

Photoinduced Electron Transfer Reactions between Ruthenium(II) Polypyridyl Complexes and Aromatic Thiolate Ions in Micellar Medium

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ABSTRACT: *The present work represents an attempt to prepare five ruthenium(II) or Ru(II) polypyridyl complexes (1a–1e) by a one-pot solvothermal synthesis in a manner that is greener than that in which the complexes are conventionally synthesised. Here, target compounds in very good yields have been achieved. The photochemical reduction of five different $^*[\text{Ru}(\text{NN})_3]^{2+}$ (triplet excited) species (where NN (a–e) = 2,2'-bipyridine, 4,4'-dimethyl-2,2'-bipyridine, 4,4'-di-tert-butyl-2,2'-bipyridine, 1,10-phenanthroline and 4,7-diphenyl-1,10-phenanthroline) with various aromatic thiolate anions (ArS^-) with different electronic and steric properties was studied in aqueous and anionic micellar (sodium dodecyl sulphate, SDS) solutions by the luminescence-quenching technique. The quenching rate constants, k_q , for each photoredox reaction were determined by Stern-Volmer analysis. The results exhibit an interesting trend for all the quenchers depending on the type of quencher and medium used. Although the incremental increase in the SDS concentration initially hampered the rate, further increasing SDS did not alter the quenching rate. In very few cases, micellar catalysis was observed, which may be attributed to the hydrophobic interaction that overcomes the electrostatic repulsion.*

Keywords: One-pot synthesis, fluorescence-quenching studies, micellar catalysis, Stern-Volmer analysis, aromatic thiolate anions

1. INTRODUCTION

Thiols play a key role in biological systems and are found in numerous peptides, proteins and low-molecular-weight compounds.^{1,2} Generally, alternation in the level of cellular thiols has been linked to a number of diseases, such as leucocyte loss, psoriasis, liver damage, cancer, AIDS,^{3,4} slow growth in children, hair depigmentation, oedema, lethargy, liver damage, loss of muscle and fat, skin lesions, weakness,⁵ Alzheimer's disease, vitamin B₁₂ deficiency^{6,7} and cardiovascular diseases (CVDs).⁸ On the other hand, thiols can be used as optical

probes and in the realms of cell imaging, redox and ligand exchange reactions and nanochemistry, etc. Additionally, the photophysics and photochemistry of thiols are of great interest in various fields of science and technology^{9,10} because of thiols' low ionisation potential and relatively weak S–H bond, and their role in radical repair and deactivation as well as in cellular redox processes.^{11,12} Thiols are often believed to act as protectors against ionising radiation via their radical scavenging activity. Thiyl radicals also cause biologically important chemical changes, such as the efficient cis-trans isomerisation of mono- and polyunsaturated fatty acid residues in model membranes via a catalytic action.^{13,14} Furthermore, these free radicals contribute to more than one hundred disorders in humans, including atherosclerosis, arthritis, ischaemia and reperfusion, the injury of many tissues, central nervous system injury and gastritis.¹⁵

Ruthenium(II) or Ru(II) complexes based on bipyridine ligands are highly interesting due to their photophysical and redox properties.¹⁶ The Ru(II) ion offers a series of advantages: (a) due to the ion's octahedral complex geometry, specific ligands can be introduced in a controlled manner; (b) the photophysical, photochemical and the electrochemical properties of these complexes can be tuned in a predictable way; and (c) the ruthenium metal ion possesses stable and accessible oxidation states ranging from Ru(I) to Ru(III). Ru(II) forms kinetically stable bonds with bipyridine, making the synthesis of heteroleptic compounds possible.

The rate of electron transfer (ET) from a donor to an acceptor molecule is influenced by exothermicity, reorganisation energy and distance.^{17–20} Over the past three decades, numerous theoretical and experimental studies have been directed towards understanding the abovementioned factors that affect the rate of photoinduced ET reactions of Ru(II) complexes.^{21–27} To a large extent, the ligands of Ru(NN) (NN being the polypyridine ligand) and the type of quencher determine the distance over which ET occurs.^{28–30} The distance dependence of ET has become increasingly important as attempts have been made to unravel the complexities of ET reactions in biological systems and in natural and synthetic solar energy conversion systems.^{31,32}

The photophysics and photochemistry of Ru(II) polypyridyl complexes are highly affected by the solvent used as well as the change in medium from homogeneous to microheterogeneous.^{33,35} Dressick et al.³⁴ performed a systematic investigation of the binding, partitioning and photosensitisation of these Ru(II) complexes in both ionic and nonionic surfactant media. The main aim of studying the photoredox reactions of Ru(II) polypyridyl complexes in microheterogeneous media is to develop photocatalytic systems, including those for solar energy conversion, by controlling the thermal back ET.^{31,32} Ionic Ru(II) polypyridyl complexes can be designed with hydrophobic ligands and thus

provide an opportunity for binding to crucial interfacial regions in microheterogeneous systems. Aqueous micelle-bound catalytic systems of this type are attractive alternatives to toxic, expensive organic solvents and are precursors to future designs of surfactant assemblies that may mimic redox events in biological membranes. Again, a major focus emerging with respect to this self-assembly of monomeric units has been the observation of modified reactivity or properties of "guests" entrapped within or associated with these microphases. Furthermore, organised media such as micelles are well documented as novel environments for photochemical conversion because micellar systems can promote ET from electron donor to acceptor by concentrating them. In addition to the abovementioned advantages, micelles affect the lifetimes of photoexcited states and the efficiency of reverse ET by providing an appropriate microenvironment composed of a hydrophobic core, an aqueous phase and a charged interface.³³

Reports on greener solvothermal one-pot synthesis and fluorescence-quenching studies of different metal complexes with various biologically important quenchers have already been published by our research group.^{36–41} To explore the key role of the electronic, steric as well as hydrophobic properties of acceptors (1a–1e) on the electron transfer reactions between donors (ArS^-) and acceptors in the micellar medium, in the present study we examined five Ru(II) complexes with ligands of varying hydrophobicity. The oppositely charged nature of the probes (positive) and the environments (negative anionic surfactant, sodium dodecyl sulphate, SDS) ensure strong electrostatic attractive forces that will assist in binding.

In the case of Ru(II) complexes containing hydrophobic ligands, binding with micelles is favoured by hydrophobic forces.⁴² Although the negatively charged thiolate ions chosen in the present study as quenchers may face Coulombic repulsion from the anionic surfactant, the repulsive forces can be circumvented to some extent by introducing hydrophobic alkyl groups into the thiolate ion. Thus the study of the photoredox reactions of Ru(II) polypyridyl complexes with alkyl-substituted thiolate ions in ionic surfactants may be interesting, and both electrostatic and hydrophobic interactions will play an important role in these reactions.¹⁷ The results obtained for the photoinduced ET reactions of $[\text{Ru}(\text{NN})_3]^{2+}$ with ArS^- in the presence of SDS have been analysed in this report.

2. EXPERIMENTAL

All chemicals, i.e., 2,2'-bipyridine (bpy), 4,4'-dimethyl-2,2'-bipyridine (dmbpy), 4,4'-di-*tert*-butyl-2,2'-bipyridine (dtbpy), 1,10-phenanthroline (phen),

4,7-diphenyl-1,10-phenanthroline (dpphen), and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Sigma Aldrich and used as received. The thiols used in this study were obtained from Fluka and Sigma Aldrich. Solvents were dried over appropriate drying agents, distilled and stored under dry nitrogen.

Absorption spectra were recorded using a JASCO V-530 UV-visible Spectrophotometer. Emission spectra were recorded using a JASCO FP-6200 Spectrofluorimeter. All sample solutions used for the emission measurements were deaerated for approximately 30 min by dry N_2 purging by keeping the solution in cold water to ensure that there was no change in the volume of the solution. All measurements were performed at room temperature. Both absorption and emission titrations were carried out by keeping the concentration of the complexes constant (1×10^{-5} M) while varying the concentration of the thiols. Distilled/recrystallised samples of the thiols were dissolved in sodium hydroxide solution such that the pH was maintained at 12.5 in all cases.

The one-pot synthetic pathway for the formation of Ru(II) polypyridyl complexes (1a–1e) is shown in Figure 1. A suspension containing a mixture of 0.261 g $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1.0 mmol) and α -diimine (3.2 mmol) in 10 ml of ethanol in a 15 ml Teflon flask was placed in a steel bomb. The bomb was placed in an oven maintained at 160°C for 48 h and then cooled to 30°C . Good-quality, red-orange-coloured crystals were separated by filtration and washed with hexane. Yield was 82%–86%. The ^1H NMR spectra of the five Ru(II) complexes (1a–1e) show good agreement with the previously published data.¹⁷

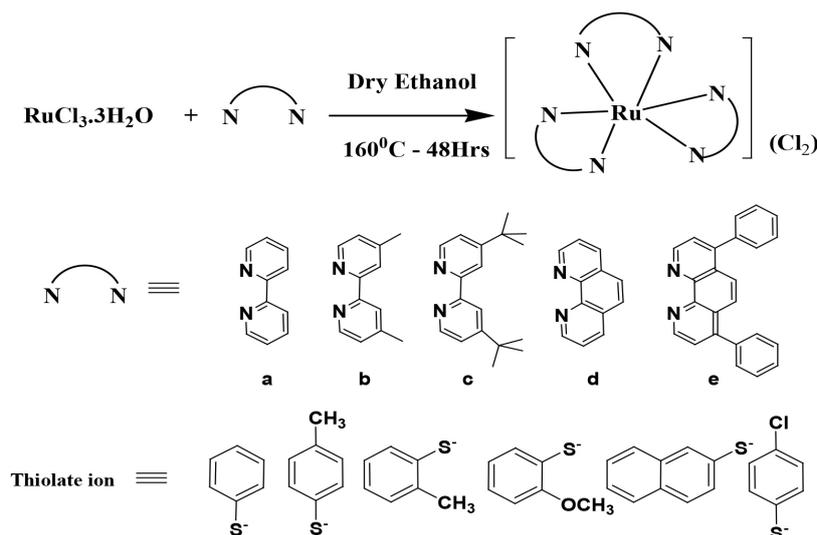


Figure 1: Formation of Ru(II) polypyridyl complexes.

3. RESULTS AND DISCUSSION

It has been established that the introduction of microheterogeneous system stabilises the emitting $^3\text{MLCT}$ states of Ru(II) polypyridyl complexes relative to the d-d state. To confirm this finding, the authors recorded both the absorption and the emission spectra of five Ru(II) complexes (1a–1e) in a water-acetonitrile mixture (Figure 2 and 3); the spectral data are shown in Table 1. It is interesting that there is a considerable red shift toward higher wavelengths (bathochromic shift) in $\lambda_{\text{max}}^{\text{em}}$ in the presence of SDS compared with the position of $\lambda_{\text{max}}^{\text{em}}$ in the absence of SDS with 1a, which is also indicated in Figure 3 and Table 1. This experimental observation clearly proves the earlier predictions that micelles lower the energy level of $^3\text{MLCT}$ states, thereby stabilising them relative to the d-d state.

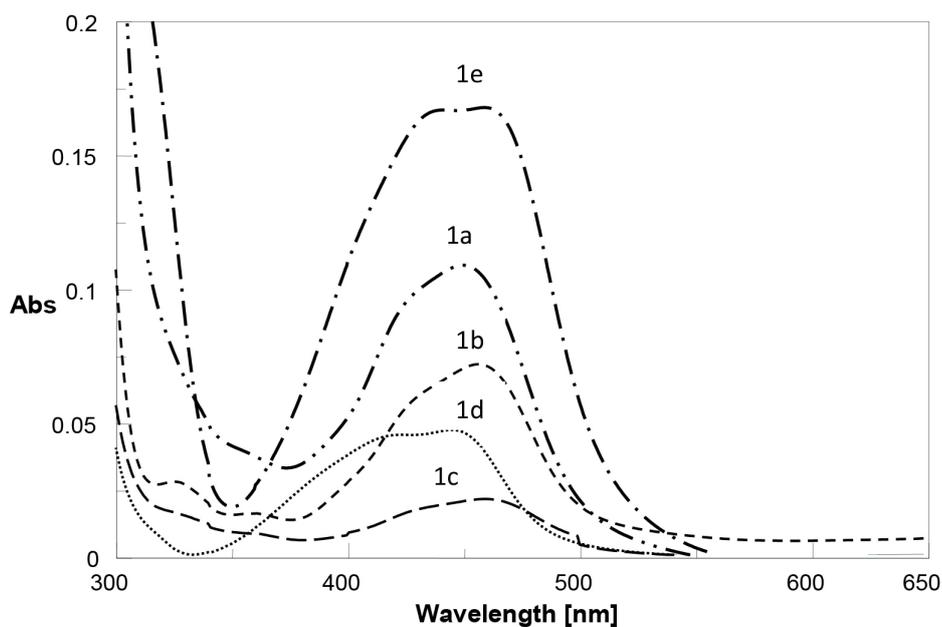


Figure 2: Overlay absorption spectrum of complexes (1a–1e) in water-acetonitrile (9:1 v/v) at 298K.

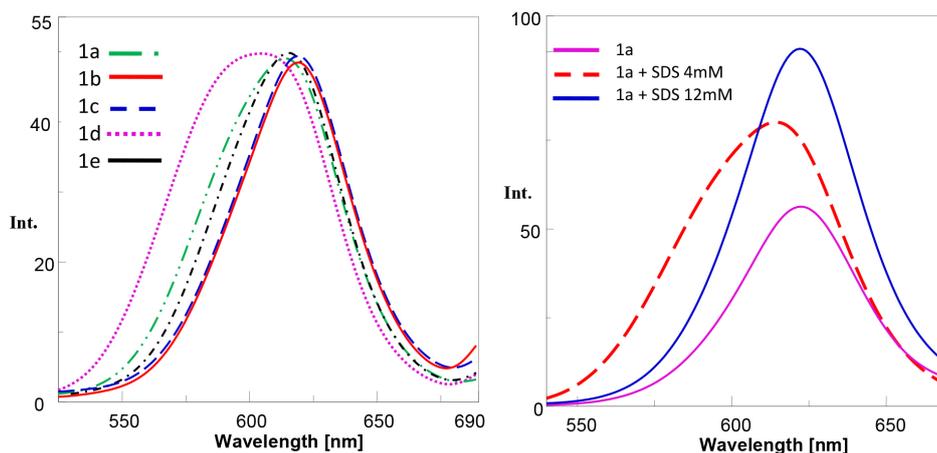


Figure 3: Overlay emission spectrum of complexes (1a–1e) (left); emission spectrum of 1a in the absence and in the presence of SDS (right) in water-acetonitrile (9:1 v/v) at 298K.

Table 1: Photophysical analytical data for complexes (1a–1e) at 298K.

Complexes	$[\text{Ru}(\text{NN})_3]^{2+}$	Absorption ^a $\lambda_{\text{max}}^{(\text{nm})}$	Emission ^a		Emission ^b	
			$\lambda_{\text{em}}^{(\text{nm})}$	$^*\tau$ (ns)	$\lambda_{\text{em}}^{(\text{nm})}$	$^*\tau$ (ns)
1a	$[\text{Ru}(\text{bpy})_3]^{2+}$	450	614	560	622	800
1b	$[\text{Ru}(\text{dmbpy})_3]^{2+}$	460	619	330	628	610
1c	$[\text{Ru}(\text{dtbpy})_3]^{2+}$	456	620	410	626	780
1d	$[\text{Ru}(\text{phen})_3]^{2+}$	447	604	960	613	1810
1e	$[\text{Ru}(\text{dpphen})_3]^{2+}$	460	615	4680	623	3960

^{*} τ = taken from the published report ⁴¹

^a recorded in water: CH_3CN (9:1 v/v)

^b recorded in water in the presence of 30 mM SDS

To study the quenching of these complexes by various thiophenolate ions, fluorescence-quenching titrations were carried out by converting the thiophenols to thiophenolate ions with sodium hydroxide and maintaining the pH at 12.5. The change in the luminescence intensity for the excited state of complexes 1a and 1e with 2-methoxythiophenolate in the absence and in the presence of SDS is shown in Figure 5, and change in the absorption is shown in Figure 4. The quenching rate constant, k_q , values were determined from the Stern-Volmer equation.^{35,36,41}

$$F_0/F = 1 + K_{\text{SV}} [\text{Q}] = 1 + k_q \tau_0 [\text{Q}]$$

where F_0 and F are the steady-state fluorescence intensities in the absence and presence of a quencher, respectively, K_{SV} is the Stern-Volmer quenching constant, $[Q]$ is the total concentration of quencher, k_q is the bimolecular quenching constant, and τ_0 is the average lifetime of the complex in the absence of a quencher. The corresponding Stern-Volmer quenching rate constants k_q are presented in Tables 2–5. All the Stern-Volmer plots represent a good linear relationship (Figure 6). As is known, linear Stern-Volmer plots represent a single quenching mechanism, either static or dynamic. It has also been proposed that in the case of non-linear Stern-Volmer plots, in addition to dynamic quenching, a second mechanism, static quenching, also prevails.⁴¹

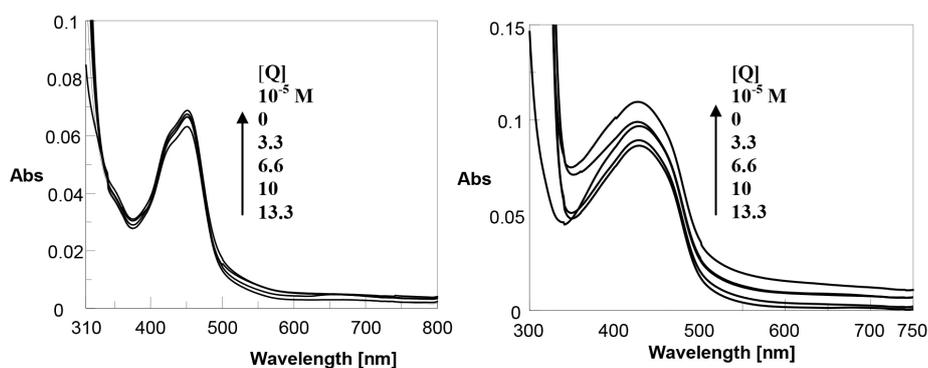


Figure 4: Overlay absorption spectrum of 1a (1×10^{-5} M) with different concentration of thiophenolate ion (left); and 1d with different concentration of 2-methylthiophenolate ion (right) (0 to 13.3×10^{-5} M) in water: acetonitrile (9:1 v/v) at 298K.

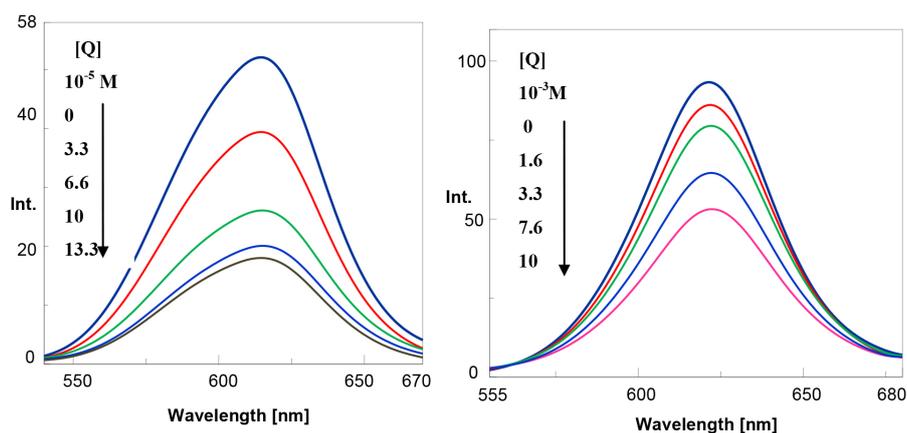


Figure 5: Emission spectral changes of 1a (top), 1e (bottom) with 2-methoxythiophenolate in the absence of SDS (left); and in the presence of 30 mM of SDS (right) in water:acetonitrile (9:1 v/v) at 298K.

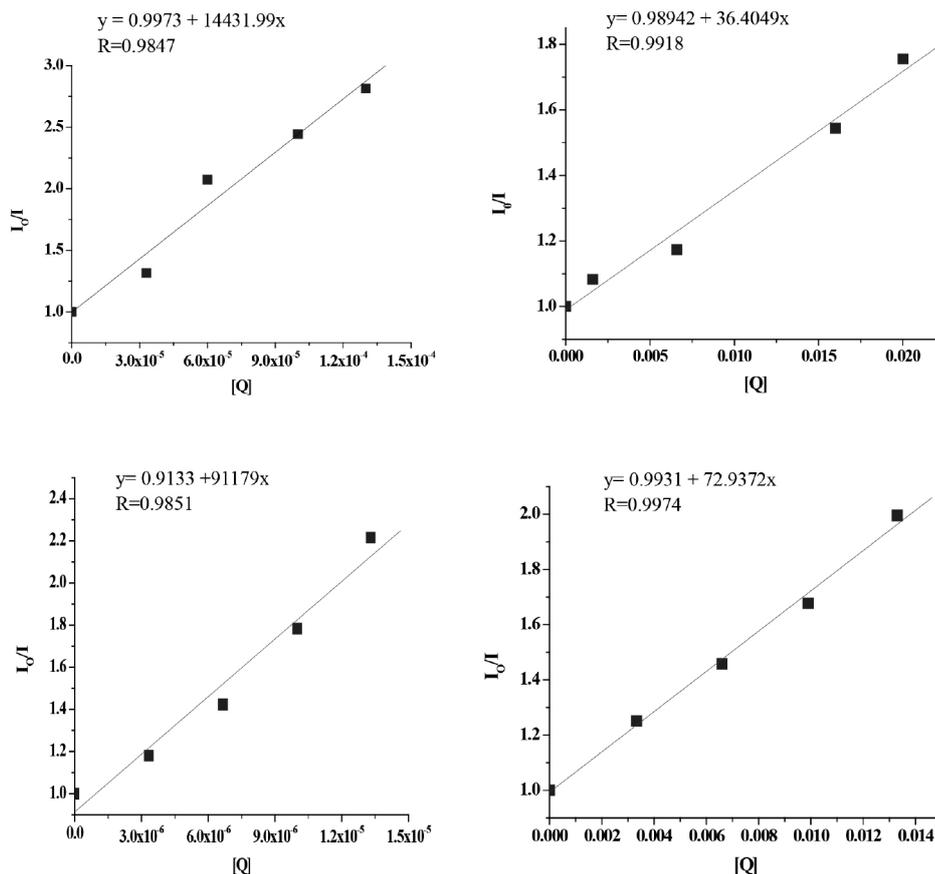


Figure 6: Stern-Volmer plot for quenching of complexes 1a (top) and 1e (bottom) with 2-methoxythiophenolate ion at 298K in the absence of SDS (left) and in the presence of 30 mM of SDS (right) in water:acetonitrile (9:1 v/v) at 298K.

The quenching rate constants for the excited state electron transfer reactions of $[\text{Ru}(\text{bpy})_3]^{2+}$ with various thiolate ions in different SDS concentrations exhibited a similar trend: an initial decrease in the rate constant by one order of magnitude in going from an aqueous to an anionic micellar medium. This trend is expected as the quenching rate constant will decrease in the anionic micellar medium because the negatively charged quencher will approach the micelle-bound dipositive Ru(II) complex due to the negative charge of the anionic micelle. In general, further increasing the concentration of SDS did not cause the rate constant to vary appreciably. At very high concentrations of SDS, k_q was greatly reduced by approximately two orders of magnitude in certain cases (such as for thiophenolate, 2-naphthalene thiophenolate) (Table 2). The electron-donating nature of the 2-methoxy thiophenolate ion caused an enormous decrease

in the rate constant due to the additional stabilisation of the thiophenolate ion by the accumulation of negative charge on it, thereby increasing the electrostatic repulsion between the quencher and the anionic micellar medium. Thus, the system exhibited rate retardation.

Table 2: Quenching rate constants k_q ($M^{-1} s^{-1}$) for the reaction of $*[Ru(bpy)_3]^{2+}$ with thiolate ions in different SDS concentration in in water:acetonitrile (9:1 v/v) at 298K.

SDS conc.	$k_q (M^{-1} s^{-1})$					
	A	B	C	D	E	F
0	8.4×10^9	1.6×10^9	5.8×10^9	2.6×10^{10}	8.6×10^9	2.3×10^9
4	1.3×10^8	4.8×10^8	1.6×10^8	1.9×10^8	3.9×10^8	1.3×10^8
8	1.5×10^8	1.2×10^8	5.6×10^8	7.5×10^7	2.7×10^8	2.6×10^8
12	1.6×10^8	1.4×10^8	6.0×10^8	5.5×10^7	2.8×10^8	1.6×10^8
20	1.7×10^8	1.5×10^8	3.8×10^8	4.0×10^7	1.4×10^8	1.8×10^8
30	1.7×10^8	1.3×10^8	3.7×10^8	4.5×10^7	1.1×10^8	1.9×10^8
40	5.7×10^7	1.2×10^8	5.2×10^8	4.8×10^7	5.8×10^7	1.7×10^8

Note: SDS conc. = SDS concentration (mM), A = thiophenol, B = 2-methylthiophenol, C = 4-methylthiophenol, D = 2-methoxythiophenol, E = 2-naphthalene thiol and F = 4-chlorothiophenol.

In the case of 2-methoxythiophenoate, 2-methylthiophenolate and 2-naphthalene-thiophenoate ions, the quenching rate constants with respect to $[Ru(dmbpy)_3]^{2+}$ exhibited the expected trend (Table 3). The k_q values were much lower with most of the quenchers in this system. This trend was expected based on the increase in the electron transfer distance; indeed, quenching rate constants exhibit a direct correlation with electron transfer distance (Table 4).

Table 3: Quenching rate constants k_q ($M^{-1} s^{-1}$) for the reaction of $*[Ru(dmbpy)_3]^{2+}$ with thiolate ions in various SDS concentration in water:acetonitrile (9:1 v/v) at 298K.

SDS conc.	k_q ($M^{-1} s^{-1}$)					
	A	B	C	D	E	F
0	7.5×10^8	1.3×10^9	2.0×10^8	1.4×10^9	3.2×10^9	1.8×10^8
4	1.5×10^8	3.6×10^7	1.6×10^8	1.0×10^8	1.9×10^8	9.2×10^7
8	7.9×10^7	5.6×10^7	3.7×10^8	8.7×10^7	1.8×10^8	1.3×10^8
12	2.3×10^8	5.7×10^7	2.2×10^8	8.6×10^7	1.4×10^8	1.5×10^8
20	1.1×10^8	4.9×10^7	2.6×10^8	6.6×10^7	7.5×10^8	1.6×10^8
30	1.1×10^8	6.5×10^7	2.6×10^8	8.9×10^7	7.0×10^8	1.8×10^8
40	1.6×10^8	5.2×10^7	3.0×10^8	8.6×10^7	2.0×10^9	1.1×10^8

Note: SDS conc. = SDS concentration (mM), A = thiophenol, B = 2-methylthiophenol, C = 4-methylthiophenol, D = 2-methoxythiophenol, E = 2-naphthalene thiol and F = 4-chlorothiophenol.

Table 4: Quenching rate constants k_q ($M^{-1} s^{-1}$) for the reaction of $*[Ru(dtbp)_3]^{2+}$ with thiolate ions in various SDS concentration in water:acetonitrile (9:1 v/v) at 298K.

SDS conc.	k_q ($M^{-1} s^{-1}$)					
	A	B	C	D	E	F
0	6.6×10^8	4.6×10^9	9.5×10^8	1.6×10^8	3.9×10^9	5.8×10^8
4	4.6×10^7	2.2×10^7	8.2×10^7	4.1×10^7	1.9×10^8	6.6×10^7
8	3.9×10^7	2.6×10^7	6.6×10^7	5.1×10^7	2.2×10^8	8.9×10^7
12	3.9×10^7	3.2×10^7	7.1×10^7	4.6×10^7	1.9×10^8	1.1×10^8
20	3.4×10^7	1.9×10^7	5.3×10^7	4.8×10^7	2.9×10^8	9.4×10^7
30	5.1×10^7	1.2×10^7	5.8×10^7	6.2×10^7	2.6×10^8	9.3×10^7
40	4.3×10^7	2.6×10^7	6.4×10^7	7.2×10^7	2.4×10^8	1.0×10^8

Note: SDS conc. = SDS concentration (mM), A = thiophenol, B = 2-methylthiophenol, C = 4-methylthiophenol, D = 2-methoxythiophenol, E = 2-naphthalene thiol and F = 4-chlorothiophenol.

Slight micellar catalysis occurred after the initial rate retardation with 2-methoxy and 4-chloro substituted thiophenolate ions. A novel observation was made with respect to the $[Ru(phen)_3]^{2+}$ complex (Table 5). We observed initial rate retardation up to the critical micellar concentration (SDS – cmc = 0.008 mole), followed by a gradual increase in the k_q values, thereby causing micellar

catalysis. This behaviour was pronounced for most of the quenchers used. Further studies are in progress to determine the possible reasons for this slight extent of micellar catalysis. The most probable reason may be that the pronounced hydrophobic nature of the phenanthroline ligand, along with the enhanced negative charge accumulation on the 2-methoxythiolate anion, causes the two oppositely charged species (complex and the quencher) to approach one another more closely, causing micellar catalysis. The enormous decrease in the k_q values in the case of $[\text{Ru}(\text{dpphen})_3]^{2+}$ with an increasing concentration of SDS was rather remarkable (Table 6). The pronounced decrease in the rate constant i.e., 2–3 orders of magnitude, with the increase in the concentration of SDS indicates that the anionic micelle was affected by almost all of the quenchers. Thus, electrostatic interaction plays a more significant role in this system than the richly hydrophobic ligands. Because most of the reaction takes place in aqueous medium, k_q exhibits a decreasing trend. The Ru(II) polypyridyl ions become attached to the Stern layer, leaving the dpphen ligand buried in the micellar phase. Because the anionic quenchers are unable to come into close proximity with the Ru^{2+} ions in the Stern layer, there is a decreasing trend in the quenching rate constant.

Table 5: Quenching rate constants k_q ($\text{M}^{-1} \text{s}^{-1}$) for the reaction of $[\text{Ru}(\text{phen})_3]^{2+}$ with thiolate ions in various SDS concentration in water:acetonitrile (9:1 v/v) at 298K.

SDS conc.	k_q ($\text{M}^{-1} \text{s}^{-1}$)					
	A	B	C	D	E	F
0	1.3×10^8	1.6×10^9	3.3×10^8	1.3×10^8	7.9×10^8	2.3×10^8
4	1.7×10^8	4.6×10^8	2.9×10^8	1.2×10^8	6.4×10^8	2.7×10^8
8	2.4×10^8	1.1×10^8	4.9×10^8	1.9×10^8	4.6×10^8	1.5×10^8
12	1.6×10^8	3.4×10^8	2.9×10^8	1.3×10^8	3.9×10^8	2.5×10^8
20	1.2×10^8	3.8×10^9	1.7×10^8	1.7×10^8	2.4×10^8	3.8×10^8
30	1.4×10^8	2.1×10^9	2.7×10^8	2.1×10^8	4.6×10^8	3.1×10^8
40	3.8×10^9	3.4×10^9	1.6×10^9	1.7×10^9	1.7×10^9	3.5×10^9

Note: SDS conc. = SDS concentration (mM), A = thiophenol, B = 2-methylthiophenol, C = 4-methylthiophenol, D = 2-methoxythiophenol, E = 2-napthalene thiol and F = 4-chlorothiophenol.

Table 6: Quenching rate constants k_q ($M^{-1} s^{-1}$) for the reaction of $[Ru(dpphen)_3]^{2+}$ with thiolate ions in various SDS concentration in water:acetonitrile (9:1 v/v) at 298K.

SDS conc.	k_q ($M^{-1} s^{-1}$)					
	A	B	C	D	E	F
0	6.8×10^9	1.2×10^{10}	1.7×10^{10}	1.9×10^{10}	7.9×10^9	2.4×10^9
4	2.8×10^7	1.3×10^7	1.2×10^8	1.2×10^7	2.9×10^8	5.8×10^7
8	2.2×10^7	1.0×10^7	3.1×10^7	8.9×10^7	2.4×10^8	5.8×10^7
12	3.9×10^7	5.6×10^7	1.6×10^7	1.4×10^7	2.6×10^8	5.4×10^7
20	2.2×10^7	1.2×10^7	3.0×10^7	1.5×10^7	4.5×10^8	7.0×10^7
30	5.2×10^7	3.9×10^7	1.6×10^7	1.8×10^7	2.5×10^8	6.9×10^7
40	4.4×10^7	8.8×10^7	2.8×10^7	2.3×10^7	1.5×10^8	1.52×10^8

Note: SDS conc. = SDS concentration (mM), A = thiophenol, B = 2-methylthiophenol, C = 4-methylthiophenol, D = 2-methoxythiophenol, E = 2-naphthalene thiol and F = 4-chlorothiophenol.

4. CONCLUSION

We prepared five Ru(II) polypyridyl complexes (1a–1e) using a new methodology, succeeding in achieving the target compounds in very good yields. Based on studies of the quenching of these complexes (1a–1e) by aromatic thiolate ions, we can conclude that, generally, an incremental increase in the SDS concentration does not alter the quenching rate after initial rate retardation. Electrostatic interaction plays a more significant role than the hydrophobic ligands in this system. In very few cases, micellar catalysis occurred, which may be attributed to hydrophobic interactions overcoming electrostatic repulsion. This behaviour was pronounced with the excited state electron transfer quenching of $[Ru(phen)_3]^{2+}$ with most of the quenchers used. Further studies are in progress to gain deeper insight into this micellar catalysis phenomenon.

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