Hirshfeld Surface Analysis of Anisylresorcinarene and Luminescence Studies of its Benzimidazolyl Appended Ru(II) polypyridyl Complexes

Ligimol Louis, D. Suresh Kumar

Supramolecular Research Laboratory, Department of Chemistry, Loyola College, Chennai-600034, India

Abstract: The macrocyclic precursor, 2,8,14,20-tetrakis(4-methoxyphenyl)-4,6,10,12,16,18,22,24-octahydroxycalix[4]resorcinarene (P1), has been synthesised and characterised using IR, NMR, ESI mass spectrometry and single crystal X-ray diffraction analysis. P1 crystallizes in the monoclinic crystal system with P2₁/c space group. Its Hirshfeld surface analysis has been carried out. The other precursor, 2-(pyridin-2-yl)-1H-benzimidazole (P2) and complex precursors, dichlorobis(phenanthroline)ruthenium(II) hydrate (P3) and dichlorobis(2,2'-bipyridine)ruthenium(II) hydrate (P4) are prepared by the modification of reported procedures. The macrocyclic ligand, benzimidazolyl functionalized anisylresorcinarene (L), has been synthesised by the aminomethylation of P1 using P2 and characterised using IR and ESI mass spectrometry. Tetranuclear ruthenium(II) phenanthroline and bipyridine complexes of L have been synthesised and characterized by IR, ESI-MS and electronic absorption spectroscopy. Upon excitation at the excitation maxima the complexes emit from the 3MLCT state at 600 and 624 nm, respectively. The emission band of complexes at 77 K in frozen CH₃CN is hypsochromically shifted to 594 and 616 nm, respectively with noticeable increase in the emission intensity and in quantum yields. The complexes show monoexponential decay profile in acetonitrile and have life times of 142 and 200 ns, respectively.

Keywords: Resorcinarene; Ru(II) complex; 2-(pyridin-2-yl)-1H-benzimidazole; Hirshfeld surface analysis

1. Introduction

The coherent design and synthesis of novel architectures are of current interest in the field of supramolecular chemistry [1]. The resorc[α]resorcinarenes, which are calixarenes formed from resorcinol building blocks linked by methylene groups [2], are utilized as supramolecular assemblies which coordinate through all three of their constituent parts: the lower rim, the phenolic groups, and the ortho position on the aromatic rings [3]. Mannich reaction is one of the main reactions employed in functionalization of resorcinarenes with polypyridine ligands [4]. The rich photochemistry of rings [3]. Mannich reaction is one of the main reactions through all three of their constituent parts: the lower rim, the phenolic groups, and the ortho position on the aromatic rings [3]. The reaction involves the synthesis, characterization and luminescence studies of tetranuclear ruthenium(II) bis(phenanthroline) and bis(bipyridine) complexes of benzimidazolyl functionalized anisylcalixresorcinarene. The Hirshfeld surface analysis of anisylresorcinarene crystal is also carried out to understand the intermolecular interaction present in the molecule.

2. Experimental Section

2.1 Reagents

Anisaldehyde, cyanopyridine, phenanthroline, 2,2'-bipyridine, ruthenium(III) chloride trihydrate, resorcinol, o-phenylenediamine, o-phosphoric acid, sodium perchlorate monohydrate (Aldrich), ammonia, hydrochloric acid (35%), and lithium chloride (Fluka) were purchased and used as such.

2.2 Physical measurements

Single-crystal X-ray structure data collections were performed on a Bruker AXS Kappa Apex II CCD diffractometer with graphite monochromatic Mo (Kα) radiation (λ) 0.71073 Å. Infrared spectra were recorded on a Perkin-Elmer spectrum RX-I FT-IR Spectrometer in the range of 4000-400 cm⁻¹. The electrospay ionization mass spectra were recorded on a micromass Quattro II triple quadrupole mass spectrometer. H NMR was recorded on Bruker AVANCE III 500 MHz (AV 500) multinuclear NMR spectrometer at 25 °C. The electronic absorption spectra were recorded on a Shimadzu UV-2450 UV-Visible spectrophotometer controlled by the UV Probe version 2.33 software. Fluorescence spectra were recorded on a Fluorolog-3 FL3-221 spectrofluorometer. The emission lifetimes were carried out using nanosecond laser flash photolysis (Applied Photophysics, U.K.). Emission quantum yields (Φ) were calculated by integrating the area under the luminescence curves and by using equation 1 [6] where OD is optical density of the compound at the excitation wavelength and A is the area under the emission spectral curve. The standard used for the luminescence quantum yield measurements was [Ru(bpy)₃]Cl₂ (Φ = 0.04) [7] and corrected for the refractive index of the solvent.

\[
\Phi = \frac{OD_{std} \cdot A_{sample} \cdot l_{sample}^2}{OD_{sample} \cdot A_{std} \cdot l_{std}^2} \cdot \Phi_{std} \quad \text{Eq. 1}
\]
2.3 Synthesis of precursor, anisylcalix[4]resorcinarene (P1)

To a solution of resorcinol (2.75 g, 25 mmol) in ethanol-water (7:3 v/v, 50 mL), was added hydrochloric acid (35%, 10 mL) stirred at 70 °C for 1 h. A solution of anisaldehyde (3.04 g, 25 mmol) in ethanol (50 mL) was added to the reaction mixture followed by water (30 mL). The resulting suspension was refluxed under stirring for 100 h and then cooled to room temperature. The solid product that separated out was filtered, washed with water, and dried to obtain a pale orange powder. The product formed was recrystallized in DMF and characterised.

Yield 4.85 g (85%), pale yellow powder, mp> 300 °C (dec.).

Analytical data calculated for $C_{56}H_{48}O_{12}$ (Mr = 913): C, 73.21; H, 5.18. Found: C, 73.67; H, 5.30. IR data $\nu_{\text{max}}/\text{cm}^{-1}$

- 3373 $\nu$(O–H)
- 2932 $\nu$(C–H) (aromatic)
- 2833 $\nu$(C–H)

Figure 1: 500 MHz $^1$H NMR spectrum of P1 in DMSO-$d_6$ at 25°C
(aliphatic), 1658, 1608 and 1510 \nu(C=\text{C}) (aromatic), 1430 \delta(C–H) (aliphatic), 1247 \nu(C–O), 822 \gamma(C–H) (aromatic). 1H NMR data (500 MHz, DMSO-d$_6$, 298 K) \delta 5.44 (4H, s, CH), 5.55 (4H, d), 6.09 (4H, s), 6.27 (8H, d), 6.50 (8H, m), 8.45 (8H, m). ESI MS: \textit{m/z} 913 \text{[M]}^+, 936 \text{[M+Na]}^+.

The volume of the filtrate was reduced to 5 mL and 50 mL of sodium perchlorate solution was added with stirring whereupon a dark red solid separated out. The product was filtered, dried and recrystallized in hot acetonitrile.

**Figure 2:** ESI-TOF mass spectrum of P1

**Figure 4:** ESI-MS spectrum of complex 1.

**Figure 5:** ESI mass spectrum of 2.

1 - Yield 0.32 g, (74%), Dark red solid. Analytical data calculated for C$_{20}$H$_{48}$N$_{16}$O$_{16}$Ru$_4$ (M = 4383.42): C, 55.90; H, 3.40; N, 8.95. Found: C, 55.75; H, 3.34; N, 8.91. IR data: \nu_{\text{max}}/\text{cm}^{-1} 3430 \nu(O-H), 3066 \nu(C=H) (aromatic), 2924 \nu(C-H) (aliphatic), 1609 and 1516 \nu(C=C) (aromatic), 1426 \delta(C-H) (aliphatic), 1097 \nu(ClO$_4$), 846 \gamma(C-H) (aromatic) 753 \omega(C-H). ESI MS: \textit{m/z} 559 \text{[M–(6ClO$_4$+4Cl$_2$H$_2$O)]}^+, 633 \text{[M+(H)-5ClO$_4$+5H$_2$O]}^+, 781 \text{[M+(H)-(4ClO$_4$+4H$_2$O)]}^+.

2 - Yield 0.31 g (75%), Dark red solid. Analytical data calculated for C$_{16}$H$_{48}$N$_{16}$O$_{16}$Ru$_4$ (M = 4191.25): C, 53.88; H, 3.56; N, 9.36. Found: C, 66.38; H, 4.13; N, 11.43. IR data: \nu_{\text{max}}/\text{cm}^{-1} 3417 \nu(O-H), 3069 \nu(C–H) (aromatic), 2920 \nu(C-H) (aliphatic), 1602 and 1597 \nu(C=C) (aromatic), 1444 \delta(C-H) (aliphatic), 1088 \nu(ClO$_4$), 763 \omega(C-H). ESI MS: \textit{m/z} 413 \text{[M–(8ClO$_4$+5H$_2$O)]}^+, 449 \text{[M–(7ClO$_4$+3Cl$_2$H$_2$O+H$_2$O)]}^+, 490 \text{[M–(7ClO$_4$+4H$_2$O)]}^+, 512 \text{[M+(H)+6ClO$_4$]}^+.

### 3.1 Synthesis and Characterisation of organic precursors, ligand and complexes.

2.4 Synthesis of ligand (L)

To a solution of P1 (1 g, 1.09 mmol) and 2-(pyridin-2-yl)-1H-benimidazole (P2) (0.85 g, 4.38 mmol) in a solvent mixture of 2-methoxyethanol–ethanol (2:1 v/v, 60 mL), was added 37% aqueous solution of formaldehyde (0.12 ml, 4.38 mmol) under argon atmosphere and refluxed for 48 h. The resulting solution was flash evaporated to get red precipitate and recrystallized.

**Figure 3:** ESI-TOF mass spectrum of L.

Yield 6.3 g (72 %) Red powder, Mp>300 °C (dec.). Analytical data calculated for C$_{10}$H$_{26}$N$_{12}$O$_{12}$ (M = 1741): C, 74.47; H, 4.86; N, 9.65. Found: C, 74.35; H, 4.68; N, 9.58. IR spectrum: \nu/cm$^{-1}$ 3316 \nu(O-H), 2926 \nu(C-H) (aromatic), 2833 \nu(C=C) (aliphatic), 1605, 1510 \nu(C=C) (aromatic), 1466 \delta(CH$_2$-N), 1246 \nu(C-O), 745 \omega(CH$_2$). ESI MS: ESI MS: \textit{m/z} 1227 \text{[M–(2P2+4OCH$_3$+H)]}^+, 1257 \text{[M–(2P2+3OCH$_3$+H)]}^+, 1354 \text{[M+(H)+2P2]}^+.

2.5 Synthesis of tetracenate ruthenium(II) polypyridyl complexes, \text{[[[Ru(phen)$_2$Cl]$_2$L]](ClO$_4$)]$^-$ (1), and \text{[[[Ru(bpy)$_2$Cl]$_2$L]](ClO$_4$)]$^-$ (2)

A solution of the ligand L (0.17 g, 0.10 mmol) and [Ru(phen)$_2$Cl]$_2$·2H$_2$O (0.21 g, 0.4 mmol) or [Ru(bpy)$_2$Cl]$_2$·2H$_2$O (0.20 g, 0.4 mmol) in DMF (50 mL) was refluxed with stirring under an argon atmosphere for 12 h. The resultant dark suspension was cooled and filtered.
The acid catalyzed condensation of resorcinol (1 equiv) with 4-methoxybenzaldehyde (1 equiv) upon refluxing in ethanol-water mixture gives P1 (Scheme 1). It is characterized by CHN analysis, IR, NMR, ESI mass spectrometry and single crystal x-ray diffraction analysis. The absence of aldehyde (C=O) stretching vibration and presence of intermolecular hydrogen bonded hydroxyl (-OH) stretching in FT-IR spectrum of P1 confirms the condensation reaction. The 1H NMR spectrum shows resonance signals for aromatic, hydroxyl, methoxy and methine bridge protons (Figure 1). The mass spectrum of P1 shows a peak at m/z 913 due to molecular ion species, [M]+ (C_{64}H_{48}O_{12}) (Figure 2). The compound 2-(pyridin-2-yl)-1H-benzimidazole (P2) was prepared by the condensation of equimolar amount of 2-cyanopyridine and o-phenylenediamine in o-phosphoric acid by using the modified procedure reported by Addison [8]. The benzimidazolyl pyridine functionalized anisylcalix[4]resorcinarene (L) was synthesized by the reaction of anisylcalix[4]resorcinarene (P1) with 2-(pyridin-2-yl)-1H-benzimidazole (P2) and formaldehyde in solvent mixture of ethanol and 2-methoxyethanol (Scheme 1). The ligand L is characterized by CHN analysis, IR, and mass spectrometry. In FT-IR spectrum of L, the band at 1466 cm⁻¹ is due to scissoring of -CH₂- connected to tertiary amine, confirming the formation of CH₂ bridge in the ligands. The ESI-TOF mass spectrum of L shows a peak at m/z 1473 corresponding to the fragment [M-(2C₆H₄OCH₁+3H₂O)]⁺ formed by the removal of two methoxyphenyl groups and three water molecules from the molecular ion. The peak at m/z 1354 is due to the fragment [(M+H)-2P₂]⁺ formed by the loss of two benzimidazolyl pyridine groups followed by the addition of one hydrogen atom to the molecular ion (Figure 3). The precursor complexes, [Ru(phen)₃Cl₂]·2H₂O (P3) and [Ru(bpy)₃Cl₂]·2H₂O (P4) were synthesized by the reaction of RuCl₃·H₂O (1 equiv) and phenanthroline or bipyridine (2 equiv) in refluxing DMF in the presence of lithium chloride as reported by Sullivan et al [9].

The reaction of ruthenium precursor complexes, P3 or P4, with the ligand L (1 equiv) in N,N-dimethylformamide, as per the Scheme 2, formed the stable complexes of 1 and 2, respectively. The tetranuclear complexes were characterized by CHN analysis, IR, ESI MS, and electronic absorption spectroscopy. The IR spectral bands at 1097 and 1088 cm⁻¹ confirm the presence of perchlorate counter ion in complexes 1 and 2, respectively. The ESI-TOF mass spectra of the complexes give the peaks corresponding to the fragment ions of the complexes (Figure 4 and 5).

3.2 Crystal structure of P1

The ORTEP representation of P1 with all atoms presented as 40% probability ellipsoid is given in Figure 6. The compound P1 crystallizes in monoclinic crystal system with P_{2₁}space group. The cell parameters are a = 17.4950(5) Å, b = 11.6056(3) Å, c = 19.7364(6) Å, α = γ = 90°, β = 74.923(3)°, V = 3630.4(3) Å³ and Z = 2. The molecule possesses a cis-trans-trans (cct) configuration and a rigid chair-like conformation. The asymmetric unit is comprised of half of the anisylresorcinarene molecule which can be completed using the two fold rotation axis (axis passing through the centre of the molecule). The solvent molecules are found to be highly disordered throughout the crystal lattice and so they are removed using SQUEEZE program. The resorcinol hydroxy groups are found to involve in the intermolecular H-bonding with the -OCH₃ group of the nearby molecule that the C-H...O interactions between the two molecules also stabilise the crystal lattice (Figure 7).
3.4 Fingerprint plots of P1

Two dimensional summaries of the intermolecular interactions in the crystal system are provided by a fingerprint plot of $d_e$ versus $d_i$. Figure 9 displays the two dimensional fingerprint plots for the P1 molecule which involve features like spike of various length and thickness corresponding to all the intermolecular interaction present within the crystal structure. The wing like peripheral spikes represent C-H contacts in fingerprint plot whereas hydrogen bonding are present as longer and thinner spikes and the non-directional H···H contacts are characterized by broader spikes.

3.5 Luminescence properties of complexes at 298 and 77 K.

The tetranuclear ruthenium(II) complexes exhibit electronic absorption bands at 263, 317 and 332 nm for 1, and 289, 317 and 333 nm for 2 assignable to the ligand centered $\pi-\pi^*$ transitions and broad absorption bands at 445 and 457 nm for 1 and 2, respectively, characteristic of the $3^{\text{MLCT}}$ transition.

The emission spectra of the complexes were recorded in CH$_3$CN at 298 K and 77 K. Upon excitation onto their excitation maxima, 1 and 2 complexes exhibit emission bands at 600 and 624 nm, respectively due to $3^{\text{MLCT}}$ emission at 298 K. The complexes show blue shift in emission maxima in comparison with the parent compound $[(\text{bpy})_2\text{Ru(P4)}]^+$ [11]. The emission band of complexes 1 and 2 at 77 K in frozen CH$_3$CN is hypsochromically shifted to 594 and 616 nm, respectively with noticeable increase in the emission intensity due to rigidochromic effect which is characteristic of typical MLCT emitters [12]. The quantum yields of 1 and 2 have increased from 0.003 to 0.04; and 0.013 to 0.23, respectively, when the temperature is decreased from 298 K to 77 K. The complexes show monoeponential decay profile in acetonitrile and have life time of 142 and 200 ns for 1 and 2, respectively. The absorption and emission spectra are depicted in Figures 10 and 11, respectively.

4. Conclusion

A new benzimidazolyl functionalized anisylicalix[4]-resorcinarene and its tetranuclear Ru(II) polypyridyl complexes have been prepared. The study demonstrates the versatility of calixresorcinarenes in the assembly of polynuclear ruthenium(II) complexes. The methodology developed in the present work can be exploited to synthesize a series of polypyridine functionalized calixresorcinarenes. The tetranuclear Ru(II) complex is stable in solution and solid state under ambient conditions and is reasonably soluble in organic solvents. The ligand offers a wide scope in constructing a plethora of complexes by inserting different metal cations to vary and fine-tune the electronic properties in such polynuclear assemblies.

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References


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