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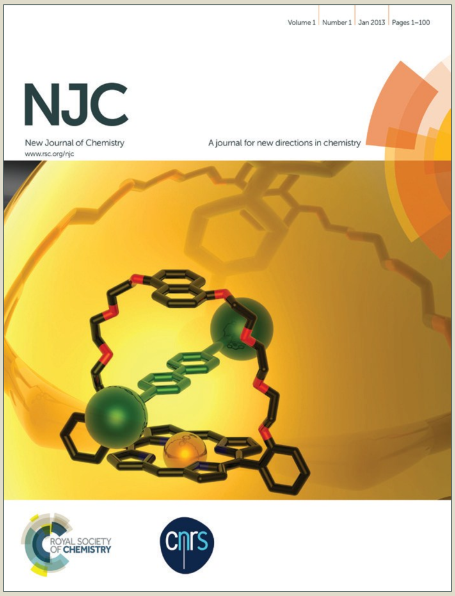

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PAPER

# Synthesis, luminescence, and electrochemical studies of a tetra- and an octanuclear ruthenium(II) complexes of tolylterpyridine appended calixarenes†

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Tetra- and octanuclear Ru(II) complexes of tolylterpyridine appended calixarenes, [{Ru(ttpy)}$_4$(**L**$^1$)](PF$_6$)$_8$ (**3**) and [{Ru(ttpy)}$_8$(**L**$^2$)](PF$_6$)$_{16}$ (**4**) [**L**$^1$ = 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(4′-*p*-benzyloxy-(2,2′:6′,2″-terpyridinyl))calix[4]-arene; **L**$^2$ = 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octa(4′-*p*-benzyloxy-(2,2′:6′,2″-terpyridinyl))-calix[8]arene; and ttpy = 4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine] have been synthesized and characterized. 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (**1**) is characterized by single crystal X-ray diffraction, whereas 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (**2**) is characterized by NMR and mass spectrometry. The tetra- and octanuclear complexes **3** and **4** are nonluminescent at 298 K, but exhibit $^3$MLCT emission at 650 nm at 77 K in acetonitrile. In the solid state at 298 K they exhibit $^3$MLCT emission at 663 and 666 nm, respectively. The polynuclear complexes **3** and **4** containing four- and eight [Ru(ttpy)$_2$]$^{2+}$ moieties undergo one-electron oxidation at 1.27 and 1.25 V versus Ag/Ag$^+$, respectively, in acetonitrile. The study demonstrates the versatility of the tolylterpyridine appended calix[4]arene and calix[8]arene in forming polynuclear Ru(II) complexes.

## Introduction

With a myriad of organic and inorganic building blocks at their disposal, chemists have been striving to design discrete molecular hosts, similar to those found in nature,[1] for applications in chemistry and biology.[2] Synthetic containers of nanoscale dimension remain rare and the structures of biological shells continue to inspire chemists towards the fabrication of nanoscale molecular frameworks[3] and the miniaturization of functional microstructures.[4] Selfassembly based on capsule components bearing complementary functional groups capable of reversible, noncovalent interactions such as hydrogen bonding and metal-ligand interactions has yielded molecular[5] and supramolecular capsules[2a] capable of packing molecular guests. Encapsulation places constraints on the translational motion of guest molecules[6] and reversible encapsulation allows the temporary isolation and characterization of guest molecules in small spaces. Although such capsules are constructed with the express purpose of isolating guest molecules from the bulk solvent, the medium must not disrupt the interactions that hold the components of the capsule together.

Calixarenes are attractive building blocks for a variety of supramolecular architectures[7] owing to their ability to bind neutral and cationic molecules inside their electron rich cavity and simultaneously to form multiple hydrogen bonds with the hydroxy groups. Appealing possibilities are offered by calixarenes which are capable of both complexing small guest molecules and binding to hydrogen bonding entities. In particular, functionalization of the lower rim of calixarenes with suitable binding groups has produced several cation receptors.[7e,8] While the native calixarenes do not generally possess significant solution affinity for organic molecules, their binding ability may be enhanced markedly by elaboration of the cavity. Calixarenes may also be transformed into effective solution hosts by elaborating the upper rim. Calixarenes are used as excellent three-dimensional anchors or molecular platforms to append other binding groups through the *O*-alkylation of the lower rim –OH functionalities.

The innate tunability of the excited-state properties of transition metal complexes has been exemplified best by the polypyridyl complexes of Ru(II), Os(II) and Re(I). Polypyridyl complexes of these $d^6$ metal ions, owing to their exceptional spectroscopic and photophysical properties are promising candidates for the construction of artificial photosynthetic devices,[9] luminescent tags and probes,[10] and molecular devices and machines.[11] Terpyridines and their structural analogs have gained much interest as functional templates in the fields of supramolecular and coordination chemistry and materials science.[12] Due to their distinct photophysical, electrochemical, catalytic, and magnetic properties, terpyridine-based metal complexes have been

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†Electronic supplementary information (ESI) available: Crystallographic data in CIF format, relevant absorption, emission, and excitation spectra of free ligands and complexes, cyclic voltammograms of complexes, mass and NMR spectra of all organic precursors, and free ligands, and mass spectra of complexes. CCDC reference numbers: 720988 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/xxxxxxxx.

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studied for a wide range of applications[13] covering light-to-electricity conversion, light-emitting electrochemical cells, electroluminescent systems and non-linear optical devices. Polynuclear arrays made up of the stereogenic $[Ru(bpy)_3]^{2+}$ motif gives rise to diastereomeric mixtures, whereas the achiral $[Ru(tpy)_2]^{2+}$ motif forms stereopure assemblies. Thus, ruthenium(II) complexes of terpyridine-based ligands are a good choice for the construction of polynuclear assemblies.

Supramolecular assemblies constructed by assembling molecular components via covalent bonds greatly enhance the possibilities to control the intramolecular intercomponent interactions. This approach has been very helpful to the study of photoinduced electron- and energy transfer processes[14] and obtain sophisticated functions such as stabilization of photoinduced charge separation,[15] multielectron collection,[16] harvesting of excitation energy in artificial antennas,[17] and in various logical and switching functions.[18] Calixarenes are excellent ligand frameworks for the construction of polynuclear assemblies by covalently conjugating multiple ruthenium(II)-based chromophores to the –OH functionalities at the lower rim. Polynuclear ruthenium(II) complexes of tolylterpyridine appended calixarenes are expected to exhibit enhanced photophysical and redox properties. The octanuclear $[Ru(ttpy)_2]^{2+}$ complexes appended onto the upper rim of the calixresorcarenes, reported by us, exhibit interesting properties.[19] Herein, we report the synthesis, luminescence and electrochemical studies of tetra- and octanuclear Ru(II) complexes of tolylterpyridine appended calixarenes **3** and **4**.

## Results and discussion

### Synthesis of calixarenes

5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (**1**) and 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (**2**) are synthesized by the base induced condensation of 4-*tert*-butylphenol with formaldehyde in refluxing phenyl ether and xylene, respectively. The mechanism of the base-induced oligomerization of phenols and formaldehyde has been discussed extensively.[20] The *p*-substituent plays a significant role in the formation of the cyclic tetramer and the methodology employed in the synthesis of the octamer in the present study is advantageous over earlier reported procedures in obtaining a single product.

### Crystal structure of calix[4]arene

The X-ray crystal structure of **1** reveals that the molecule possesses a rigid cone conformation and is isomorphous with that of the earlier reported[21] adduct of **1** with toluene ($P4/n$, $a = b = 12.754(5)$ Å, $c = 13.787(6)$ Å; $\alpha = \beta = \gamma = 90°$). The crystallographic data and ORTEP representation of **1** are presented in the electronic supplementary information section.

### Synthesis of tolylterpyridine appended calixarenes

The tolylterpyridine functionalized tetra- and octanucleating calixarenes $\mathbf{L^1}$ and $\mathbf{L^2}$ are synthesized by the *O*-alkylation of the calix[4]arene (**1**) and calix[8]arene (**2**) (1 equiv) with 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine (ttpy-Br) (4 equiv for $\mathbf{L^1}$ and 8 equiv for $\mathbf{L^2}$) in the presence of cesium carbonate (5 equiv for $\mathbf{L^1}$ and 10 equiv for $\mathbf{L^2}$) as the proton scavenger in dry DMF for $\mathbf{L^1}$ and tetrahydofuran for $\mathbf{L^2}$ under inert atmosphere.

### NMR spectra of ligands

The NMR spectra of the tetra- and octanucleating ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ show resonances corresponding to eleven and twenty different proton and carbon environments, respectively. The signal pattern indicates the presence of different electronic environments for the tolylterpyridine groups, probably as a result of the slow interconversion of the protons of the tolylterpyridine moieties on the NMR timescale.

### Synthesis of complexes

The tetra- and octanuclear complexes $[\{Ru(ttpy)\}_4(\mathbf{L^1})](PF_6)_8$ (**3**) and $[\{Ru(ttpy)\}_8(\mathbf{L^2})](PF_6)_{16}$ (**4**) are prepared by the reaction of the preformed tetra- and octanucleating calixarene based ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ (1 equiv) with $[Ru(ttpy)Cl_3]$ (4 equiv for **3** and 8 equiv for **4**) in refluxing ethylene glycol under inert atmosphere (Scheme 1). The complexes are isolated in the solid state as hexafluorophosphate salts.

### Electronic absorption and luminescence spectra of complexes

The electronic absorption spectra of the tetra- and octanuclear ruthenium(II) complexes **3** and **4** feature ligand-centered ($^1$LC) $\pi$–$\pi^*$ transitions in the UV region and MLCT ($d_\pi$–$\pi^*$) transition at 490 nm. The molar extinction coefficients of the electronic absorption bands are roughly linearly dependent on the number of metal-based chromophores. The electronic absorption spectra of the complexes are presented in Figure 1 and the electronic absorption and emission spectral data and the emission lifetimes are presented in Table 1.

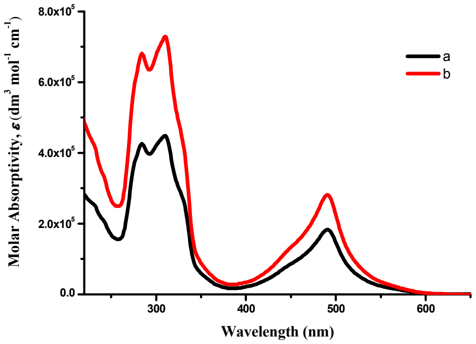

**Fig. 1** Electronic absorption spectra of (a) $[\{Ru(ttpy)\}_4(\mathbf{L^1})](PF_6)_8$ (**3**) and (b) $[\{Ru(ttpy)\}_8(\mathbf{L^2})](PF_6)_{16}$ (**4**) in acetonitrile at room temperature.

The excitation spectrum of the free ligand $\mathbf{L^1}$ consists of bands at 272 and 312 (sh) nm and that of $\mathbf{L^2}$ contains bands at 258 (sh), 275 and 311 (sh) nm. The free ligand $\mathbf{L^1}$ emits at 342 (sh) and 353 nm and $\mathbf{L^2}$ emits at 342 (sh) and 354 nm in fluid solution at room temperature. The emission bands are independent of the excitation wavelength. The complexes do not emit in solution at room temperature, but they exhibit a Ru(II) centered emission band originating from the $^3$MLCT state in the solid state at room

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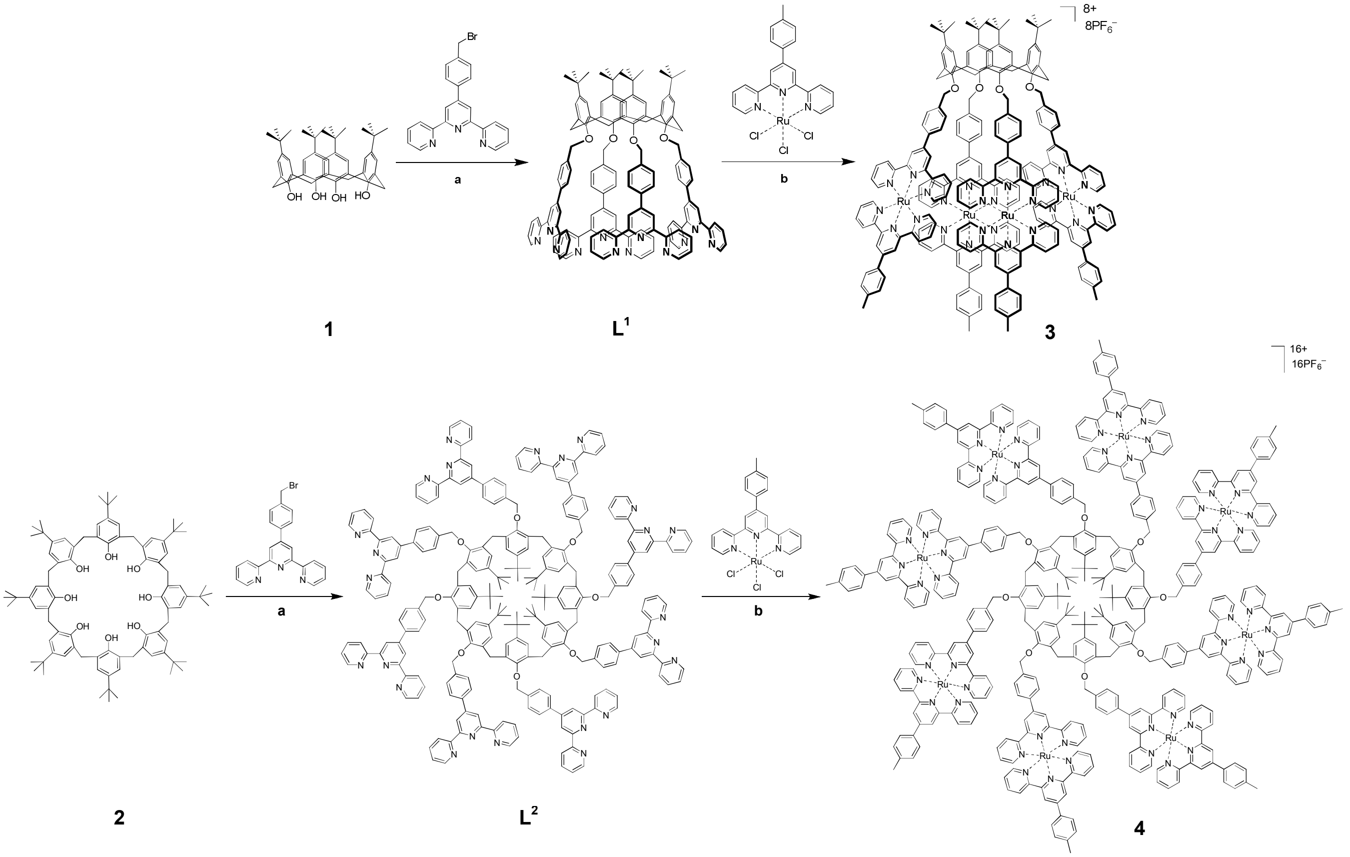

**Scheme 1** Synthesis of the polynuclear complexes [{Ru(ttpy)}$_4$(**L$^1$**)](PF$_6$)$_8$ (**3**) and [{Ru(ttpy)}$_8$(**L$^2$**)](PF$_6$)$_{16}$ (**4**): (a) Cs$_2$CO$_3$, DMF (**L$^1$**) or THF (**L$^2$**), reflux, Ar, 36 h; (b) ethylene glycol, reflux, Ar, 8 h, KPF$_6$.

**Table 1** Photophysical and electrochemical data of the complexes

| Complex | Entry no. | Electronic absorption band$^a$ (nm) ($\varepsilon \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$) | Luminescence$^a$ $\lambda_{max}$ (nm) | | | $E_{½}$$^b$ (V) | |
|---|---|---|---|---|---|---|---|
| | | | CH$_3$CN, 293 K | Solid state, 293 K | CH$_3$CN, 77 K | Metal centered oxidation | Ligand centered reduction |
| [{Ru(ttpy)}$_4$(**L1**)](PF$_6$)$_8$ | **3** | 284 (42.60)<br>309 (44.75)<br>490 (18.25) | – | 663 | 650, 690 | 1.27 | −1.18, −1.40 |
| [{Ru(ttpy)}$_8$(**L2**)](PF$_6$)$_{16}$ | **4** | 284 (68.08)<br>310 (72.92)<br>490 (28.07) | – | 666 | 650, 690 | 1.25 | −1.22, −1.44 |
| [Ru(ttpy)$_2$]$^{2+c}$ | – | 490 (2.80) | 640 | – | 628 | 1.24 | −1.24, −1.47 |

$^a$ Absorption and emission spectra were recorded using 10$^{-6}$ M solution of the complexes in acetonitrile. $^b$ The data are computed from the cyclic voltammograms recorded on a glassy carbon millielectrode in acetonitrile (10$^{-3}$ M) using tetraethylammonium perchlorate as the supporting electrolyte (0.1 M) at 293 K at the scan rate of 50 mVs$^{-1}$. Potentials are reported in volts versus Ag/Ag$^+$. $^c$ Data taken from ref. 22.

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temperature at 663 nm and 666 nm and in frozen acetonitrile at 77 K at 650 and 690 nm, respectively. The emission maxima at 77 K are bathochromically shifted compared to that of the parent complex $[Ru(ttpy)_2]^{2+}$. The acute bite angle of the tridentate tolylterpyridine ligand activates the radiationless decay process through the $^3$MC states rendering the complexes non-emissive in fluid solution at ambient temperature. The electronic absorption and luminescence spectra of the polynuclear complexes **3** and **4** exhibit similar features suggesting minimal electronic interaction among the tolylterpyridine units. Each $[Ru(ttpy)_2]^{2+}$ chromophore on the periphery of the calixarenes is spectroscopically equivalent indicating that the excited states are essentially localized on the chromophore. The emission spectra of the complexes are depicted in Figure 2.

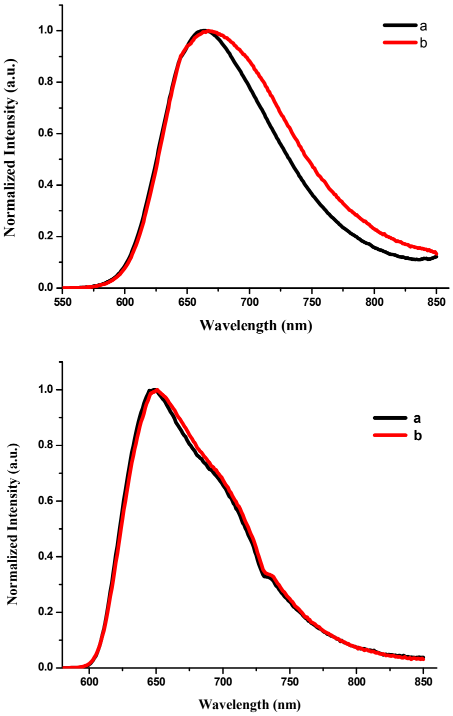

**Fig. 2** Emission spectra of (a) $[\{Ru(ttpy)\}_4(\mathbf{L^1})](PF_6)_8$ (**3**) and (b) $[\{Ru(ttpy)\}_8(\mathbf{L^2})](PF_6)_{16}$ (**4**): (**A**) solid state at room temperature, (**B**) acetonitrile at 77 K.

### Electrochemistry of complexes

The redox behavior of the complexes has been investigated in acetonitrile to complement the spectroscopic data. The cyclic voltammetric data for the complexes **3** and **4** are presented in Table 1. The complexes undergo one metal-centered oxidation in the positive potential window (0 to 1.5 V) and two successive ligand-centered reductions in the negative potential window (0 to −2 V). In ruthenium(II) polypyridyl complexes, the highest occupied molecular orbital (HOMO) is metal-based and the oxidative processes are, therefore, metal-centered, whereas the lowest unoccupied molecular orbital (LUMO) are ligand-based and the reduction processes are ligand centered.[16d,22a,23] The single metal-based redox process suggests that each ruthenium(II) chromophore is electronically “isolated” from the electrochemical viewpoint. The cyclic voltammograms of the complexes are very similar suggesting that the calixarenes have little effect on the electronic environment of the ruthenium(II) bis(tolylterpyridine) chromophores.

## Conclusions

A synthetic protocol has been established for incorporating $[Ru^{II}(ttpy)_2]$ chromophores onto the calixarene frameworks. The study demonstrates the versatility of calixarenes in the construction of polynuclear ruthenium(II) complexes. The methodology developed in the present work can be exploited to synthesize a variety of polypyridine ligands appended calixarenes and their polynuclear complexes. Further, the present work has a wide scope of developing several polynuclear compounds of differing electronic and geometric structures to assess how changes in such characteristics are manifested in polynuclear assemblies. The high nuclearity of the complexes does not affect their solubility in organic solvents, a unique feature of calixarene-based compounds. The temperature dependent Ru(II) emission confirms that the thermally activated decay via the $^3$MC states is efficient in these systems. The high molar absorption coefficients of the polynuclear complexes due to the increase in the number of ruthenium bis(tolylterpyridine) chromophores promises their use in light harvesting study.

## Experimental

### Materials

Acetamide, ammonium acetate, ammonium iron(II) sulfate hexahydrate, *N*-bromosuccinimide, dibenzoyl peroxide, ethylene glycol, formaldehyde solution (37%), hydrochloric acid (35%), potassium hydroxide, silica gel (100-200 mesh) for column chromatography, sodium hydroxide, and sodium sulfate (anhydrous) (Merck); 2-acetylpyridine, cesium carbonate, phenyl ether (99%), potassium hexafluorophosphate, ruthenium(III) chloride trihydrate, 4-*tert*-butylphenol, *p*-tolualdehyde, and xylenes (isomers) (98%) (Aldrich) were used as received. Acetone, acetonitrile, carbon tetrachloride, chloroform, dichloromethane, *N,N*-dimethylformamide, ethanol, and methanol were purified by the standard procedures.[24]

### Physical measurements

CHN microanalyses were carried out using a Perkin–Elmer 2400 Series II CHNS/O Elemental Analyzer interfaced with a Perkin–Elmer AD 6 Autobalance. Helium was used as the carrier gas. Infrared spectra were recorded on a Perkin–Elmer Spectrum RX-I FT IR spectrometer in the range 4000–400 cm$^{-1}$ using KBr pellets. NMR spectra were recorded on a Bruker AVANCE III 500 MHz (AV 500) multinuclear NMR spectrometer working at 500 MHz at 25 °C. A standard 5 mm probe was used for the $^1$H and $^{13}$C NMR measurements. The electrospray ionization mass spectra (ESI MS)

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were performed using a Micromass Quattro-II Triple Quadrupole mass spectrometer. The MALDI-TOF mass spectra were recorded on a AB Sciex 4800 MALDI TOF/TOF$^{TM}$ instrument using the TOF/TOF Series Explorer$^{TM}$ software. 2,5-Dihydroxybenzoic acid or $\alpha$-cyano-4-hydroxycinnamic acid, dissolved in chloroform and acetonitrile/methanol, was used as the matrix.

The electronic absorption spectra were recorded on a Shimadzu UV-2450 UV-Visible spectrophotometer controlled by the UV Probe version-2.33 software. The spectra were recorded in the region 190–900 nm in deaerated acetonitrile, chloroform, and *N,N*-dimethylformamide at 25 °C using a matched pair of Teflon stoppered quartz cell of path length 1 cm. Fluorescence spectra were recorded on a Fluorolog-3 FL3-221 spectrofluorometer. The excitation source was a 450 W CW Xenon lamp. The band pass for the excitation and double-grating emission monochromator was set at 2 nm. A quartz cell of path length 10 mm was used. The emission spectra of the compounds were recorded in deaerated solvents. Experiments at 77K in acetonitrile frozen glasses were carried out using quartz capillary tubes immersed in liquid nitrogen contained in a quartz dewar.

Cyclic voltammetry was performed on a EG&G PAR 273A Potentiostat/Galvanostat using RDE0018 Analytical Cell Kit consisting of a thermostated cell bottom, EG&G G0229 glassy carbon disk millielectrode, platinum counter electrode, and EG&G K0265 Ag/Ag$^+$ reference electrode. The auxiliary electrode was connected to the test solution through the counter electrode bridge tube. The reference electrode was separated from the test solution through the bridge tube containing AgCl–KCl filling solution. The cyclic voltammograms were recorded using $10^{-3}$ M solution of the complexes in oxygen free acetonitrile containing 0.1 M tetraethylammonium perchlorate as the supporting electrolyte. Oxygen free argon, saturated with the solvent vapor, was flushed through each sample solution through the purge tube assembly for 30 min before voltammetry was performed and all measurements were carried out in an atmosphere of argon at 25 °C. All operations were performed through a computer using EG&G Model 270 Software and all electrochemical parameters were obtained using the EG&G PowerSuite software. The instrument was calibrated by recording the cyclic voltammograms of ferrocene (purum, Fluka) in oxygen free acetonitrile under the same experimental conditions.

X-ray diffraction was carried out using a Bruker axs Kappa ApexII single crystal X-ray diffractometer, equipped with graphite monochromated Mo($K\alpha$) ($\lambda$ = 0.7107 Å) radiation and CCD detector. The unit cell parameters were determined from 36 frames measured (0.5° phi-scan) from three different crystallographic zones using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolution (0.8 Å). The intensity data collection, integration of frames, LP and decay corrections were done using SAINT-NT (version 7.06a) software. Empirical absorption correction (multiscan) was performed using SADABS (1999) program. The structure was solved using SIR92 and refined using SHELXL-2014 programs. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were geometrically fixed at chemically meaningful positions and were allowed to ride over the parent atoms during refinement.

### Synthesis of organic precursors

4′-(*p*-tolyl)-2,2′:6′,2″-terpyridine (ttpy),[22b] 4′-(*p*-bromomethyl-phenyl)-2,2′:6′,2″-terpyridine (ttpy-Br),[25] [Ru(ttpy)Cl$_3$],[26] and 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene (**1**)[27] were synthesized by the literature methods.

### 5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octahydroxycalix[8]arene (2)

The compound **2** was synthesized by modifying the procedure reported by Casnati et al.[28] A mixture of *p-tert*-butylphenol (10 g, 66.57 mmol), formaldehyde solution (13.5 mL, 180.00 mmol), and sodium hydroxide (1.10 g, 27.51 mmol) was heated under stirring at 100 °C for 2 h under nitrogen atmosphere in a round bottom flask fitted with a Dean-Stark apparatus. Xylene (100 mL) was added to the resulting yellow viscous substance and maintained between 100−110 °C until the reaction mixture was free from water (~ 1 h) and refluxed under nitrogen atmosphere for 6 h, and cooled to room temperature. The solid compound that precipitated out was filtered through a G4 filter funnel and washed with xylene (25 mL). The solid product was stirred in a biphasic mixture of chloroform (170 mL) and hydrochloric acid (0.1 M, 80 mL) for 20 min. The organic layer was separated, washed thoroughly with water (3x100 mL), dried over anhydrous sodium sulfate (1 h), filtered, concentrated to 50 mL, and hot acetone (100 mL) was added. The white solid that separated out was filtered, dried in vacuo, and recrystallized in chloroform. The compound was obtained as a single product. White powder: (8.65 g, 80%), mp > 360 °C. Found: C, 81.37; H, 8.62. Calc. for $C_{88}H_{112}O_8$: C, 81.44; H, 8.70. $\nu_{max}$/cm$^{-1}$ 3233 $\nu$(O−H), 3053 $\nu_s$(C−H) (aromatic), 2957 $\nu_{as}$(CH$_3$), 2903 $\nu_{as}$(CH$_2$), 2868 $\nu_s$(CH$_3$), 1602, 1486, and 1452 $\nu_s$(C=C) (aromatic), 1361 $\delta_s$(CH$_3$), 1203 $\nu$(C−O), 1026, and 986 $\delta_s$(C−H) (in-plane), 873, 815, and 783 $\gamma$(C−H) (aromatic). $\delta_H$(500 MHz; CDCl$_3$; 298 K) 1.28 (72H, s, $H_a$), 3.52 (8H, d, $J$ = 13 Hz, $H_d$), 4.39 (8H, d, $J$ = 13 Hz, $H_d$), 7.20 (16H, s, $H_b$), 9.65 (8H, s, $H_c$). $\delta_C$(125 MHz; CDCl$_3$; 298 K) 29.7, 31.9, 34.0, 125.5, 128.7, 144.7, 146.6. MALDI-TOF MS: *m/z* 1319 [(M−H)+Na]$^+$, 995 [(M+Na) − $C_{22}H_{28}O_2$]$^+$, 725 [(M+Na) − $C_{40}H_{50}O_4$]$^+$.

### Synthesis of tolylterpyridine appended calixarenes L$^1$ and L$^2$

**General Procedure.** A solution of **1** or **2** (10 mmol) and cesium carbonate (50 mmol for **L$^1$** and 100 mmol for **L$^2$**) in dry DMF (2 L for **L$^1$**) or dry tetrahydrofuran (2 L for **L$^2$**), taken in a two neck round-bottom flask, fitted with a dropping funnel, was refluxed under stirring for 1 h under argon atmosphere. A solution of 4′-(*p*-bromomethylphenyl)-2,2′:6′,2″-terpyridine (40 mmol for **L$^1$** and 80 mmol for **L$^2$**) in DMF (2 L for **L$^1$**) or tetrahydrofuran (2 L for **L$^2$**) was added dropwise over a period of 1 h and refluxed under stirring for 36 h under argon atmosphere. The solution was flash evaporated to dryness and the resulting solid product was dissolved in chloroform (4 L) and washed with water (3x4 L). The organic layer was dried over anhydrous sodium sulfate, filtered, and flash evaporated. The resulting yellow solid was dried in vacuo and purified by silica gel (100-200 mesh) column chromatography by eluting with dichloromethane-hexane (7:3 v/v for **L$^1$** and 8:2 v/v for **L$^2$**).

**5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetra(4′-*p*-benzyloxy-(2,2′:6′,2″-terpyridinyl))calix[4]arene (L$^1$).** Yellow powder: (38.40 g, 64%), mp = 200 °C (dec). Found: C, 80.76; H, 5.95; N, 8.57. Calc. for $C_{132}H_{116}N_{12}O_4$: C, 81.96; H, 6.04; N, 8.69. $\lambda_{max}$(CHCl$_3$)/nm 254 ($\varepsilon$/dm$^3$

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mol$^{-1}$cm$^{-1}$ 1 75 000), 279 (2 19 000) and 315 sh (52 750). $\nu_{max}$/cm$^{-1}$ 3052 $\nu_s$(C–H) (aromatic), 2954 $\nu_{as}$(CH$_3$), 2865 $\nu_s$(CH$_3$), 1602, 1584, 1567, 1467, and 1389 $\nu_s$(C=C) and $\nu_s$(C=N) (aromatic), 1122 $\nu_{as}$(C–O–C), 790 $\gamma$(C–H), 739 $\delta$($\beta$-ring). $\delta_H$(500 MHz; DMSO-$d_6$; 298 K) 1.16 (36H, m, $H_a$), 2.05 (4H, s, $H_c$), 2.39 (4H, s, $H_c$), 4.62 (8H, s, $H_d$), 7.53 (8H, m, $H_j$), 7.89 (8H, d, $J$ = 8.5 Hz, $H_e$), 8.02 (16H, m, $H_b$, $H_i$), 8.11 (8H, d, $J$ = 9.5 Hz, $H_f$), 8.67 (8H, m, $H_h$), 8.70 (8H, s, $H_g$), 8.76 (8H, m, $H_k$). $\delta_C$(125 MHz; DMSO-$d_6$; 298 K) 22.7, 31.4, 34.1, 62.9, 118.2, 118.7, 121.4, 124.9, 127.1, 127.7, 128.2, 130.4, 130.8, 137.9, 143.5, 144.6, 148.7, 149.8, 155.5, 156.1. MALDI-TOF MS: *m/z* 1613 [M − ttpy]$^+$, 1290 [M − 2ttpy]$^+$, 971 [M − 3ttpy]$^+$.

**5,11,17,23,29,35,41,47-octa-*tert*-butyl-49,50,51,52,53,54,55,56-octa(4′-*p*-benzyloxy-(2,2′:6′,2″-terpyridinyl))calix[8]arene ($L^2$).** Yellow powder: (18.80 g, 71%), mp = 180 °C (dec). Found: C, 80.89; H, 5.95; N, 8.59. Calc. for $C_{264}H_{232}N_{24}O_8$: C, 81.96; H, 6.04; N, 8.69. $\lambda_{max}$(CHCl$_3$)/nm 255 ($\varepsilon$/dm$^3$ mol$^{-1}$cm$^{-1}$ 2 04 814), 279 (2 49 259) and 309 sh (62 962). $\nu_{max}$/cm$^{-1}$ 3051 $\nu_s$(C–H) (aromatic), 2954 $\nu_{as}$(CH$_3$), 2865 $\nu_s$(CH$_3$), 1600, 1584, 1567, 1479, 1467, and 1389 $\nu_s$(C=C) and $\nu_s$(C=N) (aromatic), 1115 $\nu_{as}$(C–O–C), 791 $\gamma$(C–H), 740 $\delta$($\beta$-ring). $\delta_H$(500 MHz; DMSO-$d_6$; 298 K) 1.37 (72H, m, $H_a$), 2.44 (16H, s, $H_c$), 4.78 (16H, s, $H_d$), 7.39 (16H, m, $H_j$), 7.48 (16H, d, $J$ = 8 Hz, $H_e$), 7.88 (32H, m, $H_b$, $H_i$), 8.05 (16H, q, $J$ = 11 Hz, $H_f$), 8.71 (32H, m, $H_h$, $H_k$), 8.77 (16H, s, $H_g$). $\delta_C$(125 MHz; DMSO-$d_6$; 298 K) 21.3, 31.3, 34.8, 64.8, 118.6, 118.7, 118.8, 121.4, 123.8, 124.0, 127.1, 127.3, 128.0, 129.7, 130.2, 136.9, 149.1, 149.2, 155.9, 156.2. MALDI-TOF MS: *m/z* 3547 [(M+H)−ttpy]$^+$, 3226 [M−2ttpy]$^+$, 2905 [M−3ttpy]$^+$, 2583 [M−4ttpy]$^+$, 2262 [M−5ttpy]$^+$, 1941 [M−6ttpy]$^+$, 1619 [M−7ttpy]$^+$.

### Synthesis of tetra- and octanuclear ruthenium(II) complexes 3 and 4

**General Procedure.** A solution of the preformed ligand $\mathbf{L^1}$ or $\mathbf{L^2}$ (0.50 mmol) and [Ru(ttpy)Cl$_3$] (2.00 mmol for **3** and 4.00 mmol for **4**) in ethylene glycol (500 mL) was refluxed with stirring under argon atmosphere for 8 h. The dark red solution was cooled to room temperature, water (500 mL) was added, and filtered. An aqueous saturated solution of potassium hexafluorophosphate was added to the filtrate with stirring whereupon a dark red solid separated out. The compound was filtered, washed with water, dried in vacuo, and recrystallized in hot methanol.

**[{Ru(ttpy)}$_4$(L$^1$)](PF$_6$)$_8$ (3).** Dark red powder: (1.98 g, 84%). Found: C, 54.08; H, 3.73; N, 6.85. Calc. for $C_{220}H_{184}N_{24}O_4Ru_4P_8F_{48}$: C, 55.14; H, 3.87; N, 7.02. $\lambda_{max}$(CH$_3$CN)/nm 284 ($\varepsilon$/dm$^3$ mol$^{-1}$cm$^{-1}$ 4 26 000), 309 (4 47 500), 325 sh (3 10 500)and 490 (1 82 500). $\nu_{max}$/cm$^{-1}$ 3048 $\nu_s$(C–H) (aromatic), 2923 $\nu$(C–H), 1607, 1466, 1431, and 1406 $\nu_s$(C=C) and $\nu_s$(C=N) (aromatic), 838 $\nu$(P-F), 787 $\omega$(C-H), 558 $\delta$(F-P-F). ESI MS: *m/z* 952 [M−(3PF$_6$ + 2{Ru(ttpy)$_2$} + 5H)]$^{3+}$, 906 [M−(4PF$_6$ + 2{Ru(ttpy)$_2$})]$^{3+}$, 404 [(M + 4H)−8PF$_6$]$^{9+}$, 381 [M−(8PF$_6$ + 3{Ru(ttpy)$_2$})]$^{2+}$.

**[{Ru(ttpy)}$_8$(L$^2$)](PF$_6$)$_{16}$ (4).** Dark red powder: (yield 3.90 g, 83%). Found: C, 54.24; H, 3.77; N, 6.89. Calc. for $C_{440}H_{368}N_{48}O_8Ru_8P_{16}F_{96}$: C, 55.15; H, 3.87; N, 7.02. $\lambda_{max}$(CH$_3$CN)/nm 284 ($\varepsilon$/dm$^3$ mol$^{-1}$cm$^{-1}$ 6 80 769), 310 (7 29 231), 324 sh (4 97 692)and 490 (2 80 769). $\nu_{max}$/cm$^{-1}$ 3072 $\nu_s$(C–H) (aromatic), 2952 $\nu$(C–H), 1607, 1478, 1429, and 1406 $\nu_s$(C=C) and $\nu_s$(C=N) (aromatic), 846 $\nu$(P–F), 788 $\omega$(C–H), 558 $\delta$(F–P–F). ESI MS: *m/z* 908 [M−16PF$_6$]$^{8+}$, 892 [(M+K)−11PF$_6$]$^{9+}$, 382 [M−(16PF$_6$+7{Ru(ttpy)$_2$})]$^{2+}$.

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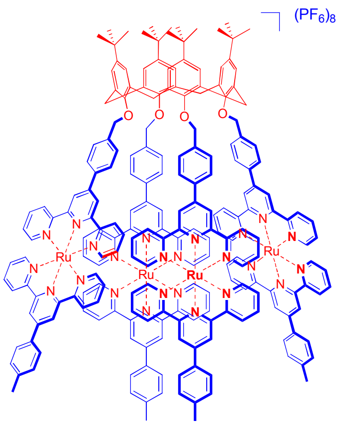
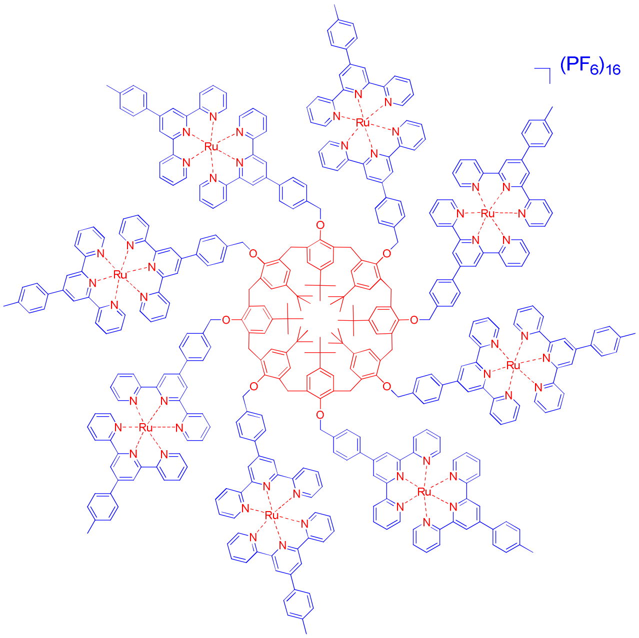
Tetra- and octanuclear ruthenium(II) complexes of tolylterpyridine appended calixarenes are synthesized and their luminescence and electrochemical properties are investigated.





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