, ~35%; $^1$H NMR (acetonitrile-*d*$_3$) δ ppm: 2.5-3.9 (br, 24H, $CH_3$), 6.50-10.50 (br m, phen/bpy-H); IR: (ν, cm$^{-1}$): 3440 b, 1637 s, 1449 w, 1426 s, 1384 vs, 1313 b, 1265 w, 1024 m, 968 s, 845 vs, 791 s, 558 m; UV/vis ($CH_2Cl_2$) $\lambda_{max}$ (log ε): 672.5 (4.52), 481.0 (4.43), 376 (4.71), 290 (4.93), 268 (5.03), 229.5 (4.65); CV ($CH_3CN$): $E_{1/2}$ = +0.61, +1.17 V Ag/AgCl; Elemental analysis of calcd. (found) % $C_{116}H_{88}N_{16}F_{24}P_4S_8MgRu_2$: C, 50.32 (50.16); H, 3.20 (2.98); N, 8.09 (7.98); S, 9.26 (9.06).

## RESULTS AND DISCUSSION

The reaction of $[Mg(OBTTAP)\{Ru(bpy)_2\}][PF_6]_2$ (**3**) or $[Mg(OBTTAP)\{Ru(phen)_2\}][PF_6]_2$ (**4**) with one molar equivalent of $[Ru(phen)_2Cl_2]\cdot 2H_2O$ or $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ in $CH_3OH$ yielded the mixture of trinuclear complexes **6** and **7** and the reaction of **5** with one molar equivalent of $[Ru(phen)_2Cl_2]\cdot 2H_2O$ in $CH_3OH/CH_2Cl_2$ (2:1) mixture yielded the mixture of trinuclear complexes **8** and **9** (**Scheme-I**). Compounds were obtained as $[PF_6]^-$ salts and separated by column chromatography over cellulose (eluent; 2:5 $CH_2Cl_2$/petroleumether in **6** and **7** and 4:1 $CH_2Cl_2$/petroleum ether in **8** and **9**). Due to strong adherence of the product mixture to the alumina surface and dissociation on silica gel, separation was achieved using a cellulose column. Two distinct bands were obtained, with the fast moving band identified as *cis* isomers **6** and **8** and the slower moving band as *trans* isomers **7** and **9**. These complexes are soluble in polar organic solvents but insoluble in non-polar solvents. They exhibit stability under ambient laboratory conditions in the air, as confirmed by conductance measurements of $CH_2Cl_2$ and acetone, which showed no dissociation even after 24 h of storage.

**$^1$H NMR spectra:** In the $^1$H NMR spectra of complexes **6** and **7**, two groups of signals were observed, upfield between δ 0.87-4.00 ppm due to alkyl protons and downfield between 6.50-10.20 ppm due to aromatic Ph/bpy/phen protons whereas in case of complexes **8** and **9**, two groups of signals were also observed, upfield between δ 2.51-4.10 ppm due to methyl protons and downfield between δ 6.50-10.50 ppm due to the aromatic bpy/phen protons. The *cis* and *trans* assignments are inferred on the basis of $^1$H NMR spectra and their mobility over the column. The *cis* isomer due to rounded shape moved faster over the column with polar eluent. Also in the *cis* isomer, the $^1$H NMR signals due to bpy/phen protons were broadened due to large mutual ring current effects in compared to that in the *trans* isomer. Both the *cis* and *trans* stereoisomers could exist in two different conformational forms, in which the two $Ru^{II}$ units could either lie on the same side of the TAP plane or on opposite sides. This is also partly responsible for the broadening of bpy/phen-H signals [23,24].

**Mass spectra:** The MALDI-TOF mass spectra of complex **6** exhibited mass peaks at *m/z* 788 and 1177, which correspond to the formation of $[M-4\{PF_6\}+DHB+AN]^{3+}$ and $[M-4\{PF_6\}+DHB]^{2+}$ fragments, respectively. In complex **7**, only mass peaks at *m/z* 1177 was observed however the ESIMS mass spectra of complexes **8** and **9** exhibit prominent ion peak at *m/z* 157.8 and 448.2 due to the formation of $[M-4PF_6]^{10+}$ and $[M+2AN]^{5+}$ ion, respectively.

**Electronic spectra:** The electronic absorption spectra of the complexes (Fig. 1) clearly showed the formation of trinuclear complexes as the characteristic intra-ligand bands are prominently seen at $\lambda_{max}$ ~ 294 nm due to $(bpy)_2Ru^{II}$ unit and ~ 267, ~ 263 nm due to $(phen)_2Ru^{II}$, with nearly equal intensity, in all of these complexes. The Q band in complexes **1** and **2** lies at 651.7 and 668.5 nm, respectively. The peripheral metallation in the case of dinuclear complexes **3**, **4** and **5** resulted in a moderate blue shift in the Q band due to the stabilization of the HOMO and destabilization of LUMO levels in TAP π-system. However, upon the formation of trinuclear complexes **6**, **7**, **8** and **9**, it undergoes a red shift with decreased intensity all of trinuclear complexes due to the LUMO higher energy ($e_g$) orbitals will be lifted and the HOMO also the same symmetry, causing

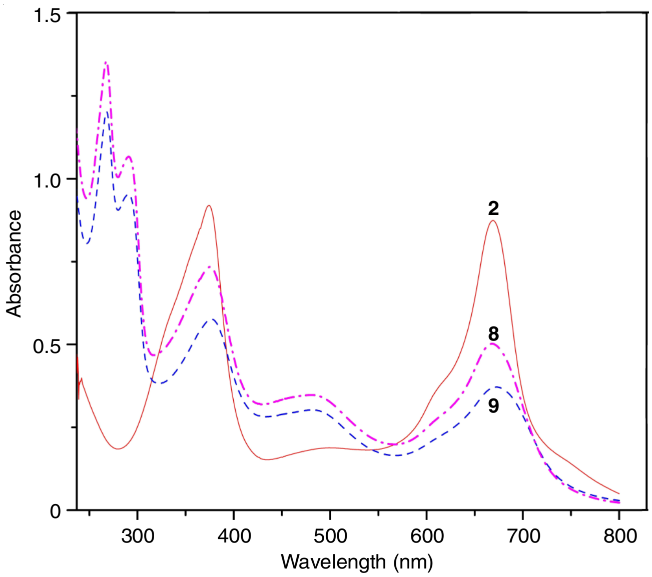


Fig. 1. Electronic absorption spectra of complexes **2**, **8** and **9** in $CH_2Cl_2$

a stronger configuration interaction. Besides, they also exhibited the moderate intensity Ru-diimine centered MLCT absorption $\lambda_{max}$ 480-490 nm. Unlike that in the dinuclear complexes **3**, **4** and **5** in which the MLCT bands are feeble, in the trinuclear complexes **6**, **7**, **8** and **9** they are prominent seen, having relatively higher intensity. Furthermore, the MLCT band is broader than that in the dinuclear precursors due to the differing absorptions of the two peripheral Ru(II) units.

**Fluorescence spectra:** The fluorescence excitation emission spectra of complex **6** are shown in Fig. 2. It could be seen that Soret excitation leads to three prominent emissions with maxima at $\lambda_{max\ em}$ 450, 550 and 700 nm having nearly equal emission intensities. The excitation profiles of these emissions show their origin to Soret, MLCT and Q-band excitations of the complex, respectively. The important aspect of the emission spectra of the trinuclear complex was that the Soret excitation led to emissions from $S_2$, MLCT and $S_1$, all three states with comparable intensity. It appears that energy being sieved through the possible emitting states and deactivation processes are uncompetitive enough to completely quench the higher lying emitting states. The MLCT and $S_1$ emissions in *trans* complexes **7** are significantly weaker than in *cis* complex **6**. The MLCT excitation also leads to $S_1$ emission but is of much lower relative intensity than that observed due to Soret excitation, which is indicative of direct $S_2$-$S_1$ internal conversion (IC) under lower symmetry environment, because of the MLCT mediated efficient $S_2 \rightarrow$ MLCT $\rightarrow S_1$ cascading. The $S_1$ emissions in the trinuclear complexes **6** and **7** are more pronounced than that in corresponding dinuclear complexes **3** and **4** or precursor complex **1**. This indicates presence of effective intercomponent electronic interaction between the peripheral $(bpy)_2Ru^{II}$/$(phen)_2Ru^{II}$ and [Mg(OBTTAP)] units.

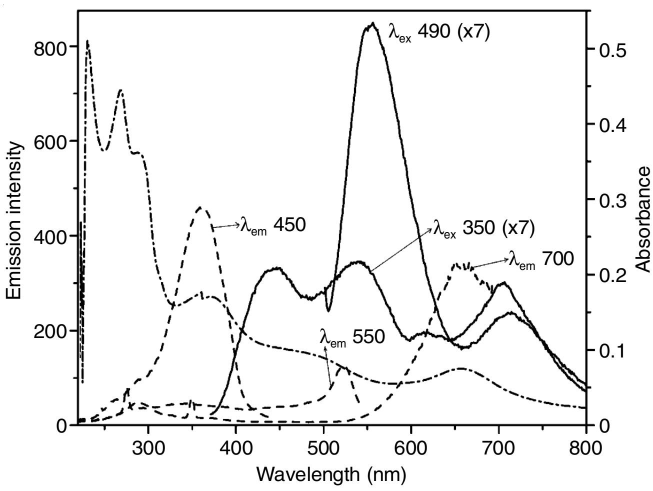


Fig. 2. Electronic absorption (‒ · ‒ · ‒), emission (———) and excitation spectra (– – – –) of complexes **4** in $CH_2Cl_2$

**Cyclic voltammetry:** In precursor complex **3**, two reversible oxidation waves were observed at $E_{1/2}$ 0.45 and 1.05 V *vs.* Ag/AgCl with nearly equal peak currents whereas in complex **5** two reversible and one irreversible oxidation wave were observed at $E_{1/2}$ 0.45, 1.03 V and 1.45 V *vs.* Ag/AgCl. Upon binding of the second Ru(II) unit in complexes **6**, **7**, **8** and **9** the oxidation waves were only moderately shifted to more positive potentials, at $E_{1/2}$ +0.50 and +1.09 V in **6** and $E_{1/2}$ +0.49 and +1.06 V *vs.* Ag/AgCl in **7** and $E_{1/2}$ +0.50 and +1.09 V in **8** and $E_{1/2}$ +0.61 and +1.17V in **9**. The two oxidation waves could tentatively be attributed to Ru(II)/Ru(III) and TAP/$TAP^+$ processes. Due to weaker $d\pi(S) \rightarrow d\pi(Ru)$ $\pi$-back bonding the Ru(II)/Ru(III) processes is being observed at less positive potential.

## Conclusion

A set of trinuclear complexes (**6-9**) was synthesized by attaching $(bpy)_2Ru^{II}$ and $(phen)_2Ru^{II}$ moieties to the periphery of [Mg(OBTTAP)] and [Mg(OMTTAP)] complexes. The spectroscopic and electrochemical investigations of the diruthenated complexes (**6-9**) revealed significant intercomponent electronic interactions between the peripheral $(bpy)_2Ru^{II}$/$(phen)_2Ru^{II}$ units and [Mg(OBTTAP)], even in the cyclic voltammetry. The binding of second Ru(II) unit resulted in moderate shifts of the oxidation waves. The stepwise synthetic approach employed in this study produced stable trinuclear complexes with reversible redox behaviour, strong fluorescence and a high degree of interchromophore connectivity. These findings demonstrate the potential of these complexes as redox-active materials. Furthermore, the stepwise synthesis strategy used in this research lays the groundwork for developing new materials with enhanced properties. This study enhances the understanding of the intercomponent electronic interactions and presents promising prospects for designing and synthesizing innovative materials for diverse applications.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledge to The Head, Department of Chemistry, Indian Institute of Technology Roorkee, India, for providing the access to the instrumental facilities. The authors also acknowledge to Regional Sophisticated Instrumentation Centre, Central Drug Research Institute (CSIR), Lucknow, India, for recording NMR and mass spectra.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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