Tetrahedron 65 (2009) 2196–2200

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An efficient phosphate sensor: tripodal quinoline excimer transduction

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ARTICLE INFO

Article history:
Received 29 September 2008
Received in revised form 12 January 2009
Accepted 14 January 2009
Available online 20 January 2009

ABSTRACT

A novel quinoline based tripodal receptor that shows intermolecular excimer emission has been designed and synthesized. The excimer emission has been used to confirm the selective recognition of phosphate ion. It combines three different types of N-donor with the elegant fluorescent signaling properties.

1. Introduction

Selective recognition and sensing of anions by artificial receptors have attracted considerable attention during the past decades, because of their significant importance and potential applications in biological, environmental, and supramolecular sciences.[1] Recognition of anionic guests is a combine effect of non-covalent interactions between host–guest, the geometry, basicity of the anion and the nature of the solvent.[2] Among these non-covalent interactions, hydrogen bonding is directional, a feature, which allows for the possibility of designing receptors with specific shapes that are capable of differentiating between anionic guests with different geometries. Due to the many possible applications in analytical chemistry and biomedical research considerable attention has been focused on the design of receptors that have the ability to selectively bind and sense anions through an optical response.[3]

Phosphate ions and their derivatives play important roles in signal transduction and energy storage in biological processes.[4] Cyclic peptides, combined amine–amide systems have been used to recognize phosphate as well as other anions in 80% H_2O/MeOH[5] and polar organic solvents.[6] However, we have reported here tripodal aminoquinoline based ligand, which have three chemically different types of nitrogen donating sites. The sensitivity provided by the fluorimetric analysis (ranging from 10^{-5} to 10^{-8} M for the concentration of the fluorescent probe) provides a rich field for this development. Moreover, the additional circumstance of having a host (containing the fluorescent probe), whose fluorescence properties are not only based on its fluorescence intensity but also presents new emission bands, resulting from specific movements and interactions with the guest molecules, provides additional and useful information on the nature of host–guest interactions. The mechanisms used in the signaling process for anion sensing are generally photo-induced electron transfer (PET),[7] metal-to-ligand charge transfer (MLCT),[8] excimer/exiplex formation, and intramolecular charge transfer (ICT),[9,10] etc. Excimer-based sensors have often been used to probe host–guest interactions with anions and/or cations in organic solvent media.[11] However, most of the studies related to excimer-based sensors are confined to host containing polyaromatic unit.

In our continuing effort to design and synthesis of new supramolecular fluorescent host molecules, which can encapsulate various types of guest,[12] in this report we describe the synthesis of a new aminoquinoline based tripodal ligand ($\mathbf{L_1}$) following the literature procedure.[13] Herein we have reported the selective chemosensing properties toward phosphate anion.

2. Results and discussion

The tripodal ligand $\mathbf{L_1}$ has been synthesized using a mixture of 8-hydroxyquinoline and tris-(2-aminoethyl) amine in the presence of sodium metabisulfite (Scheme 1) under reflux condition.

Single crystal X-ray structure analysis shows that three arms are disposed in a non-parallel arrangement, which prevents the intramolecular π-stacking arrangement (Fig. 1a). However, all the aromatic quinoline moieties are disposed in the same side in the solid state. As a result it forms an open bowl shape cavity (see Supplementary data), which can accommodate spherical anions via N–H⋯X^- type hydrogen bonding. Bridge head tertiary N atom is also present in *endo*-conformation, which can also enhance the anion binding in the semi-flattened cavity. In the solid state it forms several weak C–H⋯π interactions and results in the formation of brick-wall type 3D network (Fig. 1b).

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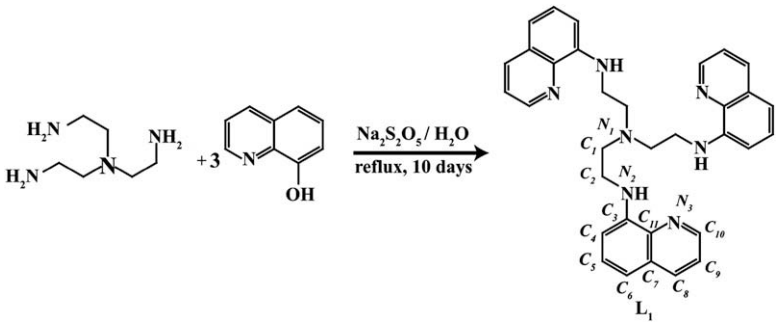
doi:10.1016/j.tet.2009.01.049



Scheme 1. Synthesis of $\mathbf{L_1}$.

The UV–vis spectrum of $\mathbf{L_1}$ shows a high-intensity band in the UV region (256 nm, ε=47,427 $M^{-1}\,cm^{-1}$) and a relatively intense band at 366 nm (ε=9427 $M^{-1}\,cm^{-1}$) with a shoulder at 340 nm (ε=7639 $M^{-1}c\,m^{-1}$) in the near visible region (Fig. 2). Peak in the UV region is corresponds to the $n\rightarrow\pi^*$ transition while that of in the near visible region (340 nm and 366 nm) is most likely due to the $\pi\rightarrow\pi^*$ transitions as seen in the other similar 8-aminoquinoline systems.[13,14] These bands are expected to shift upon protonation of amine/quinoline nitrogen atoms in the presence of different acid like HF, HCl, HBr, CH_3CO_2H, H_3PO_4, etc. In the presence of dilute H_3PO_4, peak corresponding to $n\rightarrow\pi^*$ transition has shifted to longer wavelength (276 nm) while peak due to $\pi\rightarrow\pi^*$ transition has shifted to shorter wavelength (325 nm). In addition, protonated ligand shows a broad band centered on 450 nm corresponds to intramolecular charge transfer (ICT). Similar changes in the absorption spectra were observed in case of other acids (see Supplementary data). However, addition of salt of the corresponding anions shows no significant changes in the absorption spectrum.

$\mathbf{L_1}$ shows monomer emission at 310 nm when excitated at 270 nm. With gradual increase in concentration of $\mathbf{L_1}$ the peak corresponds to monomer decreases gradually with simultaneous increase of an additional red-shifted and non-structured emission band, centered at 475 nm. The peak at 475 nm is assigned to the excimer emission which is characteristic to the similar quinoline based systems[15] (Fig. 2, inset). The excimer emission resulted from the intermolecular excimer formation, rather than intramolecular interaction, as indicated that dilute solution shows only the presence of monomer emission. The spectrum shows an isoemissive point at 410 nm. Anions are known to form strong N–H$\cdots X^-$ type of hydrogen bond with amine groups. However, anions do not interact with the aromatic ring or quilinoline nitrogen atoms of the ligand. Figure 3 shows the emission spectra of $\mathbf{L_1}$ with increasing concentrations of sodium phosphate (Na_3PO_4) in THF at 298 K. Addition of Na_3PO_4 leads to a decrease in the emission intensity of the excimer band only without showing isoemissive points (Fig. 3). Protonation of amine/quinoline nitrogen atoms prevents the intermolecular excimer formation due to charge repulsion. Moreover, it is already known that protonated pyridine moieties quench the fluorescence of known fluorophore.[16] Hence in the presence of acid, we have encountered the quenching of monomer as well as excimer fluorescence (Fig. 3, inset). However, the degree of quenching of excimer emission is dependent on the nature of the anion, which

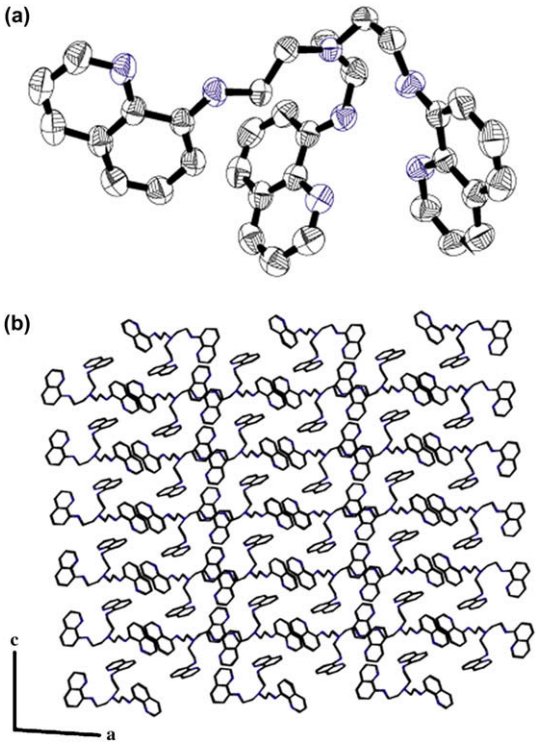


Figure 1. (a) ORTEP plot (50% probability) and (b) packing diagram of $\mathbf{L_1}$.

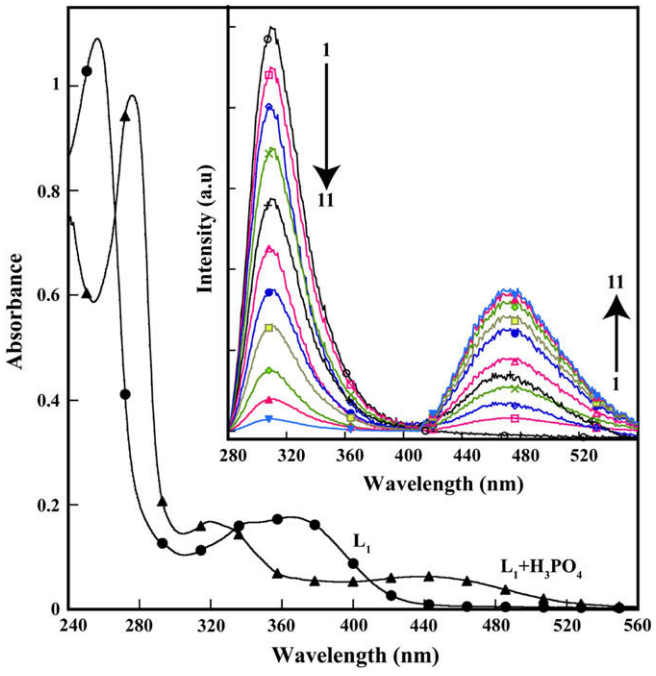


Figure 2. UV–vis spectra of $\mathbf{L_1}$ and in the presence of H_3PO_4 in THF. Inset: Fluorescence spectra of $\mathbf{L_1}$ of different concentration in THF at 298 K. [$\mathbf{L_1}$]: (1) 0.2, (2) 0.4, (3) 0.6, (4) 0.8, (5) 1.0, (6) 1.2, (7) 1.4, (8) 1.6, (9) 1.8, (10) 2.0, and (11) 2.2 μM.

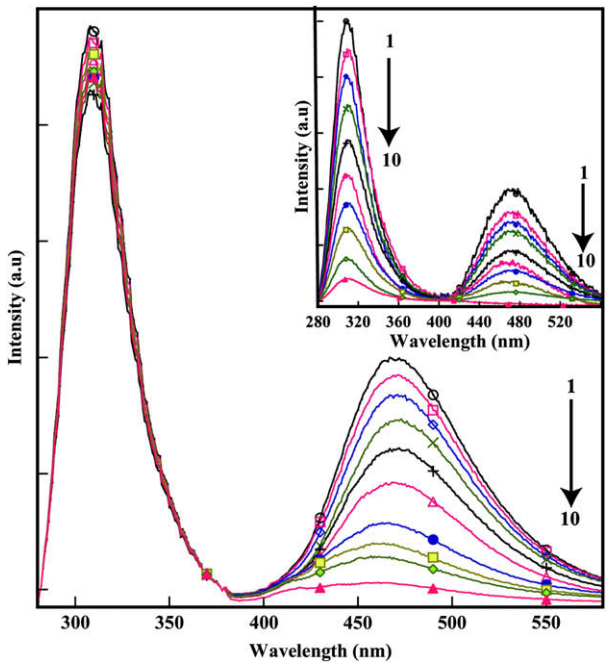


Figure 3. Fluorescence spectra of $\mathbf{L_1}$ in the presence of Na_3PO_4 in THF at 298 K. [Na_3PO_4]: (1) 0.0, (2) 1.0, (3) 2.0, (4) 3.0, (5) 6.0, (6) 10.0, (7) 15.0, (8) 20.0, (9) 25.0, and (10) 30.0 μM. Inset: Fluorescence spectra of $\mathbf{L_1}$ in the presence of H_3PO_4 in THF solution at 298 K. [H_3PO_4]: (1) 0.0, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0, (6) 6.0, (7) 8.0, (8) 12.0, (9) 15.0, and (10) 20.0 μM.

is highly selective to phophate ion (Fig. 4). The magnitude of the quenching efficiency (ϕ_Q)[17] follows the order of PO_4^{3-} (0.98)>SO_4^{2-} (0.33)>CH_3COO^- (0.23)>Br^- (0.20)>Cl^- (0.13)>NO_3^- (0.08), which is a result of combine steric and electronic effect. Excitation spectrum of the L_1 monitoring the peak at 475 nm resembles to the absorption spectra of the ligand (see Supplementary data).

Upon gradual addition of Na_3PO_4 to the THF solution of $\mathbf{L_1}$, the intensity of the emission bands decreases. The dissociation constant[18] K_d was estimated from the change in fluorescence quantum yield resulted from the titration data of $\mathbf{L_1}$ against Na_3PO_4 solution.

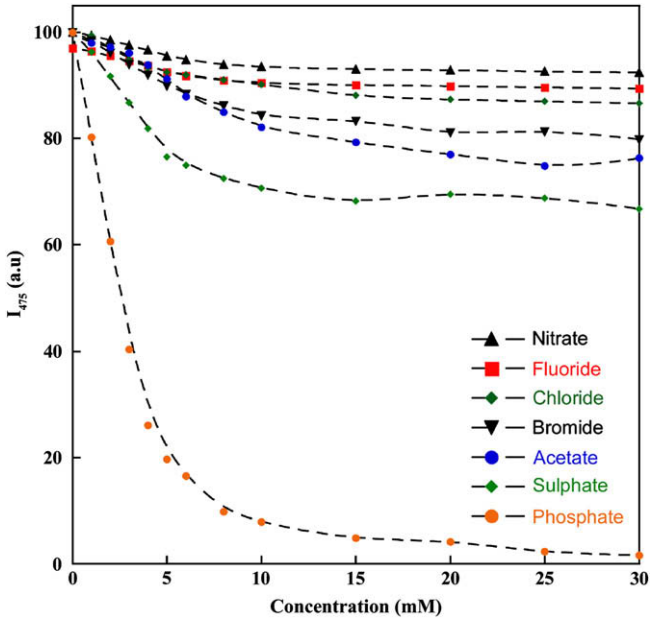


Figure 4. Plot of the emission intensity (at 475 nm) of $\mathbf{L_1}$ as a function of concentration of anions.

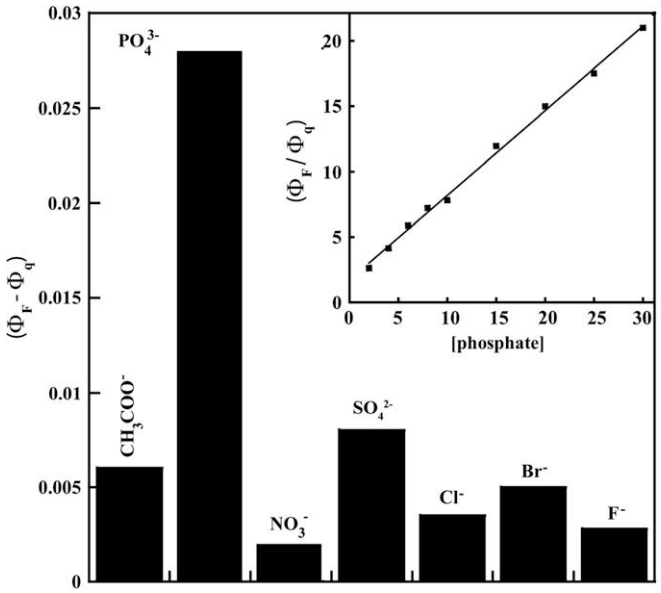
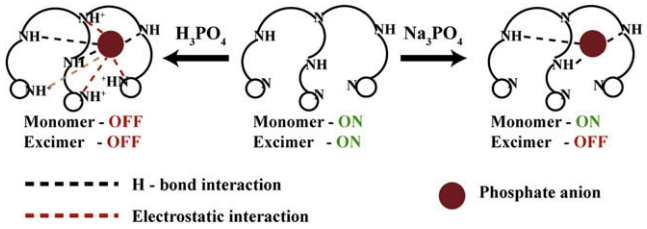


Figure 5. Schematic representation showing the change of fluorescence quantum yield ($\Phi_F - \Phi_q$) of $\mathbf{L_1}$ upon addition of the different acids. Φ_F and Φ_q are quantum yields of $\mathbf{L_1}$ in absence and presence of guest, respectively. Inset: Stern–Volmer plot with sodium phosphate.

The linear fit of the data (see Supplementary data) for Na_3PO_4 inclusion complex was obtained by plotting $\log[(F-F_{min})/(F_{max}-F)]$ as a function of logarithm of Na_3PO_4 concentration and the intercept of the linear regression determines K_d value of 6.76 μm in THF. This value indicates the formation of a stable inclusion complex and is in consistence with good correlation coefficients (>0.99). To demonstrate the selectivity of $\mathbf{L_1}$ toward phosphate, we have monitored the change in fluorescence quantum yields in the presence of different anions. Figure 5 clearly shows that $\mathbf{L_1}$ has a remarkably high selectivity toward phosphate anion in terms of change of fluorescence quantum yield. The linear Stern–Volmer response (Fig. 5, inset) with Na_3PO_4 as quencher is consistent with well-behaved fluorescence quenching systems.[19]

It is expected that N–H···PO_4^{3-} hydrogen bonding will takes place in solution. Two types of molecular interactions are possible in this mixture: (i) hydrogen bonding interactions between amine hydrogen and anion and (ii) electrostatic interaction of cationic protonated amine or quinoline group with anions. In the presence of H_3PO_4 both the interactions takes place in solution. Hence, addition of H_3PO_4 perturbs the monomer as well as excimer emission of ligand $\mathbf{L_1}$. However, in the presence of Na_3PO_4, only electrostatic interaction is possible, which results in the selective perturbation of the excimer emission of $\mathbf{L_1}$ (Scheme 2).



Scheme 2. Schematic representation of supramolecular host–guest complexes of $\mathbf{L_1}$ in the presence of phosphoric acid and its salt.

Interaction of the PO_4^{3-} with the $\mathbf{L_1}$ was further confirmed by ^1H NMR study (see Supplementary data). Broadening of the –NH signal in phosphate salt is observed compared to the pure $\mathbf{L_1}$. On the other hand, selective large downfield shift (C8 $\Delta\delta_H$=0.18, C6 $\Delta\delta_H$=0.25, C4

$\Delta\delta_H$=0.23, C7 $\Delta\delta_H$=0.27, C5 $\Delta\delta_H$=0.12, C3 $\Delta\delta_H$=0.15) occurs in aromatic protons. Overall downfield shift has been confirmed to the formation of supramolecular host–guest complexes.

3. Conclusions

In conclusion, we have reported the design and synthesis of a new quinoline based tripodal fluorescent sensor. Ligand contains three different types of N-atoms with varying pK_a values and hydrogen bond forming capabilities. An X-ray crystallographic study shows the 3D orientation of the aromatic ring on the same side resulting in the formation of bowl shape cavity for preferential binding of different type of anionic systems. This tripodal system is efficient phosphate sensor. Protonated form of phosphate is monomer as well as excimer quencher whereas unprotonated form is only excimer quencher. It shows the emission of intramolecular excimer in solution. This excimer emission is moderate and convenient for practical use to distinguish selectively phosphate ion from others anions present in the common biological systems. The excimers emission is also sensitive to the presence of acid in the solution.

4. Experimental

4.1. Materials and methods

All reagents were obtained from commercial sources and used as received. Solvents were distilled freshly following standard procedure. The IR spectra were recorded on a Perkin Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000–400 cm^{-1}. The absorption spectra were recorded on a Perkin Elmer Λ 25 UV-Visible Spectrometer at 298 K. NMR spectra were recorded on a Varian FT-400 MHz instrument. The chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) as a reference. Elemental analyses were carried out on a Perkin–Elmer 2400 automatic carbon, hydrogen, and nitrogen analyzer. HRMS spectra were recorded in WATERS LC-MS/MS system, Q-Tof Premier™ in the Central Instrument Facility (CIF) of IIT Guwahati.

4.2. X-ray crystallography

The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo Kα radiation (λ=0.71073 Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s/frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP[20] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[21] Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least squares on F^2 using SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 for Windows.[23]

Crystal data for **L_1**: CCDC # 689113; $C_{33}H_{33}N_7$, M=527.66, monoclinic, $P2(1)/c$, a=19.580(10) Å, b=8.752 (4) Å, c=16.305(7) Å, β=92.72(3)°, V=2791(2) $Å^3$, Z=4, D_c=1.259 g cm^{-3}, μ=0.075 cm^{-1}, Mo Kα radiation, R_1=0.0521, wR_2=0.1277, S=0.955.

4.3. Synthesis of tris-(*N*-ethyl-8-aminequinoline)amine (L_1)

A mixture of 8-hydroxyquinoline (1.45 g, 1 mmol), tris-(2-aminoethyl)amine (0.34 mL, 0.33 mmol), sodium metabisulfite (1.90 g, 1 mmol), and water (10 mL) was reflux for 10 days with continuous stirring. Upon cooling, the solution was made strongly alkaline (pH=12) by the addition of aqueous sodium hydroxide. The resulting mixture was cooled to rt and then filtered. The solid was extracted twice with dichloro methane (400 mL), and the dichloro methane extracts were combined, dried ($MgSO_4$), and the solvent was removed under reduced pressure. The solid obtained was triturated with hot ethanol (15 mL), filtered, and air-dried to give a yellow solid (2.43 g, 45%). It was crystallized from methanol/water mixture by slow evaporation at rt. Straw yellow solid, mp 126 °C, R_f=0.60 (EtOAC/hexane15:85). IR (KBr) ν_{max}/cm^{-1} 3445, 2956, 2932, 2865, 1615, 1512, 1460, 1243, 1118 cm^{-1}. ^{1}H NMR ($CDCl_3$; 400 MHz): δ_H 8.53 (3H, dd, J_1=2.0 Hz, J_2=2.4 Hz, ArH), 7.99 (3H, dd, J_1=2.0 Hz, J_2=6.4 Hz, ArH), 7.27 (6H, m, ArH), 6.99 (3H, dd, J_1=0.8 Hz, J_2=7.2 Hz, ArH), 6.54 (3H, m, J_1=2.0 Hz, ArH), 3.43 (9H, q, J=6.0 Hz, NH–CH_2), 3.04 (6H, t, J=6.4 Hz, N–CH_2); ^{13}C NMR ($CDCl_3$; 100 MHz): δ_c 147.2, 144.7, 137.8, 136.1, 128.6, 128.0, 121.9, 113.4, 104.6 (ArC), 53.3, 41.4 (H_2C). HRMS (ESI): m/z 527.2797 (M^+) Found: 527.2795. Elemental analysis: C, 75.10; H, 6.30; N, 18.59. Found: C, 75.15; H, 6.26; N, 18.60.

4.4. Synthesis of phosphate salt of L_1

L_1 (1 mmol) in 50% aqueous THF (20 mL) was added drop wise to a stirred alcoholic solution (20 mL) of H_3PO_4 (~1.1 mmol) at rt. The mixture was continued to stir for another 1 h at rt. This solution was evaporated to dryness under reduced pressure. A red solid powder was obtained. IR (KBr) ν_{max}/cm^{-1} 3460, 2965, 2941, 2881, 1631, 1534, 1478, 1213, 1257, 1156, 1135, 1077, 944, 879, 521. ^{1}H NMR (DMSO-d_6; 400 MHz): δ_H 8.70 (3H, d, J_1=2.8 Hz, ArH), 8.24 (3H, d, J_1=6.8 Hz, ArH), 7.50 (3H, dd, J_1=4.0, 4.4 Hz, ArH), 7.26 (3H, t, J_1=8.0 Hz, ArH), 7.11 (3H, d, J_1=8.0 Hz, ArH), 6.70 (3H, d, J_1=7.6 Hz, ArH); ^{13}C NMR (DMSO-d_6; 100 MHz): δ_c 147.22, 143.59, 137.35, 136.06, 128.72, 128.06, 122.18, 114.94, 105.72 (ArC), 52.38, 38.04 (H_2C) MS ($^+$EI): m/z 625.2566 (M^+) Found: 625.2568. Elemental analysis: C, 66.33; H, 5.80; N, 15.67. Found: C, 66.35; H, 5.82; N, 15.65.

4.5. Synthesis of phosphate salt of L_1

L_1 (1 mmol) in 50% aqueous THF (20 mL) was added drop wise to a stirred alcoholic solution (20 mL) of Na_3PO_4 (~1.1 mmol) at rt. The mixture was continued to stir for another 1 h at rt. This solution was evaporated to dryness under reduced pressure. A yellowish-red solid powder was obtained. IR (KBr) ν_{max}/cm^{-1} 3450, 2962, 2936, 2871, 1622, 1518, 1467, 1197, 1248, 1123, 1080, 990, 855, 541. However, due to the lack of solubility of the phosphate salt in the common organic solvent NMR could not be recorded. The complex was further confirmed by MS ($^+$EI): m/z 691.2024 (M^+) Found: 691.2026. Elemental analysis: C, 57.29; H, 4.81; N, 14.18. Found: C, 57.27; H, 4.84; N, 14.19.

Acknowledgements

G.D. acknowledges DST (SR/S1/IC-01/2008) and CSIR (01-2235/08/EMR-II) New Delhi India for financial support and DST-FIST for single crystal X-ray diffraction facility and CIF, IIT Guwahati. A.P. wish to thank CSIR for JRF (09/731(0045)/2007-EMR-I).

Supplementary data

Supplementary data contain crystallographic parameters, 3D space filling figure and spectra. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.01.049.

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