Synthesis, characterization and electrochemistry of 4′-functionalized 2,2′:6′,2″-terpyridine ruthenium(II) complexes and their biological activity

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The synthesis and characterization of Ru(II) terpyridine complexes derived from 4′-functionalized 2,2′:6′,2″-terpyridine ligands by a multi step procedure have been described. The complexes are redox-active, showing both metal-centred (oxidation) and ligand-centred (reduction) processes. The antibacterial and antifungal activity of the synthesized ruthenium(II) complexes $[Ru(attpy)_2](PF_6)_2$ (attpy = 4′-(4-acryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine); $[Ru(mttpy)_2](PF_6)_2$ (mttpy = 4′-(4-methacryloyloxymethylphenyl)-2,2′:6′,2″- terpyridine); $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ (MeOPhttpy = 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine); and $[Ru(mttpy)(ttpy)](PF_6)_2$ (ttpy = 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine) were tested against four human pathogens (*Proteus vulgaris, Proteus mirabilis, Pseudomonas aeruginosa* and *Escherichia coli*) and five plant pathogens (*Curvularia lunata, Fusarium oxysporum, Fusarium udum, Macrophomina phaseolina* and *Rhizoctonia solani*) by the well diffusion method and MIC values of the complexes are reported. A biological study of the complexes indicated that the complexes $[Ru(mttpy)_2](PF_6)_2$ and $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ exhibit very good activity against most of the test pathogens and their activity is better than those of some of the commercially available antibiotics like tetracycline and the fungicide carbendazim.

Introduction

Many metal complexes have been shown to possess bioactivity and several drugs based on metal complexes have been developed. These include platinum, gold, ruthenium and bismuth compounds used in the treatment of certain types of cancer, arthritis and stomach ailments.[1,2] In clinical applications and biochemistry, functionalized terpyridines have found a wide range of potential uses, ranging from colorimetric metal determination to DNA binding agents and anti-tumor research.[3] Some of these metal complexes have been reported to be potential anticancer drugs.[4] There are three main properties that make ruthenium complexes well suited for medicinal applications: (i) the rate of ligand exchange, (ii) the range of accessible oxidation states and (iii) the ability of ruthenium to mimic iron in binding to certain biological molecules. There has been considerable interest in ruthenium complexes, in recent years, because of their redox stability, excited state reactivity and excited state lifetime.[5] Owing to the octahedral structure of Ru(II) and Ru(III) complexes as opposed to the square-planar geometry of Pt(II) systems, ruthenium antitumor complexes exhibit a behavior different from cisplatin, which appears to bind DNA by cross-linking guanine, thereby causing a class of DNA-binding proteins to adhere to the site.[6–8] The useful incorporation of terpyridine complexes into an oligonucleotide probe containing a terpyridine attached to a serinol, which can also act as a building block in DNA sequencing, was designed in order to target a 159mer fragment of the HIV gag gene messenger RNA.[9] Another approach in combining biochemistry with terpyridine supramolecular chemistry is the coupling of biotin to a 4′-aminopyridine, applying the well-known isocyanate coupling reaction.[10] Biotin is known to bind strongly to the protein avidine *via* multiple hydrogen bonding with a geometry comparable to a "lock and key" system. Collectively these lend ruthenium complexes to redox activation and photodynamic approaches to therapy as well as the development of radiopharmaceuticals containing one of several radionuclides of ruthenium.[11,12] Ru(II) complexes are currently used as antileukaemic and antiviral agents, and for treatment against several types of other serious disorders such as Crohn's disease.[13–16]

The synthesis and characterization of symmetrical and unsymmetrical Ru(II) terpyridine complexes and the antibacterial activity of four terpyridine ruthenium(II) complexes against four human and five plant pathogens under *in vitro* conditions are reported in the present investigation.

Results and discussion

Synthesis of 4′-functionalized terpyridine ligands and complexes

Several methods are available for the synthesis of terpyridine ring systems.[17–23] These methods suffer from some significant drawbacks and limitations that can be overcome by using low molecular weight PEG 300 (PEG = poly(ethylene glycol)) as a reaction medium as developed by Smith *et al.*[24] 4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine (**ttpy**) was synthesized by the reaction of 2-acetylpyridine with 4-methyl benzaldehyde in the molar ratio 2 : 1 at 0 °C (Scheme 1).

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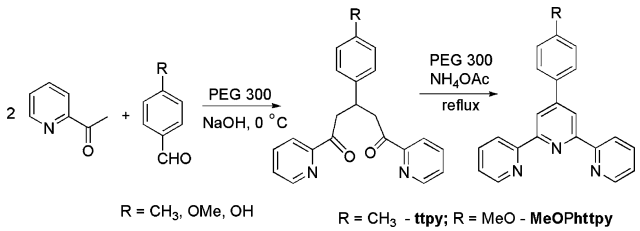
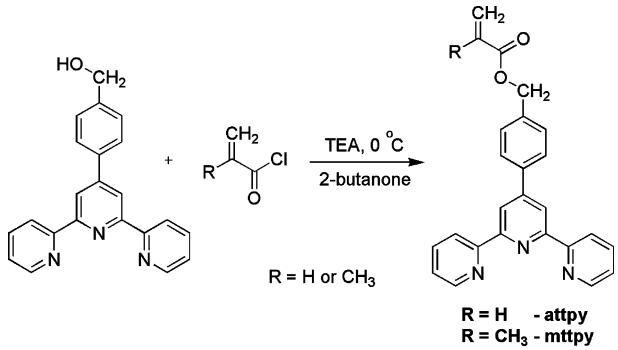


Scheme 1

4′-(4-Bromomethylphenyl)-2,2′:6′,2″-terpyridine (**Brttpy**) was synthesized according to the literature method.[25] **Brttpy** was converted into 4′-(4-hydroxymethylphenyl)-2,2′:6′,2″-terpyridine in 54% yield.[26] The hydroxy terpyridine was treated with acryloyl chloride or methacryloyl chloride in 2-butanone at 0 °C to afford 4′-(4-acryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine (**attpy**) or 4′-(4-methacryloyloxy methylphenyl)-2,2′:6′,2″- terpyridine (**mttpy**) in 80% yield (Scheme 2).

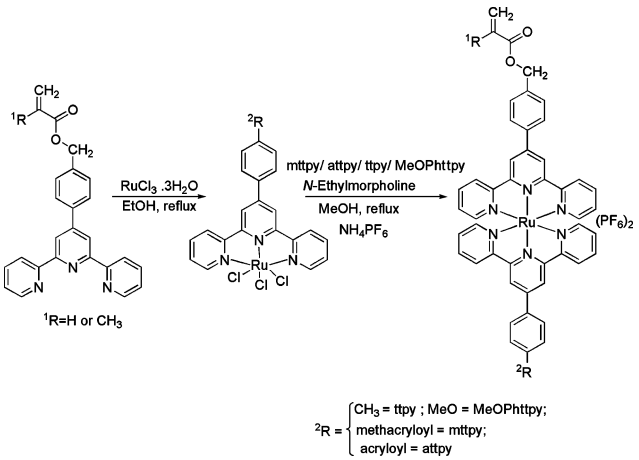


Scheme 2

Ruthenium(II)–bis(2,2′:6′,2″-terpyridine) species are conveniently prepared by the stepwise addition of the two terpyridine ligands to the ruthenium center.[27,28] The reaction of **mttpy** or **attpy** or **ttpy** or **MeOPhttpy** (MeOPhttpy = 4′-(4-methoxyphenyl)-2,2′:6′,2″-terpyridine) with hydrated ruthenium(III) chloride in refluxing ethanol afforded a dark brown insoluble ruthenium(III) mono terpyridine complex in 70% yield. Subsequently the mono complex was reacted with another equivalent of **mttpy** at reflux in methanol under reductive conditions. The resulting ruthenium(II) bis(terpyridine) complex was precipitated by the addition of a large excess of ammonium hexaflurophosphate salt and the $[Ru(mttpy)_2](PF_6)_2$ or $[Ru(attpy)_2](PF_6)_2$ was isolated as a red solid (yield 65–70%) (Scheme 3).

Characterization of 4′-functionalized terpyridine ligands and complexes

The terpyridine ligands were characterized by UV-VIS, IR, ^{1}H NMR, ^{13}C NMR spectroscopy, EI mass spectrometry and elemental analysis. In the ^{1}H NMR spectra of **mttpy** and **attpy** ligands, the signals for aromatic protons of the terpyridine rings were observed in the region δ 7.30–8.72. The vinylic protons were observed as two singlets in the region δ 5.80–6.18. The benzylic protons appear as a singlet at δ 5.18 with an increase in downfield shift by δ 0.7 for both **mttpy** and **attpy**, which is attributed to the absence of the strong electron withdrawing bromine group[29] when compared to the ligand **Brttpy**. The ^{13}C NMR spectra of **ttpy** ligands show



Scheme 3

a carbonyl carbon peak in the region δ 167.12–168.45. The **MeOPhttpy** was dissolved in acetonitrile and allowed to evaporate slowly to give golden yellow colored needle shaped crystals. An ORTEP diagram[30] of **MeOPhttpy** with atomic labeling scheme is shown in Fig 1. The **MeOPhttpy** exhibits a transoid (*trans–trans*) arrangement of pyridine rings about the interannular C–C bonds. The transoid arrangement has been previously reported for similar terpyridine ligands in the literature.[31,32] The three pyridine rings are approximately coplanar to each other and the two terminal pyridine rings N2/C6–C10 and N3/C11–C5 make dihedral angles of 1.66(7) and 3.30(7)° respectively with the central pyridine ring (N1/C1–C5). The dihedral angle of the methoxyphenyl substituent is 6.17(1)° with the N1/C1–C5 pyridine ring.

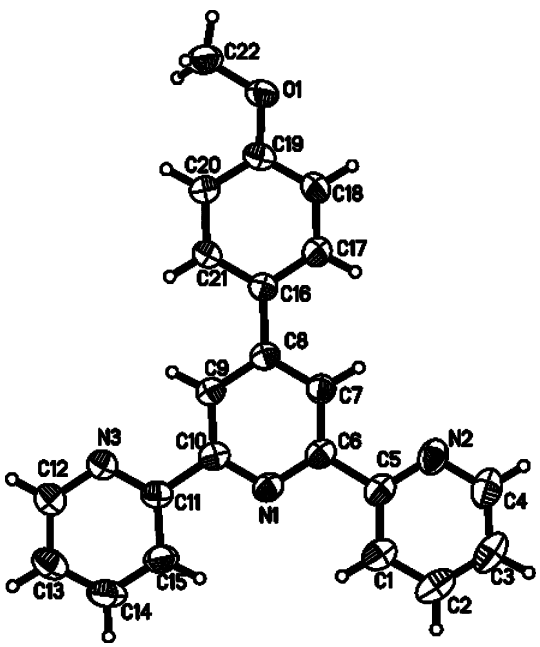


Fig. 1 ORTEP diagram of **MeOPhttpy** at 30% probability level along with its atom labeling scheme.

The ^{1}H NMR spectra of $[Ru(mttpy)_2](PF_6)_2$ and $Ru(attpy)_2](PF_6)_2$ complexes were recorded in DMSO-d_6 solution and all other unsymmetrical complexes were in CD_3CN solution and the

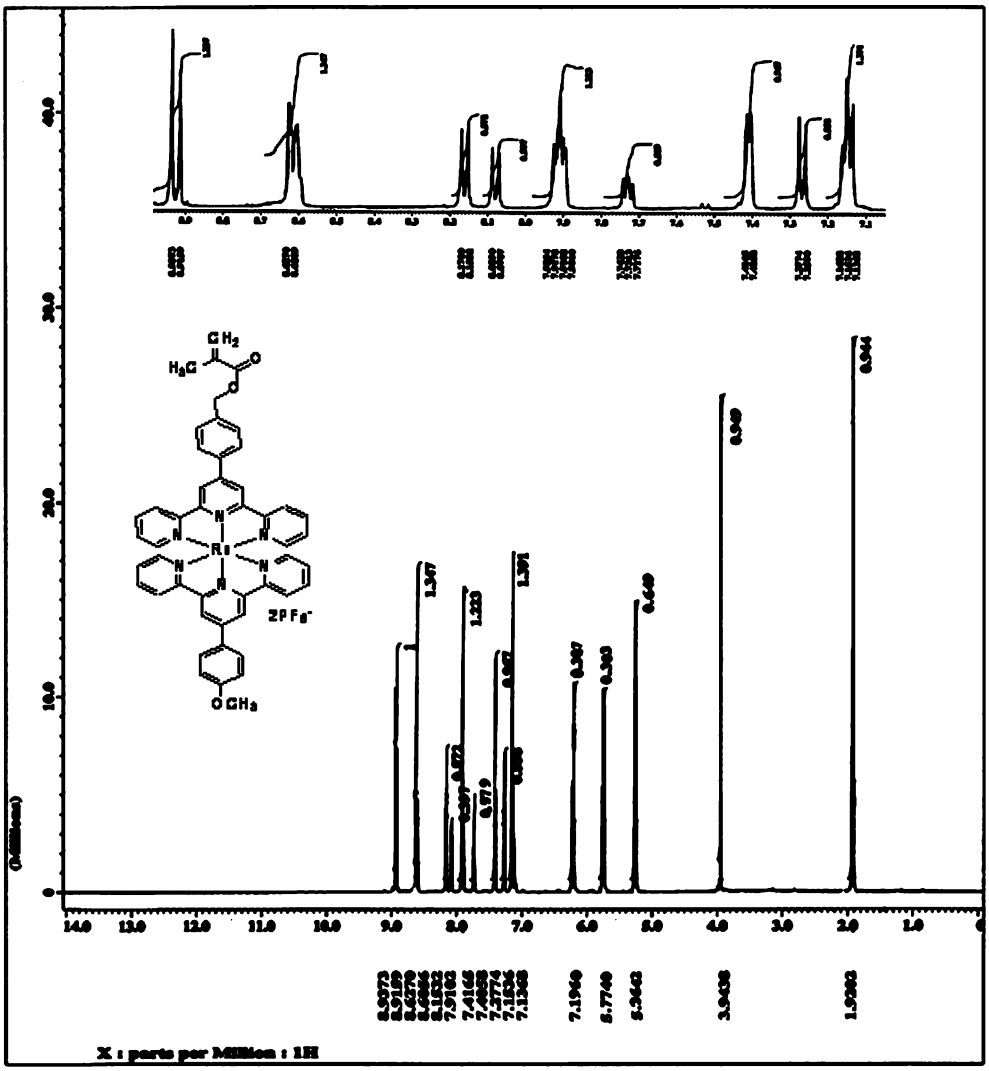


Fig. 2 ^{1}H spectrum of [Ru(mttpy)(MeOPhttpy)](PF$_6$)$_2$.

representative spectrum is shown in Fig 2. The signals for aromatic protons of the terpyridine rings of all the complexes appear in the region δ 7.13–9.51. An upfield shift for the 6,6″-protons was observed while comparing the spectrum of the free ligand with that of the corresponding complex and all other terpyridine protons undergo a downfield shift. The upfield and downfield shifts observed in the case of the pyridine ring protons were in good agreement with those previously reported in the literature.[33–35] The positive ion FAB mass spectra of ruthenium(II) terpyridine complexes, provide compelling evidence for the formation of the complexes. For example, the symmetrical complex [Ru(mttpy)$_2$](PF$_6$)$_2$ shows a molecular ion peak at m/z = 917, which is assignable to the [Ru(mttpy)$_2$ – 2PF$_6$]$^+$ fragment. The overall fragmentation pattern in the FAB mass spectra of the respective complexes strongly supports the proposed formulation of the complexes.[36,37]

Electronic spectra of the complexes

The electronic spectra of the ruthenium complexes were recorded in acetonitrile medium and the relevant data are summarized in Table 1. The UV-VIS spectrum of Ru(mttpy)$_2$(PF$_6$)$_2$ exhibits the typical metal to ligand charge transfer (MLCT) transition of the Ru(II)–terpyridine system at λ_{max}= 492 nm (ε = 29 400 dm^3 mol^{-1} cm^{-1}) and the bands at 289 nm (ε = 72 00 dm^3 mol^{-1} cm^{-1}) and 312 nm (ε = 78 200 dm^3 mol^{-1} cm^{-1}) are due to ligand centered (LC) transitions. A small red shift when compared to that of the model ruthenium(II) terpyridine complex [Ru(ttpy)$_2$](PF$_6$)$_2$ (λ_{max}= 490 nm; ε = 28 000 dm^3 mol^{-1} cm^{-1}) has been observed.[27] The spin allowed metal to ligand charge transfer (MLCT) band in the visible spectral region undergoes an increase in intensity and a red shift, regardless of the electron-donor or electron-acceptor nature of the substituents.

Table 1 Electronic spectral data for the ruthenium(II) terpyridine complexes

	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	
Complexes	MLCT	LMCT
[Ru(mttpy)$_2$](PF$_6$)$_2$	492 (29 400)	312 (78 200), 289 (72 000)
[Ru(attpy)$_2$](PF$_6$)$_2$	490 (28 496)	309 (78 124), 284 (70 612)
[Ru(mttpy)(ttpy)](PF$_6$)	491 (29 386)	312 (78 400), 289 (72 100)
[Ru(mttpy)(MeOPhttpy)](PF$_6$)$_2$	491 (28 436)	310 (78 100), 289 (71 800)

The $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ complex exhibits a typical metal to ligand charge transfer (MLCT) transition of the Ru(II)–terpyridine complex at λ_{max} = 491 nm (ε = 28 436 $dm^3\ mol^{-1}\ cm^{-1}$) and the ligand centred (LC) transitions at 289 nm (ε = 71 800 $dm^3\ mol^{-1}\ cm^{-1}$) and 310 nm (ε = 78 100 $dm^3\ mol^{-1}\ cm^{-1}$), which shows that there is a small blue shift when compared to the symmetrical $[Ru(mttpy)_2](PF_6)_2$ complex.[27,28,38]

Electrochemistry of the ruthenium terpyridine complexes

The electrochemical properties of the monomer ruthenium complexes were examined in acetonitrile medium and the relevant data are shown in Tables 2 and 3. The ferrocene–ferrocenium (+1) couple was used as an internal standard. The complexes are redox-active, showing both metal-centered (oxidation) and ligand-centered (reduction) processes. The metal based oxidation potentials of the present complexes are significantly higher than those observed for the model complexes $[Ru(tpy)_2](PF_6)_2$ ($E_{1/2}$ = + 0.92 V) and $[Ru(ttpy)_2](PF_6)_2$ ($E_{1/2}$ = +1.25 V). For example, the cyclic voltammogram of the $[Ru(mttpy)_2](PF_6)_2$ complex exhibits a reversible oxidation peak at +1.29 V ($E_{1/2}$) which can be attributed to the Ru^{II}/Ru^{III} process and the first and second ligand reductions are observed at −1.19 V and −1.43 V ($E_{1/2}$) respectively. The oxidation potential increases by 40 mV and the reduction potential decreases by 50 mV when compared to those of the model complex[27,38] $[Ru(ttpy)_2](PF_6)_2$. The cyclic voltammogram of the crylated $[Ru(attpy)_2(PF_6)_2]$ complex (Fig. 3) exhibits a quasi-reversible oxidation peak at +1.27 V ($E_{1/2}$) which can be attributed to the Ru^{II}/Ru^{III} process and the first and second ligand reductions are observed at −1.20 V and −1.41 V ($E_{1/2}$) respectively. These redox processes are assigned to the successive reduction of the two tpy ligands, assuming that each ligand can be reduced within one cycle. Presumably, the first peak belongs to terpyridine ligand, since the additional aromatic ring (tolyl) lowers the lowest unoccupied molecular orbital π* due to an increased conjugation.[39] The presence of strongly electron-releasing OMe substituent, in the unsymmetrical $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ complex allows the stabilization of the Ru(III) state and a shift of 50 mV ($E_{1/2}$ +1.24 V, quasi-reversible processes) has been observed in the oxidative processes when compared to $[Ru(mttpy)](PF_6)_2$ ($E_{1/2}$ +1.29 V, quasi-reversible processes).

Table 2 Electrochemical data for the ruthenium(II) terpyridine complexes (oxidation process)

	Oxidation			
Complexes	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V	ΔE/mV
$[Ru(tpy)_2](PF_6)_2$[a]	+0.95	+0.89	+0.92	60
$[Ru(ttpy)_2](PF_6)_2$[a]	+1.28	+1.22	+1.25	60
$[Ru(mttpy)_2](PF_6)_2$	+1.32	+1.26	+1.29	60
$[Ru(attpy)_2](PF_6)_2$	+1.30	+1.23	+1.27	70
$[Ru(mttpy)(ttpy)](PF_6)$	+1.33	+1.23	+1.28	100
$[Ru(mttpy)(MeOPhttpy)](PF_6)_2$	+1.28	+1.20	+1.24	80

[a] Model complexes.[27,38]

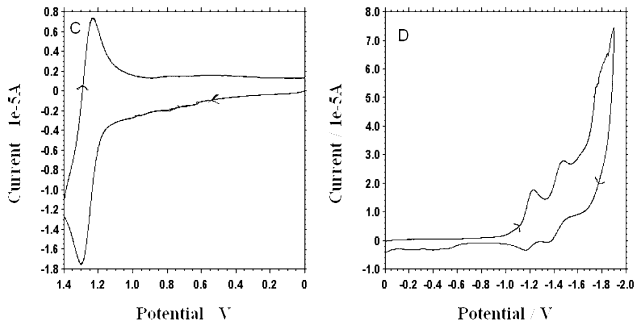


Fig. 3 Cyclic voltammograms of $[Ru(attpy)](PF_6)_2$ (scan rate: 100 mV s^{-1}) (C oxidation and D reduction process).

Biological activity of the ruthenium(II) terpyridine complexes

Escherichia coli is an important cause of gastroenteritis and hemorrhagic colitis. Infection with *E. coli* O15:H7 can affect all age groups and it causes more than 20 000 infections and as many as 250 deaths each year in the USA alone.[40] *E. coli* also produces Vero toxins resulting in hemorrhagic colitis and hemolytic uremic syndrome.[41] Chronic colonization and infection of the lung with *Pseudomonas aeruginosa* is a major cause of morbidity and mortality in cystic fibrosis (CF) patients.[43] Root emergence, damping off of seedlings, crown and root of mature plants caused by *Rhizoctonia solani* is a serious disease of sugar beet.[42] Chronic ulcers are constantly colonized or infected by bacteria such as *P. aeruginosa* and *Proteus mirabilis*.[44] *P. mirabilis*, a motile gram negative enteric bacterium, is an important pathogen of the urinary tract and is the primary infectious agent in patients with indwelling urinary catheters.[45] In people whose immune systems are suppressed, *Proteus vulgaris* can be an opportunistic pathogen causing urinary tract infection, pneumonia or septicemia. It is not sensitive to ampicillin and cephalosporins. *R. solani*, a soil borne fungus, causes seedling blight, root rot, fruit rot, or above ground aerial blight. *P. aeruginosa* is a bacterium which is difficult to control while *R. solani* causes banded leaf and sheath blight.[46]

The human pathogens namely *Escherichia coli, Proteus vulgaris, Proteus mirabilis* and *Pseudomonas aeruginosa* were maintained on nutrient agar (NA) consisting of the following (g L^{-1}): beef extract 1.0; yeast extract 2.0, peptone 5.0, NaCl 5.0, agar 15.0; distilled H_2O 1 L; pH 7.2. The plant pathogens *viz*., *Curvularia lunata, Fusarium oxysporum, Fusarium udum, Macrophomina phaseolina*

Table 3 Electrochemical data of ruthenium(II) terpyridine complexes (reduction process)

	ttpy/ttpy$^-$				ttpy/ttpy^{2-}			
Complexes	$^1E_{pa}$/V	$^1E_{pc}$/V	$^1E_{1/2}$/V	$^1\Delta E$/mV	$^2E_{pa}$/V	$^2E_{pc}$/V	$^2E_{1/2}$/V	$^2\Delta E$/mV
$[Ru(mttpy)_2](PF_6)_2$	−1.22	−1.16	−1.19	60	−1.48	−1.38	−1.43	110
$[Ru(attpy)_2](PF_6)_2$	−1.23	−1.16	−1.20	70	−1.47	−1.35	−1.41	120
$[Ru(mttpy)(ttpy)](PF_6)$	−1.20	−1.16	−1.18	40	−1.46	−1.37	−1.42	90
$[Ru(mttpy)(MeOPhttpy)](PF_6)_2$	−1.26	−1.18	−1.22	80	−1.47	−1.38	−1.43	90

Table 4 *In vitro* antibacterial activity against human pathogens (MIC[a]/μg ml^{-1})

Complexes	*P. vulgaris*	*P. mirabilis*	*P. aeruginosa*	*E. coli*
$[Ru(attpy)_2](PF_6)_2$	20	28	25	22
$[Ru(mttpy)_2](PF_6)_2$	20	17	17	12
$[Ru(mttpy)(MeOPhttpy)](PF_6)_2$	12	15	14	10
$[Ru(mttpy)(ttpy)](PF_6)_2$	25	10	13	12
Tetracycline	15	20	20	15
DMSO (control)	NI	NI	NI	NI

[a] MIC: Minimum inhibitory concentration; NI: no inhibition.

Table 5 *In vitro* antifungal activity against plant pathogens (MIC[a]/μg ml^{-1})

Complexes	*R. solani*	*M. phaseolina*	*F. oxysporum*	*F. udum*	*C. lunata*
$[Ru(attpy)_2](PF_6)_2$	36	14	11	30	9
$[Ru(mttpy)_2](PF_6)_2$	12	15	10	29	10
$[Ru(mttpy)(MeOPhttpy)](PF_6)_2$	17	9	14	19	11
$[Ru(mttpy)(ttpy)](PF_6)_2$	34	7	28	11	8
Carbendazim	25	18	15	12	8
DMSO (control)	NI	NI	NI	NI	NI

[a] MIC: Minimum inhibitory concentration; NI: no inhibition.

and *Rhizoctonia solani* were maintained on potato dextrose agar (PDA) containing the following (g L^{-1}): potato 200; dextrose 20; agar 15; distilled H_2O 1 L and the pH was maintained at 6.5. All the above cultures were maintained in slants or Petri plates at room temperature (28 ± 2 °C). The minimum inhibitory concentration (MIC) is defined as the lowest concentration of an antimicrobial that will inhibit the visible growth of a microorganism after overnight incubation. If there is nil growth of the organism, it is indicated by a + sign and if there is no retardation in its growth, it is indicated by a − sign.

Antibacterial activity

All four complexes exhibit different levels of inhibition against the tested human pathogenic bacteria. The antibacterial activity of the test compounds was dose dependent and it was pronounced at higher concentrations. The complex $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ shows remarkable antibacterial activity against all the test pathogens compared to rest of the complexes and a commercial antibiotic, *viz*. tetracycline. The minimum inhibitory concentration of the complex $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ against human pathogens was determined to be between 10 and 15 μg ml^{-1} as compared to between 15 and 20 μg ml^{-1} in tetracycline. The complexes $[Ru(mttpy)(ttpy)](PF_6)_2$ and $[Ru(mttpy)_2](PF_6)_2$ exhibit superior antibacterial activity towards four human pathogens *viz*. *P. vulgaris, P. mirabilis, P. aeruginosa* and *E. coli* when compared to the antibiotic tetracycline. The minimum inhibitory concentration of the complexes $[Ru(mttpy)(ttpy)](PF_6)_2$ and $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ against the above three bacterial pathogens ranges from 10–25 μg ml^{-1} and 10–15 μg ml^{-1}, respectively compared to 15–20 μg ml^{-1} in tetracycline (Table 4). However, the complex $[Ru(attpy)_2](PF_6)_2$ was comparatively less effective against all four human pathogens.

Antifungal activity

Similar to the antibacterial activity, all four complexes exhibit different levels of antifungal activity against the five tested plant pathogenic fungi compared to a DMSO control. The relevant data are reproduced in Table 5. Further, the antifungal activity of the test compounds was dose dependent and it was appreciable at higher concentrations. Among the four complexes tested, the complexes $[Ru(mttpy)_2](PF_6)_2$ and $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ show remarkable antifungal activity against three economically important test pathogens *viz*. *R. solani, M. phaseolina* and *F. oxysporum* compared to the rest of the complexes and the commercial fungicide, carbendazim. The minimum inhibitory concentration of the complexes $[Ru(mttpy)_2](PF_6)_2$ and $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ against the above three plant pathogens range from 10 to 15 μg ml^{-1} and 9 to 17 μg ml^{-1}, respectively compared to 15 and 25 μg ml^{-1} in carbendazim (Table 5). These results are comparable with those of other ruthenium complexes like $[Ru(M)_2(U)]^{2+}$, where M = 2,2′-bipyridine/1,10-phenanthroline and U = tpl (Ru1), 4-Cl-tpl (Ru2), 4-CH_3-tpl (Ru3), 4-CH_3O-tpl (Ru4), and 4-NO_2-tpl (Ru5), -pai (Ru6), where tpl = thiopicolinanilide and pai = 2-phenyl-azo-imidazole as well as $[Ru(\eta^6\text{-}p\text{-cymene})X_2]_2$, $[Ru(\eta^6\text{-}p\text{-cymene})X_2(pta)]$ (where pta= 1,3,5-triaza-7-phosphatricyclo[3.3.1.1.]decane), $[H_4\ Ru_4(\eta^6\text{-}p\text{-benzene})_4]^{2+}$ and $[Ru(PPh_3)_2(LH)_2]ClO_4$(where L= 4-phenyl/4-cyclohexyl thiosemicarabazones of pyridine 2-aldehyde and thiophene-2-aldehyde) previously reported in the literature.[47–49]

Conclusion

The synthesis of a Ru(II) complex with the 4′-(4- methacryloyloxymethylphenyl)-2,2′: 6′,2″-terpyridine ligand has been achieved by a multi step procedure. All four complexes investigated in the present study exhibit antimicrobial activity against four human and five plant pathogens. The biological study of the complexes $[Ru(mttpy)_2](PF_6)_2$ and $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$ can be investigated further as these systems exhibit very good activity against most of the test pathogens and their activity is better than some of the commercially available antibiotics and fungicide.

Experimental methods

Materials

2-Acetylpyridine, *p*-methoxybenzaldehyde, *p*-tolualdehyde, triethylamine, *N*-bromosuccinimide, azobis(isobutyronitrile), $RuCl_3 \cdot 3H_2O$ and *N*-ethylmorpholine were received from E.Merck. Acryloylchloride and methacryloylchloride were synthesized according to the literature method.[50]

Instrumentation

Infrared spectra of the precursor compounds, ligands and their complexes were recorded in the range 4000–400 cm^{-1} using KBr pellets on a Shimadzu FTIR 8000 spectrophotometer/Perkin Elmer Spectrum RX1 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra of the ligands and complexes were obtained using a JEOL GSX400 Fourier Transform NMR spectrophotometer operating at 400 MHz and 100 MHz respectively. Electronic spectra of the complexes were recorded on a Hitachi 320 double beam spectrophotometer. Acetonitrile or DMF were used as the solvent for all measurements. The FAB mass spectra of complexes were obtained on a JEOL SX 102/DA-6000; *m*-nitrobenzylalcohol (NBA) was used as the matrix. Electron impact mass spectra of the ligands were obtained on a JNS-DX 303 HF mass spectrometer. The C, H, N contents of the ligands and complexes were carried out using Carlo Erba Elemental analyzer Model 1106 and Haereus CHN rapid analyser. The cyclic voltammograms of 10^{-3} M solutions of complexes were obtained on a CHI600A electrochemical analyzer. The measurements were carried out under oxygen free conditions using a three electrode cell in which a glassy carbon electrode was the working electrode, a saturated Ag/AgCl electrode was the reference electrode and a platinum wire was used as an auxiliary electrode. The ferrocene–ferrocenium (+1) couple was used as an internal standard and $E_{1/2}$ of the ferrocene–ferrocenium couple under these experimental conditions was 470 mV in DMF medium and ΔE_p for Fe/Fe^+ is 70 mV. Tetra(n-butyl)ammonium perchlorate (TBAP) was used as supporting electrolyte (**CAUTION!** TBAP is potentially explosive; hence care should be taken in handling the compound) and the concentration of TBAP was 10^{-1} M.

Test organisms

The cultures of human and plant pathogens used in this study were obtained from the culture collections of Biocontrol and Microbial Metabolites Lab, Centre for Advanced Studies in Botany, University of Madras.

General synthetic procedure for 4′-functionalized terpyridines[24]

2-Acetylpyridine (10.0 g, 82.5 mmol) was added to a suspension of crushed NaOH (3.3 g, 82.5 mmol) in poly(ethylene glycol) (PEG 300) (70 mL) and stirred at 0 °C for 10 min. *p*-Methoxybenzaldehyde (5.61 g, 41.2 mmol) or *p*-tolualdehyde (4.96 g, 41.2 mmol) or *p*-hydroxybenzaldehyde (5.04 g, 41.2 mmol) was added *via* asyringe and the suspension was kept at 0 °C for 2 h. The suspension was manually stirred with spatula every 15 min as the viscosity becomes too high for adequate mixing with a magnetic stirrer. After 2 h, NH_4OAc (20 g) was added in excess and the suspension was heated at 100 °C for 2 h. During this time, the color of the mixture changed from red to dark green and was accompanied by the formation of a fine precipitate. Millipore water (200 mL) was added and the precipitate of substituted terpyridine was isolated by filtration, washed with 100 mL of water, 20 mL of cold ethanol and dried under vacuum.

4′-(4-Methylphenyl)-2,2′:6′,2″-terpyridine (ttpy). Yield: 8.5 g (63%); mp: 167–170 °C; IR (KBr disc ν/cm^{-1}): 3386, 1589; ^1H NMR (500 MHz, $CDCl_3$) δ: 2.42 (s, 3H, CH_3), 7.30–7.34 (m, 2H), 7.82 (d, 2H, $J = 8.0$ Hz), 7.85–7.86 (m, 4H), 8.66 (d, 2H, $J = 7.5$ Hz), 8.72–8.73 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.39, 118.72, 121.48, 123.88, 127.42, 129.75, 135.53, 136.98, 149.17, 150.26, 155.90, 156.39; mass (EI, 70 eV); *m*/*z* (%): 323 (100).

4′-(4-Methoxyphenyl)-2,2′:6′,2″-terpyridine (MeOPhttpy). Yield: 9.1 g (65%); mp: 161–163°C; IR (KBr disc ν/cm^{-1}): 3055, 1565; ^1H NMR (400 MHz, $CDCl_3$) δ: 3.86 (s, 3H, CH_3), 7.02 (d, 2H, $J = 8.8$ Hz), 7.31–7.34 (m, 2H), 7.83–7.88 (m, 4H), 8.64–8.72 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.32, 114.29, 118.24, 121.34, 123.70, 128.49, 130.73, 136.79, 149.05, 149.10, 149.72, 155.35, 156.35, 160.50; mass (EI, 70 eV); *m*/*z* (%) : 339 (100).

4′-(4-Hydroxyphenyl)-2,2′:6′,2″-terpyridine (HOPhttpy). Yield: 8.6 g (64%); mp: 310–312 °C; IR (KBr disc ν/cm^{-1}): 3070, 1595, 1585; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.00 (d, 2H, $J = 8.8$ Hz), 7.33–7.36 (m, 2H), 7.83–7.87 (m, 4H), 8.64–8.78 (m, 6H), 9.85 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 114.22, 118.34, 121.39, 123.50, 128.42, 130.53, 136.79, 149.25, 149.18, 149.62, 155.45, 156.37, 160.57; mass (EI, 70 eV); *m*/*z* (%) : 325 (100).

Synthesis of 4′-(4-bromomethylphenyl)-2,2′:6′,2″-terpyridine (Brttpy)

Brttpy was synthesized according to the literature method. Yield: 3.46 g (70%).; mp: 176 °C. IR (KBr disc ν/cm^{-1}): 1584, 790; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.55 (s, 2H), 7.33–7.35 (m, 2H), 7.52 (d, 2H, $J = 8.6$ Hz), 7.85–7.89 (m, 4H), 8.65 (d, 2H, $J = 8.1$ Hz), 8.72–8.73 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 33.09, 118.89, 121.48, 123.99, 127.71, 127.85, 137.03, 138.64, 138.71, 149.19, 149.56, 156.04, 156.16; anal. calcd for : $C_{22}H_{16}BrN_3$ (402.29): calculated (%); C, 65.68; H, 4.01; N, 10.44; found (%); C, 65.40; H, 3.86; N, 10.50.

Synthesis of 4′-(4-hydroxymethylphenyl)-2,2′:6′,2″-terpyridine (HOttpy)

Brttpy (0.95 g, 2.36 mmol) was converted into **HOttpy** in 54% yield by using $NaHCO_3$ (0.240 g, 2.85 mmol) in a water–acetonitrile solvent mixture. Yield: 0.482 g (60%); mp: 197–198 °C; UV-VIS (CH_3CN); λ_{max} nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 286 (32 860), 227 (16 280); IR (KBr disc ν/cm^{-1}): 3386, 1589; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.71 (br s, 1H), 4.78 (s, 2H), 7.34–7.36 (m, 2H), 7.49 (d, 2H, $J =$ 8.1 Hz), 7.86–7.90 (m, 4H), 8.66 (d, 2H, $J = 8.0$ Hz), 8.68–8.70 (m, 2H), 8.72 (s, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ: 64.94, 118.86, 121.51, 123.96, 127.50, 127.55, 137.03, 137.69, 142.03, 149.19, 150.01, 155.99, 156.32; mass (EI, 70 eV); *m*/*z* (%) : 339 (100); anal. calcd for : $C_{22}H_{17}N_3O$ (339.39): calculated (%); C, 77.86; H, 5.05; N, 12.38; found (%); C, 77.49; H, 5.17; N, 12.26.

Synthesis of 4′-(4-methacryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine (mttpy)

HOttpy (0.486 g, 1.43 mmol) and triethylamine (0.20 mL, 1.43 mmol) were dissolved in 2-butanone and methacryloyl chloride (0.14 mL, 1.43 mmol) was added dropwise at 0 °C to the solution. After the addition was over, the mixture was stirred for another 6 h. The triethylamine hydrochloride salt formed during this reaction was filtered off and the filtrate was concentrated under reduced pressure. The crude product was recrystallized from methanol. Yield: 0.47 g (80%). UV-VIS (CH_3CN); λ_{max} nm (ε/dm^3 mol^{-1} cm^{-1}): 287 (30 640), 227 (17 202); IR (KBr disc ν/cm^{-1}): 2923, 1720, 1585, 1184; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.92 (s, 3H), 5.19 (s, 2H), 5.54 (s, 1H), 6.12 (s, 1H), 7.34–7.45 (m, 4H), 7.87 (m, 4H), 8.64–8.68 (m, 4H), 8.72 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.33, 65.92, 119.39, 121.92, 124.12, 125.95, 127.58, 128.49, 136.17, 137.28, 137.91, 142.45, 148.28, 150.01, 155.02, 155.23, 167.18; mass (EI, 70 eV); m/z (%): 407.67 (100); anal. calcd for $C_{26}H_{21}N_3O_2$ (407.46): calculated (%); C, 76.64; H, 5.19; N, 10.31; found (%); C, 76.69; H, 5.16; N, 10.26.

Synthesis of 4′-(4-acryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine (attpy)

This compound was synthesized in a similar fashion to that of 4′-(4-methacryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine by using acryloyl chloride instead of methacryloylchloride. Yield: 0.46 g (81%) UV-VIS (CH_3CN); λ_{max} nm (ε/dm^3 mol^{-1} cm^{-1}): 287 (29 622), 228 (18 202); IR (KBr disc ν/cm^{-1}): 2928, 1732, 1580, 1184; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.18 (s, 2H), 5.58 (dd, 1H, J = 2.0, 10.0 Hz), 6.18 (dd, 1H, J = 2.0, 10.6 Hz), 6.26 (dd, 1H, J = 2.0, 17.2 Hz), 7.34–7.45 (m, 4H), 7.87–7.89 (m, 4H), 8.64–8.68 (m, 4H), 8.73 (s, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.53, 64.92, 119.56, 122.02, 124.32, 126.05, 127.58, 128.79, 136.97, 137.88, 138.61, 142.85, 148.28, 150.50, 155.09, 155.28, 167.14; anal. calcd for $C_{25}H_{19}N_3O_2$ (393.44): calculated (%); C, 76.32; H, 4.87; N, 10.68; found (%); C, 76.67; H, 4.95; N, 10.25; mass (EI, 70 eV); m/z (%): 394.12 (100).

General method of synthesis of ruthenium(III) complexes

4′-(4-Methacryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine (**mttpy**) (0.50 g, 1.23 mmol) or 4′-(4-acryloyloxymethylphenyl)-2,2′:6′,2″-terpyridine (**attpy**) was added to $RuCl_3{\cdot}3H_2O$ (322 mg, 1.23 mmol) in ethanol and refluxed for 8 h under an inert atmosphere. The mixture was cooled and the dark brown precipitate was collected by filtration, washed thoroughly with methanol, water and diethyl ether and dried under vacuum. Yield: (0.530 g, 70%).

General method of synthesis of ruthenium(II) complexes

[Ru(mttpy)$_2$](PF$_6$)$_2$. **mttpy** (0.331 g, 0.812 mmol) was added to [Ru(mttpy)]Cl_3 (0.50 g, 0.813 mmol) in methanol along with *N*-ethylmorpholine (5 drops). The mixture was refluxed for 6 h under an inert atmosphere. The resulting deep red solution was filtered and a three-fold excess of methanolic ammonium hexafluorophosphate was added to the filtrate. The resulting red precipitate was filtered off and recrystallized from acetone–acetonitrile solution and dried under vacuum.[28] Yield: 0.750 g (76%); UV-VIS (CH_3CN); λ_{max} nm (ε/dm^3 mol^{-1} cm^{-1}): 492 (29 400), 312 (78 200), 289 (72 000); IR (KBr disc ν/cm^{-1}): 1712, 1608, 1161, 840; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 1.98 (s, 6H), 5.40 (s, 4H), 5.80 (s, 2H), 6.18 (s, 2H), 7.28 (t, 4H, J = 6.3 Hz), 7.54 (d, 4H, J = 4.9 Hz), 7.77 (d, 4H, J = 7.8 Hz), 8.06 (t, 4H, J = 7.8 Hz), 8.43 (d, 4H, J = 8.3 Hz), 9.08 (d, 4H, J = 8.3 Hz), 9.48 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 19.01, 65.98, 120.98, 124.05, 124.87, 125.65, 127.72, 129.56, 132.31, 135.23, 136.56, 137.90, 145.59, 152.29, 155.08, 157.79, 167.98; FAB$^+$-MS (nitrobenzyl alcohol matrix), m/z: 916 [M − 2PF$_6$]$^+$, 1061 [M − PF$_6$]$^+$; anal. calcd for : $C_{52}H_{42}F_{12}N_6O_4P_2Ru$ (1205.93): calculated (%); C, 51.79; H, 3.51; N, 6.97; found (%); C, 51.70; H, 3.59; N, 6.84.

[Ru(attpy)$_2$](PF$_6$)$_2$. Yield: 0.70 g (71%); UV-VIS (CH_3CN); λ_{max} nm (ε/dm^3 mol^{-1} cm^{-1}): 490 (28 496), 309 (78 124), 284 (70 612); IR (KBr disc ν/cm^{-1}) 1712, 1608, 1161, 840; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 5.38 (s, 4H), 5.90 (dd, 2H, J = 11.5 Hz), 6.27 (dd, 2H, J = 11.2 Hz), 6.40 (dd, 2H, J = 17.5 Hz), 7.28 (t, 4H, J = 6.5 Hz), 7.54 (d, 4H, J = 4.9 Hz), 7.77 (d, 4H, J = 7.8 Hz), 8.06 (t, 4H, J = 7.8 Hz), 8.43 (d, 4H, J = 8.3 Hz), 9.08 (d, 4H, J = 8.3 Hz), 9.48 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 65.98, 120.98, 124.05, 124.87, 125.65, 127.72, 129.56, 132.31, 135.23, 136.56, 137.90,145.59, 152.29, 155.08, 157.79, 167.98; FAB$^+$-MS (nitrobenzyl alcohol matrix), m/z: 889 [M − 2PF$_6$]$^+$, 1033 [M − PF$_6$]$^+$; anal. calcd for: $C_{50}H_{38}F_{12}N_6O_4P_2Ru$ (1177.87): calculated (%); C, 50.98; H, 3.25; N, 7.13; found (%); C, 51.60; H, 3.40; N, 6.62.

[Ru(mttpy)(ttpy)](PF$_6$)$_2$. Yield: 0.75 g (82%); UV-VIS (CH_3CN); λ_{max} nm (ε/dm^3 mol^{-1} cm^{-1}): 491 (29 386), 312 (78 400), 289 (72 100); IR (KBr disc ν/cm^{-1}): 1713, 1614, 1161, 830; ^{1}H NMR (400 MHz, CD_3CN) δ: 1.93 (s, 3H), 2.01 (s, 3H), 5.36 (s, 2H), 5.72 (s, 1H), 6.18 (s, 1H), 7.19 (t, 4H, J = 6.1 Hz), 7.45 (d, 4H, J = 5.9 Hz), 7.77 (d, 4H, J = 8.2 Hz), 7.97 (t, 4H, J = 8.0 Hz), 8.23 (d, 4H, J = 8.2 Hz), 8.66 (d, 4H, J = 7.8 Hz), 9.02 (s, 4H);^{13}C NMR (100 MHz, CD_3CN) δ: 18.34, 21.39, 65.43, 118.20, 124.52, 125.39, 126.39, 127.34, 128.83, 129.76, 136.34, 137.41, 138.84, 139.86, 153.37, 156.54, 159.23, 168.12; FAB$^+$-MS (nitrobenzyl alcohol matrix), m/z: 832 [M − 2PF$_6$]$^+$, 976 [M − PF$_6$]$^+$; anal. calcd for: $C_{48}H_{38}F_{12}N_6O_2P_2Ru$ (1121.85): calculated (%); C, 51.39; H, 3.41; N, 7.49; found (%);C, 51.50; H, 3.82; N, 7.66.

[Ru(mttpy)(MeOPhttpy)](PF$_6$)$_2$. Yield: 0.73 g (78%); UV-VIS (CH_3CN); λ_{max} nm (ε/dm^3 mol^{-1} cm^{-1}): 491 (28 436), 310 (78 100), 289 (71 800); IR (KBr disc ν/cm^{-1}): 1713, 1614, 1161, 839; ^{1}H NMR (500 MHz, CD_3CN) δ: 1.92 (s, 3H), 3.94 (s, 3H), 5.36 (s, 2H), 5.77 (s, 1H), 6.19 (s, 1H), 7.15 (t, 4H, J = 4.8 Hz), 7.28 (d, 2H, J = 5.9 Hz), 7.42 (d, 4H, J = 5.6 Hz), 7.74 (d, 2H, J = 5.3 Hz), 7.92 (t, 4H, J = 7.6 Hz), 8.07 (d, 2H, J = 8.3 Hz), 8.15 (d, 2H, J = 8.3 Hz), 8.62 (d, 4H, J = 7.8 Hz), 8.91 (s, 2H), 8.93 (s, 2H); FAB$^+$-MS (nitrobenzyl alcohol matrix), m/z: 848 [M − 2PF$_6$]$^+$, 993 [M − PF$_6$]$^+$; anal. calcd for: $C_{48}H_{38}F_{12}N_6O_3P_2Ru$ (1137.85): calculated (%); C, 50.67; H, 3.37; N, 7.39; found (%); C, 51.99; H, 3.60; N, 7.56.

Antibacterial activity of compounds against human pathogens

The antibacterial activity of the synthesized ruthenium(II) complexes [Ru(attpy)$_2$](PF$_6$)$_2$; [Ru(mttpy)$_2$](PF$_6$)$_2$; [Ru(mttpy)-(MeOPhttpy)](PF$_6$)$_2$; and [Ru(mttpy)(ttpy)](PF$_6$)$_2$ was tested

against human pathogens by the well diffusion method.[51,52] One mL inoculum of each test pathogen was added to the molten nutrient agar (NA) medium and poured into a sterile Petri dish under aseptic conditions. After solidification, a 5 mm well was made in the center of each plate using a sterile cork borer. Different concentrations of the complex were made from the stock solution which was filter sterilized using 0.25 μm filter paper. Each well received 50 μL solution of each compound and the Petri dishes were incubated at room temperature. 100 μL dimethyl sulfoxide (DMSO) 99% was used as a test control. After 48 h, the appearance of an inhibition zone around the well was observed.

Antifungal activity of compounds against plant pathogens

The antifungal activity of ruthenium(II) complexes $[Ru(attpy)_2](PF_6)_2$; $[Ru(mttpy)_2](PF_6)_2$; $[Ru(mttpy)(MeOPhttpy)](PF_6)_2$; $[Ru(mttpy)(ttpy)](PF_6)_2$ was tested on the mycelial growth of test fungi using the well diffusion technique. The DMSO solution of each compound mixed with molten potato dextrose agar (PDA) was poured into a 9 cm Petri dish and allowed to solidify. The plates were inoculated with 5 mm mycelial discs of the test fungi. The PDA with 10% DMSO was taken as control. The plates were incubated at room temperature for 6 d and the mycelial growth was measured.

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