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Aromatic guest inclusion by a tripodal ligand: Fluorescence and structural studies

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Abstract

The newly synthesized simple tripodal ligand tris-[2-(naphthalen-2-yloxy)-ethyl]-amine (L_1) act as a fluorescence signaling system for aromatic guest. It forms inclusion complexes with several electron deficient aromatic compounds. This inclusion phenomenon has been studied by steady-state fluorescence spectroscopy and solid-state structural analysis. Electron-rich L_1 shows dramatic color change and a concomitant quenching of luminescence in solution as well as solid phase when titrated with several other electron deficient aromatic guest molecules. Rather high selectivity towards the picric acid was observed. L_1 simultaneously forms inclusion complex and organic salt co-crystal with the composition $[(L_1H^+)\,(Pic^-)] \subset PicH$ (PicH = picric acid) when crystallized in the presence of picric acid. In the solid state, it forms a strong π–π, C–H$\cdots$π and C–H$\cdots$O type interactions.

Keywords: Tripodal ligand; Fluorescence; Inclusion complexes; Aromatic guest; Co-crystal; X-ray structure

1. Introduction

The field of inclusion phenomena is at the forefront of chemical research [1]. Aromatic guest sensing has been of great interest in biological and environmental sciences for several decades. Various fluorescent sensors have been developed for detections of different kinds of aromatic guest [1]. Many examples of inclusion and sensing of aromatic guests are known in the literature [1]. However, these approaches have often involved the synthesis of structurally complicated hosts. Therefore, design and synthesis of simple sensor molecules are highly desirable. Inclusion of various kinds of guest molecules by planar host in the solid state is already reported in the literature [2]. There is no covalent bonding between guest and host, the attraction being generally due to the various weak interactions. Lattice inclusion complexes are the result of the supramolecular self-assembly of molecules in their crystal lattice with voids, which are occupied by guest species. Formation of inclusion complexes relies on the recognition processes. In the molecular recognition processes the non-covalent interactions such as hydrogen bonding, aromatic π-stacking and weak intermolecular interactions (*viz.* C–H$\cdots$π and C–H$\cdots$O) play the crucial role [3]. Intermolecular interactions involving aromatic rings are important in both biological [4] and non-biological processes [5]. Much of the work has been done in the field of directed synthesis of novel host with specific properties. Within the field of supramolecular chemistry, the non-covalent interactions between a π-electron-rich donor molecules with a π-deficient acceptor moiety through hydrogen bond and/or cooperative aromatic π–π interactions has attracted much attention in recent years [6].

Therefore, it is of high importance in the field of photochemistry to discover and/or develop new simple and sensitive sensors for aromatic guest. Synthesis of these kinds of hosts should be simple enough to have a greater utility. We have been focusing on the discovery of new supramolecular fluorescent host molecules, which can encapsulate various types of guest [7]. This paper describes the simple one-step synthesis and characterization of simple electron-rich tripodal naphthalene ether ligand tris-[2-(naphthalen-2-yloxy)-ethyl]-amine (L_1) for the first time (Scheme 1). Absorption and fluorescence stud-

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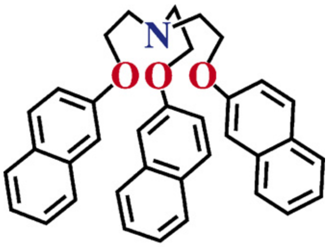

L_1

Scheme 1.

ies of the inclusion complexes with various electron deficient aromatic guests have been performed. L_1 shows a drastic change in the fluorescence intensity after guest binding in solution as well as in solid phase. We also report here the crystal structure of the inclusion complex of the organic salt co-crystal of L_1 with picric acid, which displays the formation of 3D supramolecular network.

2. Materials and methods

2.1. Materials

All the reagent grade chemicals were used without purification unless otherwise specified. Triethanol amine, thionyl chloride, 2-naphthol and all the aromatic guest molecules were obtained from Aldrich (US) and used as received. THF was dried and freshly distilled prior to use for fluorescence measurements by following the literature procedures.

2.2. Physical measurements

The ligand L_1 was characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR and mass (positive ion) spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian FT-400 (400 and 100 MHz, respectively) instrument in $CDCl_3$ with Me_4Si as the internal standard. Elemental analyses were carried out on a PerkinElmer 2400 automatic carbon, hydrogen and nitrogen analyzer. Melting points were determined with an electrical melting point apparatus by Buchi, Switzerland. The absorption spectra were recorded on a PerkinElmer Lambda-25 UV–vis spectrometer at 298 K. The steady-state fluorescence spectra were recorded on a Varian Cary-Bio spectro-fluorimeter and corrected for emission. Fluorescence quantum yield was determined in each case by comparing the corrected spectrum with that of naphthalene ($\Phi_F = 0.23$) [8] in ethanol by taking the area under the total emission using the following equation [9]:

$$\Phi_S = \Phi_R \frac{F_S A_R}{F_R A_S} \left(\frac{\eta_S}{\eta_R}\right)^2 \tag{1}$$

where Φ_S and Φ_R are the radiative quantum yields of the sample and the reference, F_S and F_R are the area under the fluorescence spectra of the sample and the reference, A_S and A_R are the absorbance of the sample and the reference (at the excited wavelength), η_S and η_R are the refractive indices of the solvent used for the sample and the reference. The quantum yield of naphthalene was measured using quinine sulfate in 1N H_2SO_4 as reference at λ_{ex} of 350 nm ($\Phi_F = 0.54$).

2.3. X-ray structure determination

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 ($\lambda = 0.71073$ Å) at 273(3) K, with increasing ω (width of 0.3° per frame) at a scan speed of 3 s per frame. The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP [10] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [11]. Structures were solved by direct methods using SHELXS-97 and refined with full-matrix least squares on F^2 using SHELXL-97 [12]. 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 [13].

2.4. Synthesis of tris-[2-(naphthalen-2-yloxy)-ethyl]-amine (L_1)

To a solution of 2-naphthol (4.32 g; 30 mmol) in 25 ml of dry *n*-propanol crushed NaOH (1.6 g; 40 mmol) was added. It was stirred for 1 h at RT. Tris-(2-chloroethyl)amine hydrochloride [14] (2.4 g; 10 mmol) was then added to the above solution at RT. For completion of the reaction, the mixture was refluxed for 6 h. The reaction mixture was poured into ice-cold water and kept overnight at low temperature. The compound was collected by filtration under suction and washed with cold ethanol. The product obtained was pale yellow in color after re-crystallization from ethyl acetate:ethanol (1:3) mixture at room temperature. Yield: 92%, mp 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 3.2 (6H, t, NCH_2), 4.24 (6H, t, OCH_2), 7.09 (3H, s, Ar*H*), 7.11 (3H, s, Ar*H*), 7.29 (3H, t, Ar*H*), 7.38 (3H, t, Ar*H*), 7.65 (9H, m, Ar*H*); ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ 54.48, 66.86, 106.60, 118.79, 123.47, 126.12, 126.59, 127.46, 128.81, 129.25, 134.33, 156.46. ESI-MS: $M^+ = 528$. Anal. Calcd. $C_{36}H_{33}NO_3$: C, 81.95; H, 6.30; N, 2.65. Found: C, 81.99; H, 6.28; N, 2.67.

3. Results and discussion

Aromatic compounds usually have electron deficient or electron-rich hydrophobic moieties, and therefore, hosts capable of forming weak complexes with aromatic guests by hydrophobic π–π interactions are extremely attractive. Presence of multiple hydrophobic electron-rich naphthalene moieties in L_1 allows us to study the inclusion phenomena with a large variety of electron deficient aromatic guest in solution and solid phase.

3.1. Synthesis

Tris-[2-(naphthalen-2-yloxy)-ethyl]-amine (L_1) has been synthesized for the first time. L_1 is synthesized via *o*-alkylation method using *n*-PrOH as a solvent. Synthesis and characteriza-

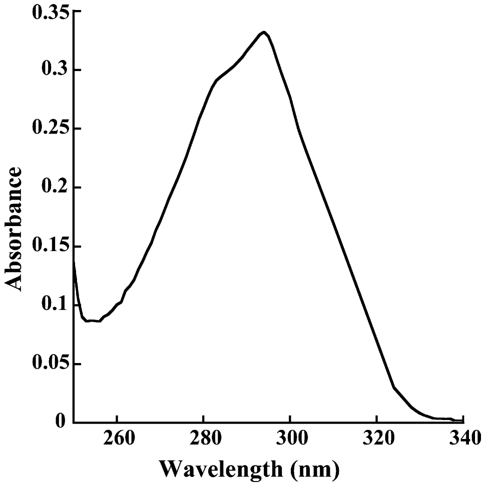

Fig. 1. UV–vis absorption spectra of L_1 ($\times 10^{-5}$ M in dry THF) at 298 K.

tion data are provided in Section 2. IR and NMR spectral data and the results of chemical analyses are in order and in complete agreement with the molecular formulae of the compound. Recrystallization from ethyl acetate:ethanol (1:3) mixture at room temperature results in the formation of thin plates, which are not suitable for single crystal X-ray diffraction studies.

3.2. Absorption spectroscopy

The UV–vis absorption spectra (Fig. 1) of L_1 ($\times 10^{-5}$ M) was recorded in dry THF at 298 K. The absorption spectrum is found to be overlapping of two transitions in the 270–310 nm regions. The $\pi \rightarrow \pi^*$ transitions of the naphthalene unit appear at 283 ($\varepsilon = 29{,}400\,(\mathrm{M\,cm})^{-1}$) and 294 nm ($\varepsilon = 33{,}300\,(\mathrm{M\,cm})^{-1}$) [7]. The band at ~250 nm is assigned [15] to the π–π interaction between the naphthalene units of the ligand. In L_1, these transitions are found to be non-solvatochromic in nature. When L_1 is titrated against different aromatic guest molecules, an absorption maximum corresponds to the guest absorption increases linearly with simultaneous decrease in the absorbance corresponds to the host molecule. In dry THF, we are unable to detect any new peak at the higher wavelength due to the formation of host–guest complex in the solution. There is also no detectable shift in the peak positions of the $\pi \rightarrow \pi^*$ transitions of the naphthalene unit upon guest addition.

Electron donor–acceptor complexes have been extensively studied in the widespread fields from biological to materials science [16]. The association behavior of the aromatic host–guest complexes and their absorption property are dependent on the ionization potential of the donor, the electron affinity of the acceptor, and environmental conditions. Formation of host–guest complex is a cumulative effect of various weak intermolecular interactions, which is much more prominent in the solid state. In polar solvents, individual stronger interactions of host and guest with the bulk solvent molecules outbreaks these weak interactions. Hence, in dry THF we have not observed any higher wavelength band in the absorption spectra due to the formation of host–guest complex. We have titrated L_1 with picric acid in a mixed solvent of ethylacetate and hexane (v/v, 1:20). The absorption spectrum of the mixed solution has a broad absorption band at ~460 nm, which is not present in the pure compounds (see supporting information). The red shifted low intensity band is attributable to the formation of host–guest complex between aromatic moieties of electron-rich L_1 and electron-poor picric acid unit [17].

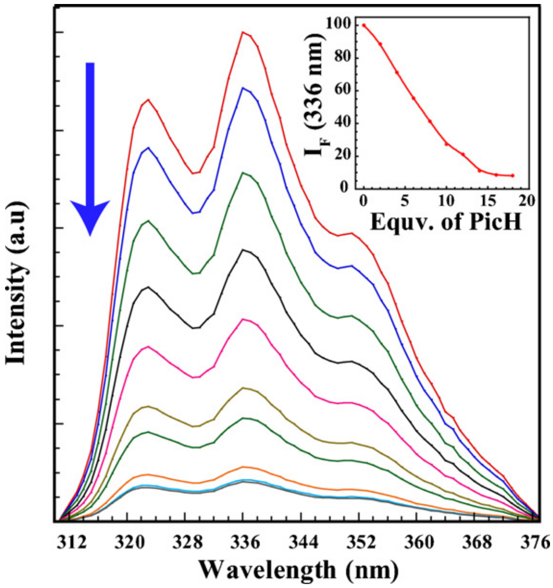

Fig. 2. Emission spectra of L_1 ($\times 10^{-6}$ M in dry THF) during the titration with picric acid. Inset: plot of the emission intensity (at 336 nm) of L_1 as a function of equivalent of picric acid added.

3.3. Fluorescence spectroscopy

The emission spectrum of L_1 was recorded in dry THF at 298 K. Free L_1 shows a locally excited structured monomer emission of naphthalene. The structured non-solvatochromic naphthalene emission of L_1 was observed with (0, 0) band centered at 323 nm (Fig. 2) along with vibrational structures at 338 and 352 nm when excited at 300 nm. The quantum yield of fluorescence monomer emission, Φ_F of the free ligand was found to be 0.19 (Table 1), which is comparable to that of naphthalene ($\Phi_F = 0.23$).

Table 1
Fluorescence quantum yield of L_1 with different aromatic guests

Sr. no.	Guest input	Φ_F	$\Phi_F - \Phi_q$
1	Nil	0.230	0.000
2	Trimesic acid	0.095	0.135
3	Trimesic acid trimethyl ester	0.102	0.128
4	Picric acid	0.019	0.211
5	*p*-Nitro aniline	0.187	0.043
6	*p*-Nitro benzoic acid	0.162	0.068
7	*p*-Nitro toluene	0.210	0.020
8	*p*-Nitro phenol	0.174	0.056
9	Nitrobenzene	0.190	0.040
10	Pyromellitic acid	0.081	0.149
11	Pyromellitic dianhydride	0.090	0.140

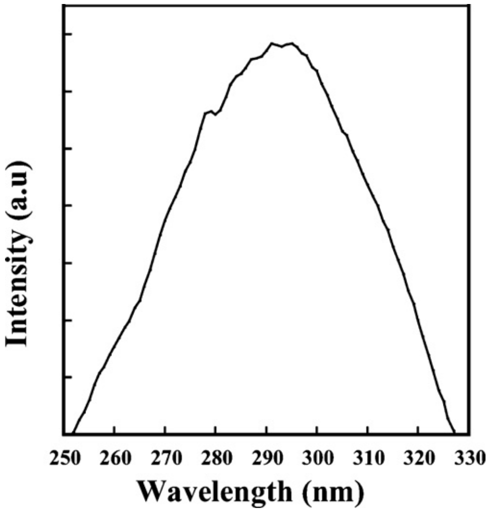

Fig. 3. Excitation spectra of L_1.

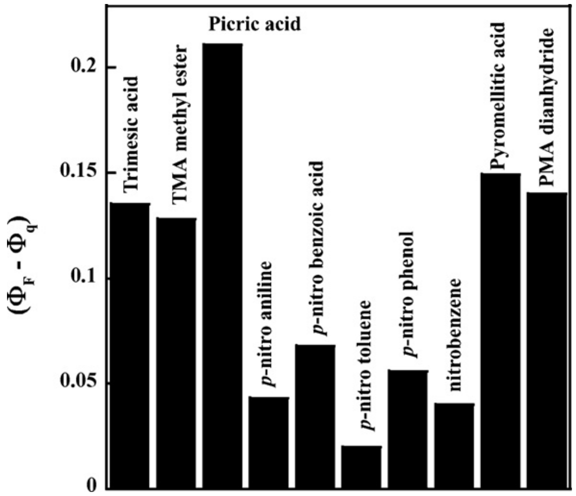

Fig. 4. Schematic representation showing the change of fluorescence quantum yield ($\Phi_F - \Phi_q$) of L_1 upon addition of the aromatic guest. Φ_F and Φ_q are quantum yields of L_1 in absence and presence of guest, respectively.

The excitation spectra monitoring the different bands of the structured emissions are the identical and match with the absorption spectra of the free ligand in dry THF at 298 K (Fig. 3). With increasing concentration of the ligand, the total intensity of fluorescence emission decreases significantly without the appearance of any broad band in the higher wavelength region. This suggests that self-quenching takes place without formation of any excimer at higher concentration [18]. The concentration of the ligand was maintained at 10^{-6} M throughout the study as the emission intensity is found to be maximum at this concentration.

When dry THF solutions of electron deficient aromatic guests were added to L_1 the fluorescence intensity was quenched to varying degrees (Figs. 2 and 4). The best results were observed for additions of picric acid to L_1, where 98% quenching was observed (Fig. 4). Fluorescence titration results revealed that maximum fluorescence quenching occurs when 16 equiv. of picric acid had been added to L_1. Fig. 4 clearly shows that L_1 exhibits relatively higher selectivity toward picric acid over other electron deficient aromatic guests such as *p*-nitro aniline, *p*-nitro benzoic acid, *p*-nitro toluene, *p*-nitro phenol, nitrobenzene, trimesic acid, trimesic acid trimethyl ester, pyromellitic acid, pyromellitic dianhydride in terms of change of fluorescence quantum yield. In order to confirm the nature of molecular interactions between host and guest in solution we have chosen a guest containing different functional groups. We have

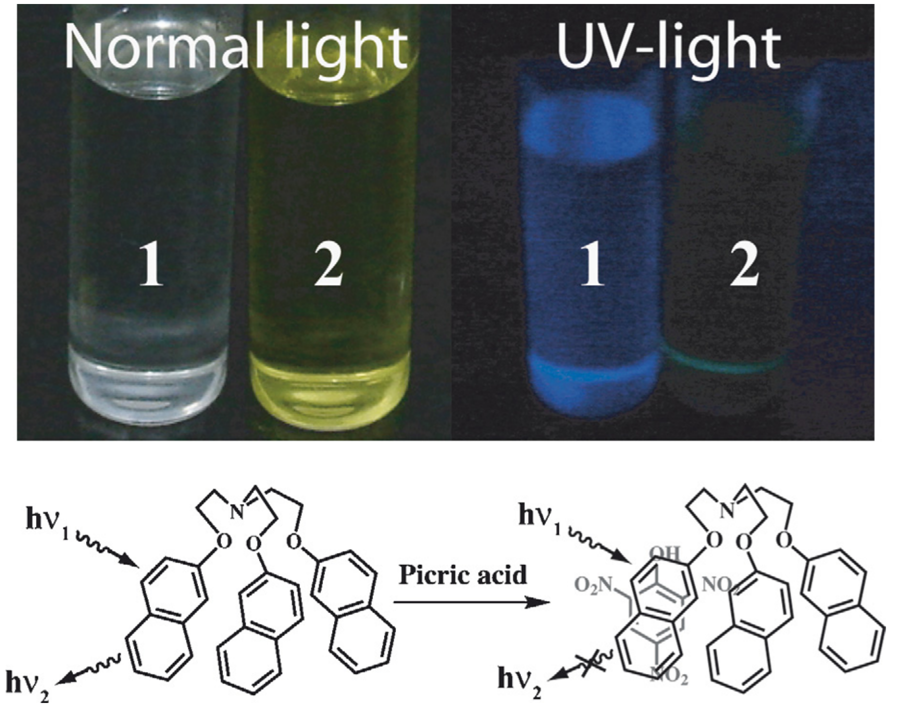

Fig. 5. Pictorial representation of fluorescence quenching of L_1 and formation of inclusion complex in presence of picric acid.

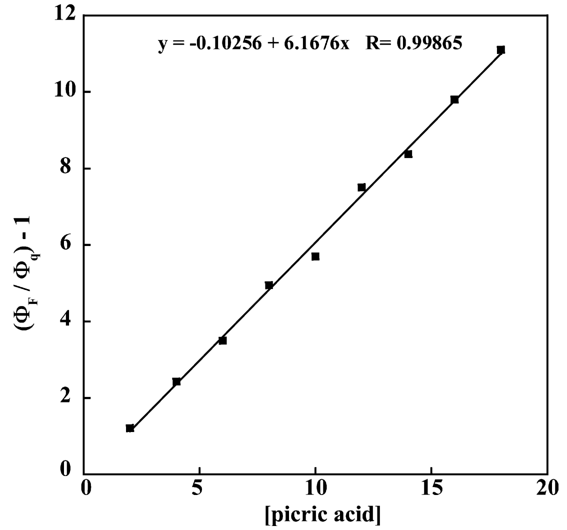

Fig. 6. Stern–Volmer plot with picric acid.

observed that fluorescence quenching of the host molecules is a cumulative effect of both acid–base and aromatic interactions.

Fig. 5 pictorially and schematically shown the quenching of fluorescence intensity of L_1 in presence of electron deficient picric acid. Due to the stereochemical requirement, L_1 adopts a flattened conformation and alone cannot exhibit intramolecular as well as intermolecular π–π interactions. Hence, it readily forms stable intermolecular π–π interactions with aromatic guest and form stable inclusion complex. The quenching of fluorescence is not a result of simple re-absorption of the guest molecules. The excitation spectra of host–guest complex resembles to the absorption spectra of the pure L_1.

Upon gradual addition of picric acid to the THF solution of L_1, the intensity of the emission bands decreases. The linear Stern–Volmer response (Fig. 6) with picric acid as quencher is consistent with well-behaved fluorescence quenching systems [19]. The dissociation constant K_d [20] was estimated from the change in fluorescence quantum yield resulted from the titration data of L_1 against picric acid solution. The linear fit of the data (Fig. 7) for picric acid inclusion complex was obtained by plotting $\log[(\Phi - \Phi_{\min})/(\Phi_{\max} - \Phi)]$ as a function of logarithm of picric acid concentration and the intercept of the linear regression determines K_d value of 5.6 μm in THF. This value indicates the formation of a stable inclusion complex and is in consistence with good correlation coefficients (>0.99). Fluorescence quenching experiment results show that the stronger acids are relatively stronger quencher. We have also shown that electron deficient guest possessing no acidic group (*viz.* nitrobenzene, *p*-nitroaniline) can also quench the fluorescence. To test the effect of protonation of the bridgehead N atom on fluorescence quenching, we have titrated L_1 with mineral acids (see supporting information). Mineral acids have negligible effect on fluorescence quenching. Hence, the formation of organic salt along with the inclusion complex is responsible for the quenching of fluorescence. The spectral characteristics of L_1 in the solid state are consistent with its solution phase behavior. In the solid state, L_1 exhibits a broad absorption band in the 250–340 nm regions. It shows a broad emission band in 315–370 nm regions. All the detail vibrational structures are lost in the solid state. All the inclusion complexes in the solid state also follow the similar trends. But these inclusion complexes show quenching in the fluorescence intensity in the solid state. However, when these solid samples are dissolved in dry THF, on an average they reproduced the solution phase spectral behavior. In the crystals host–guest ratio is smaller than that of the solution, to have a similar extent of quenching.

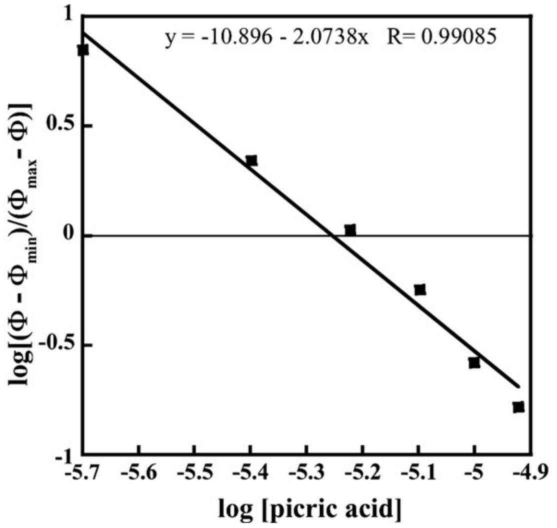

Fig. 7. Linear regression plot for K_d determination obtained from the titration data of L_1 with picric acid in THF.

3.4. Crystal structure analyses

Some of our main concerns have been to ascertain the inclusion of aromatic guest in the solid state and the consequences of weak intermolecular forces on the 3D network structure. Single crystal X-ray structural analysis [21] confirmed the host–guest relationship between L_1 and picric acid. Solid-state supramolecular organization in the crystals was discussed. X-ray quality red color crystals obtained from ethyl acetate and chloroform (1:2) mixture at low temperature. In the solid state, it forms an organic salt co-crystal. Each unit cell contains two symmetrically independent picric acid moieties (Fig. 8). One picric acid is forming organic salt and another is forming inclusion complex with the protonated L_1. We have shown that picric acid form various organic salt co-crystal with different organic amines [22]. One of the naphthalene rings is located on top of the picric acid ring. Picric acid form strong π–π stacking interactions with the L_1. The aromatic ring of guest picric acid is sandwiched between two naphthalene rings of host molecule (Fig. 9) due to intermolecular π–π stacking interactions. In comparison to the similar ligand with 1-naphthol unit [7c] L_1 exists in more flatten conformation due to its special streochemical requirement. It does not form any cavity in the structure (see supporting information). Therefore, bridgehead protonatd N atom is exposed enough to form strong hydrogen bond with the picrate anion, resulting the formation of organic salt co-crystal. Overall, solid-state structure is stabilized by several weak C–H···π and C–H···O type interactions (see

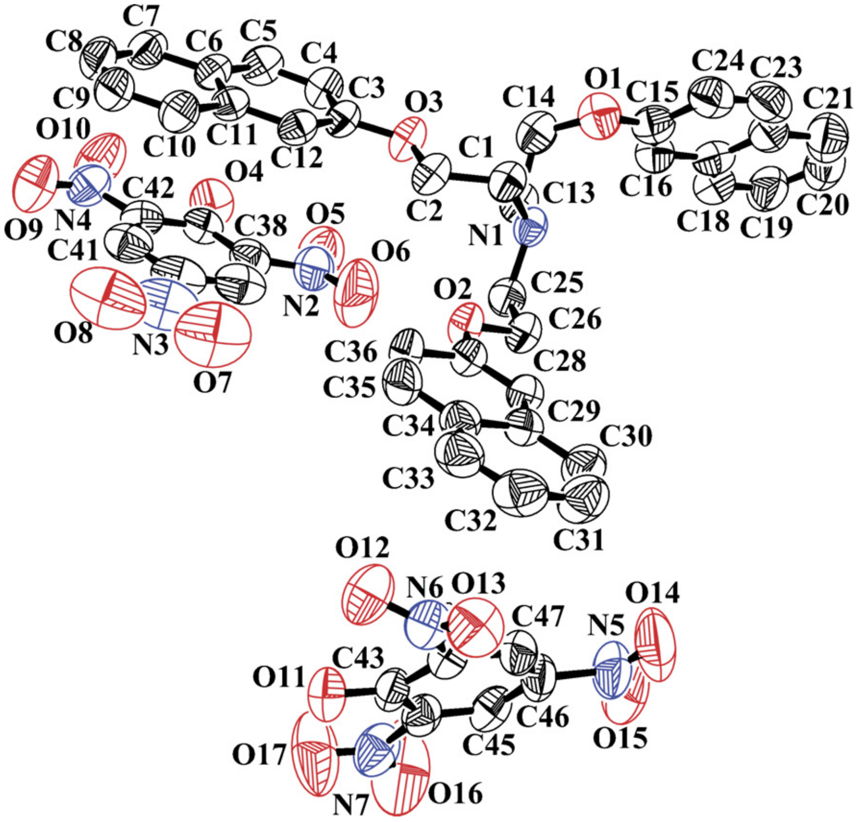

Fig. 8. ORTEP plot of $[(L_1H^+)(Pic^-)] \subset$ PicH. H-atoms are omitted for clarity.

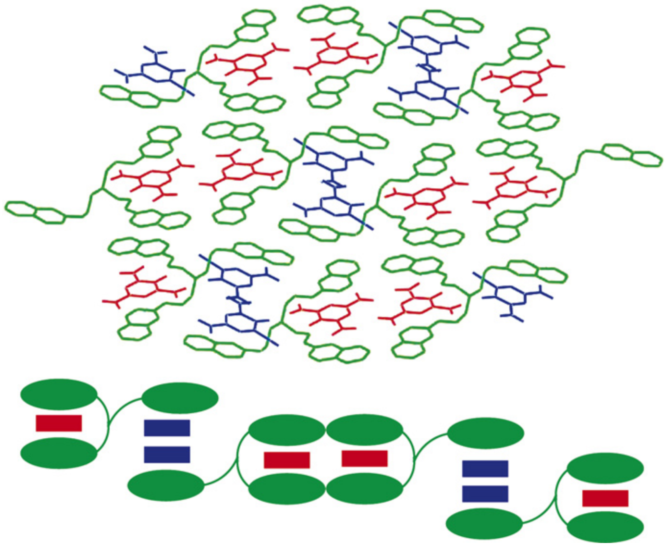

Fig. 9. Packing of $[(L_1H^+)(Pic^-)] \subset$ PicH along *a*-axis showing the π-stacking interaction scheme.

supporting information). In the solid state, L_1 forms two different types of hydrophobic void space, where picric acid is trapped in either end-on or side-on manner. Hence, there exist *aba* and *abba* type intermolecular π–π stacking interactions between L_1 and picric acid (Fig. 9). All efforts to crystallize inclusion complexes between L_1 and other electron deficient aromatic guest other than picric acid remain unsuccessful.

4. Conclusions

In conclusion, we have presented the synthesis and characterization of a simple electron-rich tripodal fluorophore L_1 for the first time. Electron-rich L_1 is an efficient fluorogenic host for inclusion of electron deficient aromatic molecules in solution. We have studied the formation of host–guest complexes with different electron deficient aromatic guest by steady-state fluorescence spectroscopy and single crystal X-ray structural studies. We found that fluorescence quenching efficiency depends on the extent of electron deficiency in the aromatic guests coupled with their acidic nature. Guest molecules with protected acid groups with similar extent of electron deficiency can also quench the fluorescence. Electron-rich L_1 can from strong intermolecular π-stacking interaction with aromatic guest bearing a stronger electron-withdrawing group. So, we can suggest that fluorescence quenching of the host molecules is a cumulative effect of both acid–base and aromatic interactions in solution. We have also shown structurally the simultaneous formation of inclusion complex and organic salt co-crystal in the solid state between picric acid and L_1. In the solid state, guest form mixed *aba* and *abba* type intermolecular π–π stacking interactions with L_1. The self-assembled structures exhibit a number of unusual weak non-covalent interactions in addition to conventional hydrogen bonding. Designing of supramolecular host–guest fluorescence signaling systems for other organic guests are in progress in our laboratory.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2007.12.020.

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[21] Crystal data for $[(L_1H^+)\ (Pic^-)] \subset PicH$: CCDC No. 645624; $C_{48}H_{39}N_7O_{17}$, $M = 985.86$, triclinic, P-1, $a = 10.5087(3)$ Å, $b = 12.1588(4)$ Å, $c = 18.2172(6)$ Å, $\alpha = 86.727(2)$, $\beta = 81.775(2)$, $\gamma = 84.839(2)$, $V = 2292.08(13)$ Å^3, $Z = 2$, $\mu = 0.110\ \mathrm{mm}^{-1}$, $d_{\mathrm{calc.}} = 1.428\ \mathrm{g/cm}^3$, $\lambda = 0.107\ \mathrm{cm}^{-1}$, Mo Kα radiation, $R_1 = 0.0532$, $wR_2 = 0.1847$, $S = 1.013$. The crystallographic data for the complexes has been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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