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# Syntheses, Spectral and Electrochemical Investigation of Coordination Complexes of Octakis(benzylthio)tetraazaporphyrinmanganese(II)

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**Synthesis of [Mn(OBTTAP)], 1 and bichromophoric, di- and pentanuclear complexes with diimine-ruthenium(II) of the type**  $\{[Mn(OBTTAP)]\{Ru(bpy)_2\}[PF_6]_2$ , 2,  $\{[Mn(OBTTAP)]\{Ru(phen)_2\}[PF_6]_2$ , 3,  $\{[Mn(OBTTAP)]\{RuCp(PPh_3)\}[PF_6]$ , 4,  $\{[Mn(OBTTAP)]\{Ru(bpy)_2\}_4-[PF_6]_8$ , 5,  $\{[Mn(OBTTAP)]\{Ru(phen)_2\}_4-[PF_6]_8$ , 6 and  $\{[Mn(OBTTAP)]\{RuCp(PPh_3)\}_4-[PF_6]_4$ , 7, (OBTTAP = octakis(benzylthio)tetraazaporphyrin) have been described. They were characterized using IR,  $^1H$  NMR, UV–visible, and mass spectral data. In the electronic absorption spectra the relative intensities and positions of the Soret and Q-bands, in the di- and pentanuclear complexes were observed shifted vis-à-vis that in the precursor complex 1. They all exhibit strong  $S_2$  emission. The emission intensity of the equimolar solutions of complexes 2, 3, 4 and 7 were found to be significantly higher than that of 1. The excitation-emission behaviors of the complexes are indicative of interchromophore energy transfer. Complexes 2–7 exhibited good electrode activity, particularly with multiple reversible redox waves in oxidative CV scans. The OBTTAP ring oxidations were observed as one or two reversible waves, depending upon number and nature of the peripheral metal units. Particularly, with four  $(bpy)_2Ru^{II}$  units bonded to the  $[Mn(OBTTAP)]$  periphery, it was observed as two reversible, one electron oxidation waves at  $E_{1/2}$  0.81 and 1.02 V vs. Ag/AgCl. Also the Ru(II)/Ru(III) oxidations were observed at significantly lower potential, in this complex, at  $E_{1/2}$  0.49 V vs Ag/AgCl due to weaker  $\pi$ -interaction with  $d\pi(S)$  orbitals.

**Keywords:** Bipyridyl; Electrochemistry; Phenanthroline; Ruthenium; Manganese(II); Tetraazaporphyrin

## INTRODUCTION

In recent years there has been a growing interest in molecular systems having multiple redox active

centers. The porphyrin and tetraazaporphyrin derivatives are generally considered as an active component for such systems. They constitute a family of very versatile materials that have potential applications in medical diagnosis [1–4], data storage devices [5,6], catalysis [7–9], radiation protection [10] and chemical sensors [11–14]. The manganese porphyrins and related compounds constitute an extremely interesting class of coordination complexes due to their role in photosynthesis and its mimicking in artificial systems [15–17]. It is believed that a manganese porphyrin functions as an oxidant for the natural photosynthetic oxidation of water to molecular oxygen. This has provided a motivation for a number of redox and photochemical studies utilizing analogous manganese(II) complexes [18–21]. The manganese complexes of porphyrin/tetraazaporphyrins show high catalytic activity for oxidation [22] and epoxidation of hydrocarbons [23–27], and are of particular interest in many fields concerning NMR image enhancement agent, food-stuff antioxidants and nonlinear optical materials.

We have recently used several metallo-tetraazaporphyrins,  $[M(OBTTAP)]$ , as ionophore materials in the fabrication of ion selective electrodes. Also the  $[M(OBTTAP)]$  are excellent dyes and many of them are weakly luminescent [28]. Hence, it would be interesting to dovetail them with the long lived and strongly luminescent units like  $(bpy)_2Ru^{II}$  and  $(phen)_2Ru^{II}$  in order to enhance luminescence yields. When coupled with additional polypyridyl ruthenium(II) chromophores, their ion sensing and recognition potential could be extended to the fluorescence based sensing of coordinating anions

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and molecules. In a previous paper we have published the synthesis of  $[M(\text{OBTTAP})]$  complexes with different bivalent transition metal ions [29], and the behaviour of modified silver and graphite electrodes using them [30]. Thus we herein report synthesis, spectroscopic and electrochemical investigations of di- and pentanuclear complexes of  $[\text{Mn}(\text{OBTTAP})]$  possessing  $(\text{bpy})_2\text{Ru}^{\text{II}}$ ,  $(\text{phen})_2\text{Ru}^{\text{II}}$  and  $\text{Cp}(\text{PPh}_3)\text{Ru}^{\text{II}}$  peripheral units as shown in Scheme 1.

## RESULTS AND DISCUSSION

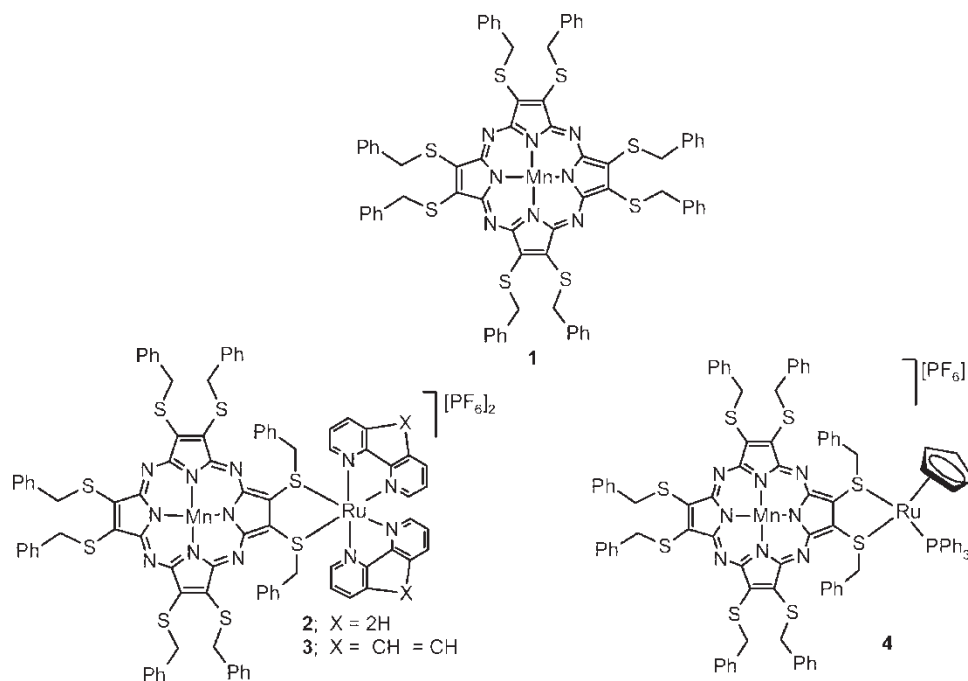
### Syntheses and Characterization

The precursor complex  $[\text{Mn}(\text{OBTTAP})]$ , **1** was synthesized by the reaction of metal free (OBTTAP) and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  in chlorobenzene-DMF mixture, under nitrogen atmosphere [29]. This complex upon reaction with equimolar amount of  $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ru}(\text{phen})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  or  $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$  yielded peripherally coordinated dinuclear complexes **2**, **3** and **4** respectively. Whereas, when the  $[\text{Ru}(\text{bpy})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Ru}(\text{phen})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  or  $[\text{RuCp}(\text{PPh}_3)_2\text{Cl}]$  were taken slightly more than four molar equivalent amounts corresponding pentanuclear complexes **5**, **6** and **7** respectively were predominantly obtained. All these complexes are highly soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{CH}_3\text{CN}$ , etc. polar solvents but are insoluble in  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_5\text{CH}_3$ , etc. nonpolar solvents. They all are air and moisture sensitive but are stable under dry ambient conditions.

In the IR spectra they all exhibited the characteristic fingerprint of the constituent units. The di- and pentanuclear complexes **2**, **3**, **5** and **6** exhibited one strong band between  $1400\text{--}1500\text{ cm}^{-1}$ , due to the  $\nu_{\text{C}=\text{C}}$ , and  $\nu_{\text{C}=\text{N}}$  vibrations of the bipyridine and phenanthroline rings and a very strong band around  $845\text{ cm}^{-1}$  due to  $[\text{PF}_6]^-$ .

Due to paramagnetic nature of the complexes the  $^1\text{H}$  NMR signals were not resolved. In the parent  $[\text{Mn}(\text{OBTTAP})]$  complex, **1**, two broad signals were observed between  $\delta$  3.98–4.10 and 7.26 ppm. The tetraazaporphyrin possesses a smaller cavity size and hence has a larger ring current, creating larger anisotropic effect in its complexes than that the normal porphyrins. The anisotropic shielding led to a substantial shift of the resonance signals particularly, for  $-\text{CH}_2$  and  $-\text{C}_6\text{H}_5$  units. The cationic di- and pentanuclear complexes possessing  $(\text{bpy})_2\text{Ru}^{\text{II}}$  and  $(\text{phen})_2\text{Ru}^{\text{II}}$  units exhibited distinct bpy/phen signals between  $\delta$  6.25–10.25 and 6.50–9.00 ppm. The complexes **4** and **7** possessing  $\text{Cp}(\text{PPh}_3)\text{Ru}^{\text{II}}$  units exhibit four groups of signals at  $\delta$  1.24, 3.03, 4.10, and 7.20–8.50 and 1.25, 4.13, 5.30 and 7.00–8.25 ppm respectively (Table I).

In the electrospray ionization (ESI) mass spectra of the complexes, molecular ion peak for complex **1** was observed at  $m/z$  1355. The base peak for this complex was observed at  $m/z$  454 that corresponds to the formation of  $[\text{M}]^{3+}$  species. Similarly, for the di- and pentanuclear complexes, **2–7** multiple charged ion peaks were observed. Thus in complex **2** the mass peak at  $m/z$  868 was observed due to  $[\text{M} - 2\text{PF}_6]^{2+}$ , in **3** at 1004 due to  $[\text{M} + \text{MeOH} - 2\text{PF}_6]^{2+}$  and in **4** at 886 due to



SCHEME 1

TABLE I IR and <sup>1</sup>H NMR spectral data

Compound	IR ( $\nu/\text{cm}^{-1}$ ) <sup>a</sup>	<sup>1</sup> H NMR ( $\delta/\text{ppm}$ ) <sup>b</sup>
1	3033m, 1650w, 1522m, 1400vs, 1256w, 1094w, 750w, 694vs	3.98–4.10 (br, CH <sub>2</sub> ), 7.26 (m, Ph-H)
2	3432b, 2926m, 2860w, 1719m, 1603s, 1543w, 1453s, 1413m, 1308w, 1258m, 1026m, 844vs, 764vs, 700m, 559s.	0.87, 1.28 (s, 16H, CH <sub>2</sub> ) 3.01 6.25–10.25 (m, 56H, Ar/bpy-H)
3	3434b, 3065w, 2924m, 2856w, 1978w, 1722m, 1606s, 1482w, 1421w, 1247w, 1026w, 845vs, 765w, 707m, 560s.	0.88, 1.28, (s, 16H, CH <sub>2</sub> ) 3.01, 6.50–9.00 (br-m, 56H, Ar/phen-H)
4	3432m, 2929m, 2852w, 1721w, 1631s, 1451m, 1265m, 1095m, 817s, 697s, 552s.	0.95, 1.24, 2.74 (2s, 16H, CH <sub>2</sub> ), 3.03, 4.10 (s, 5H, Cp-H), 7.20–8.50 (m, 55H, Ph-H)
5	3430b, 3069w, 2926m, 2847w, 1713w, 1608s, 1453s, 1313m, 1255m, 1026w, 843vs, 765s, 652w, 560s.	0.88, 1.29 (2s, 16H, CH <sub>2</sub> ), 3.01 (s, 40H, Ph-H), 6.00–10.50 (m, m, 64H, bpy-H)
6	3432b, 2925m, 2847w, 1963s, 1717w, 1628s, 1421s, 1308w, 1041m, 844vs, 710s, 559s.	0.88, 1.29 (s, 16H, CH <sub>2</sub> ), 2.92, 6.50–9.00 (br-m, 104H, Ar/phen-H)
7	3431b, 2925s, 2856w, 1633s, 1451s, 1261s, 1173w, 1096s, 1029s, 843s, 807s, 698m, 543m.	0.85, 1.25 (s, 16H, CH <sub>2</sub> ), 4.13 5.30, (2s, 20H, Cp-H), 7.00–8.25 (m, 100H, Ph-H)

<sup>a</sup>: b, broad; m, medium; s, strong; vs, very strong; w, weak; <sup>b</sup>: br, broad; s, singlet; m, multiplet.

[M–PF<sub>6</sub>]<sup>2+</sup>. Similarly in the pentanuclear complexes **5**, **6** and **7** mass peaks were observed at 668 due to [M–5PF<sub>6</sub>]<sup>5+</sup>, at 704 due to [M + MeOH-5PF<sub>6</sub>]<sup>5+</sup> and at 1068 due to [M–3PF<sub>6</sub>]<sup>3+</sup> respectively. In the MALDI-TOF mass spectra, in a matrix consisting of 2,5-dihydroxy benzoic acid (DHB) dissolved in acetonitrile (AN), complex **4** exhibited peak at *m/z* 1754, 1001 and 429 due to formation of [M–{PF<sub>6</sub>}]<sup>+</sup>, [M–{PF<sub>6</sub>} + DHB + 2AN]<sup>2+</sup> and [Cp(PPh<sub>3</sub>)Ru]<sup>+</sup>, respectively. Similarly complex **2** in MALDI-TOF mass spectra, exhibited ion peaks at *m/z* 1015, 935 and 625 that correspond to [M–2{PF<sub>6</sub>} + 3AN + DHB]<sup>2+</sup>, [M–2{PF<sub>6</sub>} + 3AN]<sup>2+</sup> and [M–2{PF<sub>6</sub>} + 3AN]<sup>3+</sup> and complex **3** exhibited an ion peaks at *m/z* 642 that correspond to [M–2{PF<sub>6</sub>} + 3AN]<sup>3+</sup>, respectively. Base peaks in the MALDI-TOF MS of complexes **2**, **3** and **4** were observed at *m/z* 567, 615 and 662 due to formation [Ru<sup>II</sup>(bpy)<sub>2</sub> + DHB]<sup>+</sup>, [Ru<sup>II</sup>(phen)<sub>2</sub> + DHB]<sup>+</sup> and [CpRu<sup>II</sup>(PPh<sub>3</sub> + DHB + 2 AN)]<sup>+</sup> fragments, respectively. The molecular ion peaks in the MALDI-TOF MS of pentanuclear complexes **5**–**7** were not observed due to their highly charged ionic nature and consequent poor desorption. Instead, they predominantly exhibited fragment peaks at *m/z* 567, 616 and 662, respectively.

## Electronic Spectra

The electronic spectra were recorded in dry CH<sub>2</sub>Cl<sub>2</sub> and the observed spectral bands are listed in Table II. Generally the metallo-tetraazaporphyrins with D<sub>4h</sub> symmetry exhibited two prominent bands in the electronic spectra *viz.* Q-band, in the visible region and Soret band in the ultraviolet region. But in the [Mn(OBTTAP)], both of these bands were found to be relatively weak and broad, particularly so was the Q-band, due the C<sub>4v</sub> symmetry. The size of Mn<sup>2+</sup> ion is large enough to exactly fit in the tetraazaporphyrin cavity. Therefore, it sits at one side of the macrocycle ring. Upon coordination of the second Ru(II) unit to the [Mn(OBTTAP)] periphery, a new low intensely shoulder was observed, between 450–500 nm, due to dπ(Ru) → π\*(bpy/phen) MLCT transition. At the same time the Soret and Q-bands get further broadened. The [Mn(OBTTAP)] complex, **1** exhibited Q-band at 662 nm and the Soret band at 328 nm [29]. The Soret band in this complex is nearly five times more intense than the Q-band. Upon binding of peripheral metal units, the Q- and Soret band maxima were both observed shifted. In the dinuclear complexes **2**, **3**, and **4** the Q-band was bathochromically

TABLE II Electronic spectral and cyclic voltammetry data

Compound	Absorption spectra $\lambda_{\text{max}} / \text{nm}$ (log $\epsilon$ )	E <sub>1/2</sub> / V (vs Ag/AgCl)
1	662(3.96), 328 (4.73)	–0.33
2	688(4.28), 480(4.67), 360(4.79), 296(5.25), 236(5.14)	+0.50, +1.04, +1.32(i.r.)
3	720(4.39), 268(4.99), 235(5.05)	+0.40, +0.91
4	711(4.02), 352(4.50), 277sh(4.60), 233(4.90)	+0.64, +0.96(i.r.); –0.23
5	673(4.07), 494(4.42), 363(4.61), 296(5.17), 233(5.05)	+0.49, +0.81, +1.02, +1.46(i.r.); (0.42(i.r.))
6	702(4.66), 381sh(5.07), 264(5.45), 231(5.50)	+0.38, +0.92; (0.86(i.r.))
7	703(4.05), 354(4.39), 231(5.20)	+0.63, +0.98(i.r.); –0.31

i.r., irreversible

shifted by 26, 58 and 49 nm, respectively, whereas in the pentanuclear complexes **5**, **6** and **7**, the shift was less prominent than that in the dinuclear complexes i.e., **11**, **40** and **41** nm, respectively. The Soret absorption in complexes **2**, **3**, **5** and **6**, on the longer wavelength side also overlaps with the LMCT transitions occurring in the (bpy)<sub>2</sub>/(phen)<sub>2</sub>Ru<sup>II</sup> units, and therefore its shape was deformed in these complexes. These complexes also possessed an intra ligand bipyridyl ( $\lambda_{\text{max}} \sim 296$  nm) and phenanthroline ( $\lambda_{\text{max}} \sim 267$  nm) centered absorptions. Complexes **4** and **7** possessing Cp(PPh<sub>3</sub>)Ru<sup>II</sup> moiety, exhibited intense LMCT bands at  $\lambda_{\text{max}}$  352 and 354 nm, respectively [31,32].

The Soret and Q-bands position shifts arise from the stabilization of the vacant  $e\pi$  and filled  $a_1$  molecular orbitals. In the C<sub>4v</sub> symmetry, which is the case with the [Mn(OBTTAP)] complexes, the vacant  $e$  MO's and the filled  $a_1$  HOMO, due to their interaction with  $p_z$  and  $d_{z^2}$  (Mn) atomic orbitals, get stabilized, whereas the  $a_2$  MO's energy remains unchanged. Consequently the configuration interaction between the two E states arising from  $a_1 \rightarrow e$  and  $a_2 \rightarrow e$  transitions is decreased. Peripheral binding of the metal unit causes slight gain in the Q-band intensity, due to further extension of the  $\pi$ -interaction, and perturbation of macro symmetry to C<sub>2v</sub>. But upon binding of four such units, their mutual relative intensity decreased again.

### Emission Spectra

The fluorescence emission and excitation spectra of the complexes were recorded in deoxygenated dichloromethane solutions at room temperature and the data obtained are summarized in Table III. Complexes **2**, **3**, **5** and **6** consisted of two different chromophore units, viz., [Mn(OBTTAP)] and (bpy)<sub>2</sub>Ru<sup>II</sup>/(phen)<sub>2</sub>Ru<sup>II</sup>, both of which are proven luminophores that are datively bonded to each other. Hence, these supramolecular systems exhibited luminescence features that are hybrid of the two. The emission spectra may get complicated in cases where complexes decomposed forming solvated luminescent species. Hence, in order to ensure that dissociation should not occur, the

fluorescence spectra were recorded in a non-coordinating solvent, CH<sub>2</sub>Cl<sub>2</sub>. The dichloromethane solutions of the complexes were very stable and conductance, electronic absorption spectra and voltammograms remained unchanged even after two days of storage under ambient laboratory conditions.

The precursor [Mn(OBTTAP)], **1**, as well as the di- and pentanuclear complexes **2–7** exhibited S<sub>2</sub> fluorescence in the visible region. The [Mn(OBT-TAP)] exhibited a strong emission at  $\lambda_{\text{max}}$  435 nm. The excitation profile of this emission is suggestive of its origin to the Soret band absorption. Upon binding of a (bpy)<sub>2</sub>Ru<sup>II</sup> or (phen)<sub>2</sub>Ru<sup>II</sup> moiety with [Mn(OBT-TAP)] in complexes **2** and **3**, emission maxima were observed at 500 and 464 nm with a shoulder towards longer wavelength side. From Fig. 1 it could be seen that the 296 and 483 nm excitations in complex **2** resulted into appearance of a very weak emission maxima at  $\lambda_{\text{em}}$  500 and at 560 nm, respectively. Similarly, in complex **3** the 300 and 490 nm excitations caused appearance of the emission maxima at 466 and 566 nm, respectively. As compared to that in the dinuclear complexes **2** and **3**, emission maxima in the pentanuclear complexes **5** and **6** were observed moderately hypsochromic shifted (Fig. 2). The Q-band excitation did not lead to any observable emission upto 800 nm. Neither the excitation spectra for  $\lambda_{\text{em}}$  705 nm (probable S<sub>1</sub> wavelength) showed any appreciable excitation maxima between 350–700 nm (Fig. 1).

Unlike the porphyrin derivatives that primarily emit through their S<sub>1</sub> state (33,34), the strong S<sub>2</sub> emission in these complexes is a unique feature. A comparison of the electronic absorption spectra of [Mn(OBTTAP)] vis-à-vis of [MnP] shows that although the S<sub>2</sub>–S<sub>1</sub> energy gap is nearly comparable, the S<sub>1</sub> state (i.e. Q-Band) in the former has much lower transition probability. The S<sub>2</sub> state also decays rapidly in [Mn(OBTTAP)], hence lifetime measurements using a nanosecond fluorescence spectrophotometer were not successful. Similar configurations of the S<sub>2</sub> and S<sub>1</sub> levels and large energy gap between them, absence of allowed intermediate states and cushioning effect of

TABLE III Fluorescence spectral data

Complex	Emission spectra		Excitation spectra	
	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{max,em}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\lambda_{\text{max,exc}}/\text{nm}$
<b>1</b>	331	435	435	330
<b>2</b>	296 483 702	500(w) 560 N.E.	500 525 560 705	425, 360 365, 458 360, 425 450, 555, 600
<b>3</b>	300 490 716	464(w) 566 N.E.	464 529 565 625	370 400 460 500
<b>4</b>	360	436	435	355
<b>5</b>	296 450 694	420 516 N.E.	363 425 514 581	363 252, 345 260 446
<b>6</b>	354 441 702	448 521 N.E.	448 523 590	371 425 459
<b>7</b>	360	435	435	355

N.E., non emitting; w, weak.



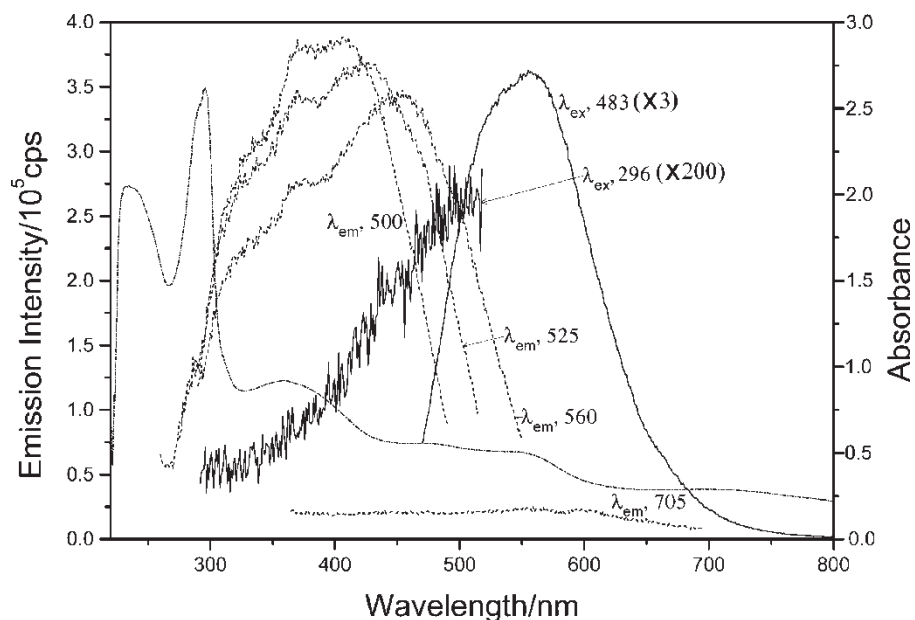


FIGURE 1 Fluorescence emission spectra (—), excitation spectra (---) at different wavelength and electronic absorption spectra (-.-) of complex **2** in  $\text{CH}_2\text{Cl}_2$ .

the  $-\text{S}-\text{CH}_2\text{C}_6\text{H}_5$  groups for the solvent mediated collisional deactivation have been primarily responsible for the  $\text{S}_2$  emission. The geometry of these molecules is such that the peripheral thiobenzyl substituents, possessing stereochemical non-rigidity [35–38], provide hairy cushion for the solvent mediated collisional cascading of the OBTTAP centered  $\text{S}_2$  to  $\text{S}_1$  state.

A comparison of the emission intensities of the equimolar solutions of di- and pentanuclear complexes was made for the excitation at 360 nm. As seen from Fig. 3, binding of one  $(\text{bpy})_2\text{Ru}^{\text{II}}$  unit to the

$[(\text{Mn}(\text{OBTTAP}))]$  in **2** caused nearly eight fold increase in the emission intensity, while binding of four such units in **5** caused a drop in the emission intensity to nearly half of that of complex  $[(\text{Mn}(\text{OBTTAP}))]$ , **1**. Similar behaviors were observed for  $(\text{phen})_2\text{Ru}^{\text{II}}$  binded complexes **3** and **6**, but contrary to this in the  $\text{Cp}(\text{PPh}_3)\text{Ru}^{\text{II}}$  binded di- and pentanuclear complexes **4** and **7** a 2.2 and 3 fold increase in the emission intensities respectively were observed vis-à-vis that of **1**. The enhancement of the emission intensities in the di- and pentanuclear complexes could arise due to efficient

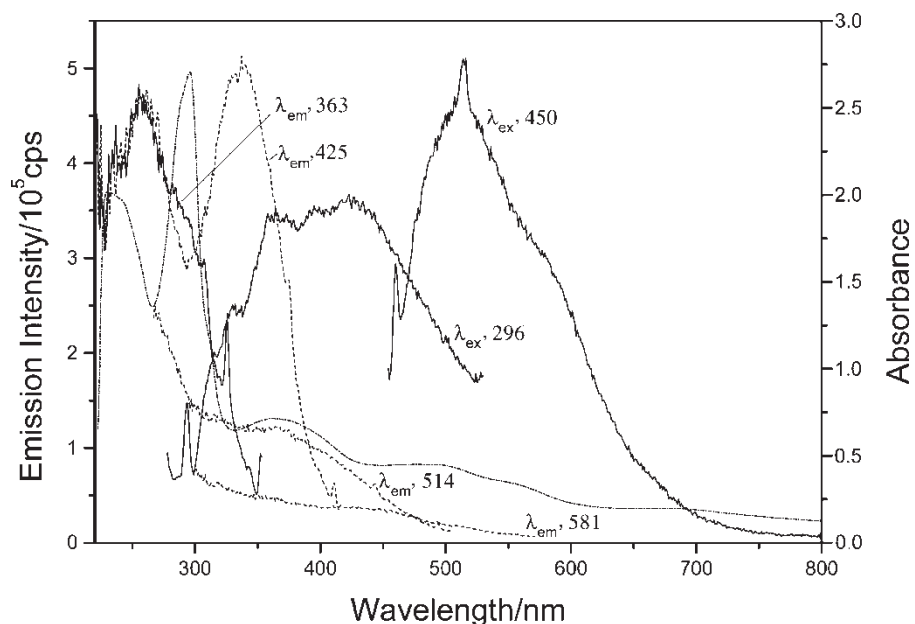


FIGURE 2 Fluorescence emission spectra (—), excitation spectra (---) at different wavelength and electronic absorption spectra (-.-) of complex **5** in  $\text{CH}_2\text{Cl}_2$ .

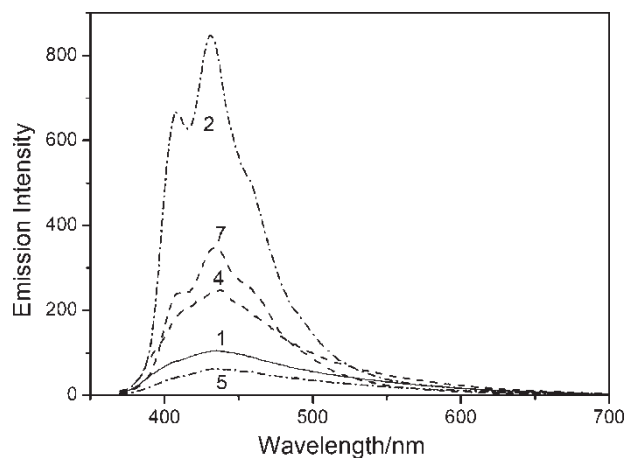


FIGURE 3 Fluorescence emission spectra of  $1.1 \times 10^{-5}$  M solutions of complexes 1, 2, 4, 5 and 7 in dichloromethane.

energy transfer from the LMCT absorption states of the peripheral Ru(II) units to the [Mn(OBTTAP)] core. The opposite trend in the pentanuclear complexes 5 and 6 might be due to steric crowding and consequent deformation of the TAP core.

### Cyclic Voltammetry

The cyclic voltammetry experiments were carried out at room temperature under nitrogen atmosphere in dry acetonitrile and the data are summarized in Table II. The precursor complex, 1 exhibited a low lying reversible oxidation wave at  $E_{1/2}$   $-0.33$  V vs Ag/AgCl. This wave seems to arise from  $Mn^{2+}/Mn^{3+}$  process as similar oxidation wave was neither observed in the metal-free OBTTAP- $H_2$ , nor in [Mg(OBTTAP)] (39,40) under identical conditions. The complex 1, in the oxidative scan exhibits little electrode activity between 0.0 and 2.0 V, particularly for the OBTTAP centered oxidations. However, upon binding of the  $(bpy)_2Ru^{II}$ ,  $(phen)_2Ru^{II}$  and  $Cp(PPh_3)Ru^{II}$  units to the [Mn(OBTTAP)] in complexes 2–7 two or more prominent, additional oxidation waves appeared at  $E_{1/2}$  0.50, 1.04 and 1.32 (i.r) V vs Ag/AgCl in 2, 0.49, 0.81, 1.02 and 1.46 (i.r) V in 5, 0.40, 0.91 V in 3, 0.38, 0.92, V in 6, 0.64, 0.96 (i.r.) V in 4 and 0.63, 0.98 (i.r.) V in 7. The representative voltammograms of complexes 2 and 5 are shown in Fig. 4. It could be seen that upon binding of one  $(bpy)_2Ru^{II}$  unit in complex 2, the electrode activity of the complex for the oxidative scan improved significantly, exhibiting two oxidation waves at  $E_{1/2}$  0.50 and 1.04 V vs. Ag/AgCl. Since there are two oxidizable centers, viz the OBTTAP and the peripheral Ru(II), the former could be attributed to the Ru(II)/Ru(III) process, while the latter to OBTTAP/OBTTAP $^{2+}$ . In the pentanuclear complex, 5 the first oxidation appeared at the same position as in 2, but the second wave is split into two waves (having equal peak currents), as expected for the two successive one

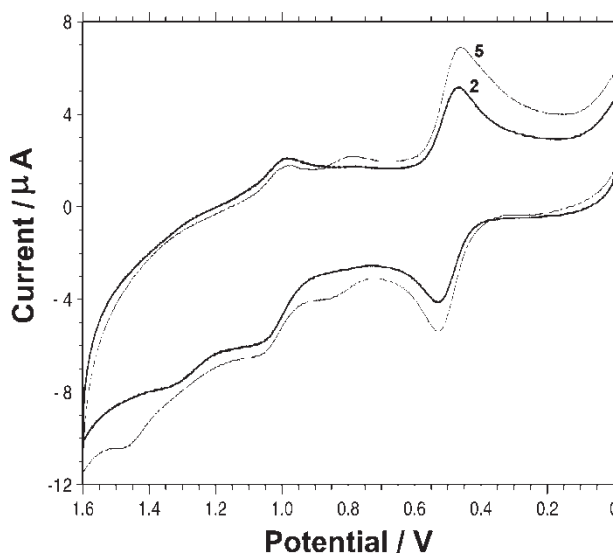


FIGURE 4 Cyclic voltammograms of complexes 2 and 5 in acetonitrile in presence of 0.1 M TEAP as supporting electrolyte at glassy carbon electrode (scan rate  $200 \text{ mV s}^{-1}$ ).

electron oxidations of the OBTTAP core (41–45). Hence, the second wave in complex 2, which had comparatively larger peak current value and was observed at higher  $E_{1/2}$ , could be attributed to the two electron oxidation of the OBTTAP. The voltammograms are not simple composites of the constituent units and suggest significant mutual electronic influence over each other. The Ru(II)/Ru(III) process is being observed at significantly lower potential than that in  $[(bpy)_2Ru(S_2Bn_2C_2(CN)_2)]^{2+}$  ( $E_{1/2}$ , 1.01 V), suggesting much lower stabilization of metal  $d\pi$  orbitals. Also the redox behaviour of the OBTTAP was changed upon binding of one or four peripheral Ru(II) units. The behaviour of  $(phen)_2Ru^{II}$  linked complexes 3

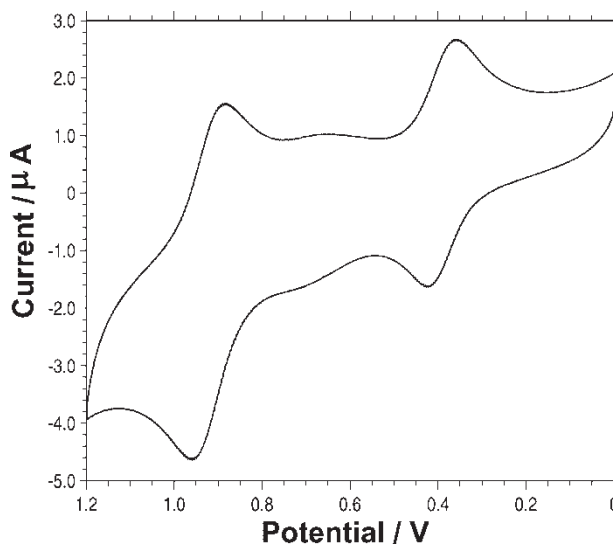


FIGURE 5 Cyclic voltammogram of complex 6 in acetonitrile in presence of 0.1 M TEAP as supporting electrolyte at glassy carbon electrode (scan rate  $200 \text{ mV s}^{-1}$ ).

and **6** is similar (Fig. 5). In case of complexes **4** and **7** having Cp(PPh<sub>3</sub>)Ru<sup>II</sup> moiety only one reversible oxidation wave was observed between 0 and 2.0 V due to Ru(II)/Ru(III) process. In the cathodic sweep they also exhibited an additional irreversible wave due to the Ru(II)/Ru(I) process occurring at the peripheral Cp(PPh<sub>3</sub>)Ru<sup>II</sup> unit. The OBTTAP centered oxidations are distinctly observed only when the (bpy)<sub>2</sub>Ru<sup>II</sup> or (phen)<sub>2</sub>Ru<sup>II</sup> units are bonded to them. This is probably due to the fact that (bpy)<sub>2</sub>Ru<sup>II</sup> units provide effective electron transfer channel to the OBTTAP core which is otherwise shielded by the SCH<sub>2</sub>Ph groups.

## EXPERIMENTAL SECTION

All common chemicals were of AR grade and were used as received unless otherwise mentioned. Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, RuCl<sub>3</sub>·H<sub>2</sub>O, 2,2'-bipyridine, 1,10-phananthroline and LiCl used, were obtained from Loba Chemie, India. Tetraethyl ammonium perchlorate, (TEAP) used in CV studies was obtained from Fluka. Spectroscopic grade CH<sub>2</sub>Cl<sub>2</sub> was used for electronic spectral and fluorescence studies. Dry benzene and acetonitrile were used for cyclic voltammetry studies. Benzene was dried over sodium, and the acetonitrile was dried by passing through activated neutral alumina (preheated at 450 °C for 24 h). All syntheses were carried out under nitrogen atmosphere. The precursors [Mn(OBTTAP)] **1**, [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O, [Ru(phen)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O and [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl] were synthesized by the literature methods [29,46,47].

IR spectra were recorded on a Perkin Elmer-1600 FTIR spectrophotometer or Thermo Nicolet-Nexus, with KBr pellets, electronic spectra on a Shimadzu-1601 spectrophotometer, in CH<sub>2</sub>Cl<sub>2</sub> solutions and fluorescence excitation and emission spectra were recorded on a Perkin Elmer LS 50B spectrofluorimeter, in deaerated dichloromethane solutions. <sup>1</sup>H NMR spectra were recorded on a Bruker DRX-300 FTNMR spectrometer in acetone-d<sub>6</sub> solutions. The ESI mass spectra were recorded on a Micromass

Quattro II spectrometer using methanolic solutions of the complexes. MALDI-TOF mass spectra were recorded on a Micromass TofSpec 3E, in 3,5-dihydroxybenzoic acid matrix dissolved in acetonitrile (AN). Voltammetry studies were carried out on a CHI 600A voltammetric analyzer instrument using three-electrode assembly. 0.1 M TEAP was used as supporting electrolyte. All voltammetric measurements were made in the degassed solutions under nitrogen atmosphere. Platinum working microelectrode (0.2 mm dia.), platinum wire auxiliary electrode and Ag/AgCl reference electrodes were used. C, H, N analyses were carried out on a Elementar Vario EL III autoanalyser (Table IV).

### Synthesis of [Mn(OBTTAP)Ru(bpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>, **2**

The [Mn(OBTTAP)] (0.067 g, 0.05 mmol) and [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O (0.026 g, 0.05 mmol) were taken in 30 mL methanol-benzene (2:1 v/v) mixture. The suspension was stirred for 10 h at room temperature followed by heating at reflux for 5 h under nitrogen atmosphere. The resultant solution was filtered and its volume was reduced to ca. 1 mL by evaporation under reduced pressure. Addition of a few drops of concentrated methanolic solution of NH<sub>4</sub>PF<sub>6</sub> to this solution precipitated out the cationic salt **2**. It was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether and was purified by passage through a neutral alumina column (15 × 2.5 cm) eluting with CH<sub>2</sub>Cl<sub>2</sub>-C<sub>6</sub>H<sub>6</sub> (2:1 v/v) mixture. The initial minor green band was discarded and a second major band was collected. Solvent was removed at reduced pressure and the residue was finally recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether. Solid compound was dried over CaCl<sub>2</sub> under vacuum. Yield 0.057 g (ca. 55%).

### Synthesis of [Mn(OBTTAP)Ru(phen)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>, **3**

The [Mn(OBTTAP)] (0.067 g, 0.05 mmol) and [Ru(phen)<sub>2</sub>Cl<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O (0.027 g, 0.05 mmol) were

TABLE IV Elemental analyses data

Compound	Analyses, Found (Calcd.)				
	C%	H%	N%	S%	Mn%
<b>1</b>	65.5 (64.3)	4.9 (4.2)	7.8 (8.3)	19.5 (19.1)	4.6 (4.1)
<b>2</b>	54.2 (53.9)	3.6 (3.5)	8.0 (8.2)	11.8 (12.5)	2.4(2.6)
<b>3</b>	56.5 (55.0)	4.2 (3.5)	8.4 (8.0)	11.5 (12.2)	2.2 (2.6)
<b>4</b>	62.2 (59.7)	4.4 (4.0)	5.4 (5.8)	12.8 (13.4)	2.7 (2.9)
<b>5</b>	44.8 (43.9)	3.5 (2.9)	8.4 (8.1)	6.3 (6.2)	1.1 (1.3)
<b>6</b>	45.0 (46.4)	2.9 (2.8)	8.0 (7.7)	5.5 (5.9)	1.2 (1.3)
<b>7</b>	54.8 (54.1)	4.3 (3.7)	3.4 (3.1)	6.8 (7.0)	1.4 (1.5)



reacted in 30 mL methanol–benzene (2:1 v/v) mixture as described for **2** to obtain 0.060 g (ca. 57%) of **3**.

#### Synthesis of [Mn(OBTTAP)CpRu(PPh<sub>3</sub>)] [PF<sub>6</sub>]<sub>4</sub>, **4**

The [Mn(OBTTAP)] (0.067 g, 0.05 mmol) and [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl] (0.037 g, 0.05 mmol) were reacted in 30 mL methanol–benzene (2:1 v/v) mixture as described for **2**. The solution was stirred for 10 h at room temperature followed by heating at reflux for 5 h and was processed as described above. Yield 0.063 g (ca. 65%).

#### Synthesis of [Mn(OBTTAP){Ru(bpy)<sub>2</sub>Cl<sub>2</sub>}]<sub>2</sub> [PF<sub>6</sub>]<sub>8</sub>, **5**

The [Mn(OBTTAP)] (0.067 g, 0.05 mmol) and [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (0.125 g, 0.24 mmol) were reacted in methanol–benzene (1:1 v/v) (40 mL) mixture. The resulting suspension was stirred for 10 h at room temperature followed by heating at reflux for 10 h under nitrogen atmosphere. It formed a red solution, which was filtered and volume was reduced to ca. 1 mL by evaporation under reduced pressure. Addition of a few drops of concentrated methanolic NH<sub>4</sub>PF<sub>6</sub> to this solution precipitated out the cationic salt **5**. It was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether and purified by passage through a (15 × 2.5 cm) neutral alumina column eluting with CH<sub>2</sub>Cl<sub>2</sub>–C<sub>6</sub>H<sub>6</sub> (2:1 v/v) mixture. The initial minor green band was discarded and second major band was collected, solvent was removed at reduced pressure and the residue was finally recrystallized from CH<sub>2</sub>Cl<sub>2</sub> petroleum ether mixture. Solid compound was dried over CaCl<sub>2</sub> under vacuum. Yield 0.148 g (ca. 72%).

#### Synthesis of [Mn(OBTTAP){Ru(phen)<sub>2</sub>Cl<sub>2</sub>}]<sub>2</sub> [PF<sub>6</sub>]<sub>8</sub>, **6**

The [Mn(OBTTAP)] (0.067 g, 0.05 mmol) and [Ru(phen)<sub>2</sub>Cl<sub>2</sub>]·2H<sub>2</sub>O (0.130 g, 0.24 mmol) were reacted in methanol–benzene (1:1 v/v) (40 mL) mixture as for complex **5** to obtain 0.175 g (ca. 80%) of **6**.

#### Synthesis of [Mn(OBTTAP){CpRu(PPh<sub>3</sub>)<sub>4</sub>}] [PF<sub>6</sub>]<sub>4</sub>, **7**

The [Mn(OBTTAP)] (0.067 g, 0.05 mmol) and [CpRu(PPh<sub>3</sub>)<sub>2</sub>Cl] (0.178 g, 0.24 mmol) were reacted in methanol–benzene (1:1 v/v) (40 mL) mixture as for complex **5** to obtain 0.135 g (ca. 75%) of **7**.

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