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Synthesis and characterization of bis[N'-(4-carboxybenzylidene)]pyridine-2,6-dicarbohydrazide: Colorimetric and fluorometric modulation in presence of F⁻ ions



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HIGHLIGHTS

• Bis[N'-(4-carboxybenzylidene)]pyridine-2,6-dicarbohydrazide has been prepared and characterized.

• Colorimetric and fluorometric modulations in presence of F⁻ has been studied.

• DFT calculation carried out in DMSO medium supported the experimental results.

G R A P H I C A L A B S T R A C T

 F^- ion recognition with a novel organic compound bis[N'-(4-carboxybenzylidene)]-pyridine-2,6-dicarbohydrazide (L) is monitored using UV-vis, fluorescence and ¹H NMR spectroscopic titrations and DFT/TD-DFT calculations which supported the experimental results.



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ABSTRACT

A novel organic compound bis[N'-(4-carboxybenzylidene)]-pyridine-2,6-dicarbohydrazide (L) was synthesized and characterized using spectroscopic and X-ray diffraction techniques.

Tetrabutyl ammonium halides [(Bu)₄N⁺X⁻] X = F, Cl, Br and I were allowed to react separately with a solution of L in DMSO (1×10^{-5} M). The solution of L turned to shining yellow colour in the presence of F⁻ ion only. The binding properties have been studied using absorption, emission and ¹H NMR titrations. Theoretical studies on compound L and compound L + X⁻ (X = F, Cl and Br) in DMSO medium were carried out using density functional theory (DFT) at the B3LYP/6–31G(d,p)/6–31G+(d,p) level. The theoretical calculations agreed to the experimental results.

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Introduction

Design and synthesis of chemical sensors for the recognition of anions is demanding area of current research. The importance of anions in nature as fertilizers, industrial raw materials and corresponding environmental concerns necessitated the development of highly sensitive anion sensors [1–7]. Anion-compound interactions, mainly through hydrogen bonding or electrostatic interaction are different than that of metal–ligand coordination in cation-compound interactions. The design of anion compounds differs substantially from that of cation compounds [8–17]. Most of the anion compounds bear amide or urea derivatives and pyrrole groups as binding sites and form N–H \cdots anion bonds or the positively charged ammonium groups (or guanidinium groups) that involve N⁺–H \cdots X type hydrogen bonds [18–23]. One of the

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frequently used strategies to design anion sensors involves the constructions of compounds showing luminescent and colorimetric responses [24-26]. Such systems are generally composed of anion binding sites and the chromogenic groups. When anions interact with the sensor via electrostatic, hydrogen bonding, coordination to a metal centre, hydrophobic interaction, or a combination of any two or more of these interactions, the sensor can output binding information either by its altered fluorescence, absorption spectra or both [27-29]. Colour changes as signalling event detected by the naked eye are widely used owing to the low cost of equipment required. Among various anions, fluoride ion has attracted the interest of chemists due to its applications in many industrial products. It has been used in dental care and in the human diet. A large intake of fluoride ions can lead to osteoporosis, fluorosis and other diseases [30,31]. Keeping these precedence in view, a simple bis-hydrazide containing amido and imino groups at 2.6-positions of a pyridyl ring has been synthesized and characterized. It selectively detected F⁻ anion by naked-eye as well as by changes in the optical signals in DMSO solution.

Experimental

Materials and methods

Tetra-n-butylammonium (TBA) halides were purchased from Sigma–Aldrich Chem Co. All solvents were purchased from E. Merck and freshly distilled prior to their use. The compound L was prepared and characterized using reported procedure [32].

X-ray structural studies

Single crystal X-ray diffraction data of L was collected in the temperature range of 100(2)–293(2) K on a Oxford diffraction XCALIBUR-EOS diffractometer using graphite monochromatized MoKa radiation ($\lambda = 0.71073$ Å). Intensities of these reflections were measured periodically to monitor crystal decay. The crystal structure was solved by direct methods and refined by full matrix least squares (SHELX-97) [33]. Drawings were carried out using MERCURY [34].

Absorption titrations

UV–vis absorption spectra were recorded on "Jasco V-630" spectrophotometer at 25 °C. The absorption titrations of L with fluoride salt was performed by monitoring the changes in the absorption spectrum of L (10^{-5} M) in DMSO. The concentration of L was kept constant a 10^{-5} M while the concentrations of fluoride salt was varied within (1-10) × 10^{-6} M. The absorption of guest molecule is eliminated initially by keeping their equal quantities separately in host L and reference solution. From the absorption data, the intrinsic association constant K_a was determined from a plot of [guest]/($\varepsilon_a - \varepsilon_f$) vs [guest] using [35] Eq. (1).

$$[guest]/(\varepsilon_a - \varepsilon_f) = [guest]/(\varepsilon_b - \varepsilon_f) + [k_a(\varepsilon_b - \varepsilon_f)]^{-1}$$
(1)

where [guest] is the concentration of fluoride salt. The apparent absorption coefficients ε_a , ε_f , and ε_b correspond to $A_{obsd}/[L]$, the extinction coefficient of the free L and extinction coefficient of L in fully bound form respectively. K_a is given by the ratio of slope to the intercept.

Fluorescence titrations

Fluorescence spectra were measured using a Perkin–Elmer LS-45 luminescence spectrometer. Host (L) displayed fluorescence at λ_{emiss} 556 nm at excitation wavelength λ_{ex} 315 nm. Fluorescence titration experiments were performed by maintaining the concentration of L constant at 10^{-5} M while varying the concentration of the fluoride anion within $(1-10) \times 10^{-6}$ M and the fluorescence was measured after each addition until fluorescence intensity was found maximum.

¹H NMR titrations and ESI–MS studies

¹H NMR titrations were carried out in DMSO – d_6 solution (TMS as internal standard) using JEOL AL-300 MHz spectrometer. Concentration of host (L) as 10^{-3} M was titrated against guest (F⁻) concentration 10^{-2} M. Chemical shift was measured in δ ppm. ESI-MS was recorded on micromass LCT (Waters) mass spectrometer.

Computational method

Geometry optimization was performed using Gaussian 09 suite of programs [36]. A hybrid version of DFT and Hartree–Fock (HF) methods was used, namely, B3LYP density functional theory method in which the exchange energy from Becke's exchange function was combined with exact energy from Hartree–Fock theory [37,38]. LanL2DZ was used for I while for the C, H, N, F, O and Br atoms, 6-31G^{**} basis set was used for compound L. 6-31G+^{**} basis set used for compound L + X⁻(X = F, Cl, and Br). The calculations for compound L + I⁻ tried but it did not satisfy energy convergence criteria. In addition, we also performed time dependent density function theory (TD-DFT) [39,40].

Synthesis and characterization

Preparation of compound L

L was synthesized in three steps starting from 2,6-pyridine dicarboxylic acid (1 mmol, 0.167 g). Its methyl ester was prepared by stirring it in excess methanol in the presence of catalytic amount of concentrated thionyl chloride (SOCl₂) at room temperature for one day. The ester (1 mmol, 0.171 g) thus isolated was then reacted with aqueous hydrazine hydrate (2.1 mmol, 0.12 mL) in methanol under reflux for 3 h which resulted solid 2,6-pyridine dicarboxylic acid, 2,6-dihydrazide. It (1 mmol, 0.195 g) was finally reacted with 4-formyl-benzoic acid (2 mmol, 0.300 g) in methanol at room temperature. Reaction was monitored using TLC. The product thus obtained was filtered and then purified by repeated recrystallization from hot ethanol. Yield: 85%, ¹H NMR (DMSO- d_{6} , 300 MHz): δ (ppm) 13.20 (b, 2H, -COOH), 12.44 (s, 2H, -NH), 8.81 (s, 2H, CH=N), 8.37 (m, 2H, CHpy), 8.33 (m, 1H, CHpy), 8.04 (d, 4H, ArH), 7.92 (d, 4H, ArH). 13 C NMR (dmso-d₆, 300 MHz): δ (ppm) 166.98 (C1, -COOH), 138.18 (C2, ArH), 127.41 (C4, ArH), 132.12 (C₅, ArH), 140.11 (C₆, -CH=N), 159.70 (C₇, -C(0)NH), 148.89–148.15 (C₈, C₉, Py), 125.79 (C₁₀, Py). IR (KBr pellet, cm⁻¹): 3463 (>CONH), 1671 (-COOH), 1609 (-C=N).

Crystal data: C27H35N5O11S2, M = 669.74, Monoclinic, a = 26.7068(15), b = 10.1394(4), c = 12.4951(6), $\alpha = 90$, $\beta = 110.310(6)$, $\gamma = 90$, space group C 2/c, Z = 4, V/Å³ = 3173.2(3), Reflections collected/unique = 6463/3552 [*R*(int) = 0.0196], Final *R* indices [*I* > 2sigma(*I*)] = *R*1 = 0.0360, *wR*2 = 0.0871.

Preparation of adduct of L with tetrabutylammonium fluoride

Crystalline solid of L (1 mmol, 0.459 g) was added to a solution of tetrabutylammonium fluoride in DMSO (1 mmol) and stirred for 5 h, filtered to get pale yellow solid. This compound was washed with methanol followed by diethyl ether. Yield: 60%, ¹⁹F NMR (DMSO-*d*₆, 300 MHz): δ (ppm) – 47.45 ppm, IR (KBr pellet, cm⁻¹): 3418 (>CONH), 1681 (—COOH), 1654 (—C=N). ESI-MS: calcd. *m*/*z* 720.46, found 721.53.



Fig. 1. Molecular structure of L.

Results and discussion

As shown in Scheme 1, compound L was synthesized using twosteps simple-controlled reactions from diester to dihydrazide, then to final compound L in good yields. Elemental analysis and spectroscopic characterizations (¹H NMR, ¹³C NMR, IR, UV-vis and fluorescence) supported the formation of the bis-hydrazide, L. It showed characteristic infrared band of amido and imino groups at 3463 and 1609 cm⁻¹ respectively. The structure of compound L was supported by its ¹H and ¹³C NMR spectra (S1, S2). The most deshielded protons of COOH group of compound L appeared as broad peak at δ 13.20 ppm where as protons of amido and imino groups appeared as singlet at δ 12.44 ppm and 8.81 ppm respectively. Pyridyl protons were observed as multiplet at δ 8.38–8.26 ppm where as phenyl protons appeared at δ 8.04 (*J* = 8.1 Hz) and 7.92 (*J* = 9 Hz) respectively. The UV-vis spectrum of compound L showed a peak at λ_{max} 315 nm where as an emission band from L was displayed at λ_{emiss} 556 nm at excitation wavelength of $\lambda_{excitation}$ 315 nm.

Crystal structure of compound L

The proposed molecular structure of L was further supported by its single crystal X-ray diffraction study. Crystal structure analysis of compound L exhibited a special configuration with two amide – carboxy phenyl arms disposed at 2 and 6 positions of pyridyl group with space group C2/c (Fig. 1). The two parts of the molecule are symmetrically related with the nitrogen atom N(1) of the pyridine ring lying on the twofold axis to form a helical species. In the crystal lattice, one molecule of DMSO and two molecules of water are present. One of water molecule is present in its cleft (S3). The oxygen atom (O5) involved in H-bonding with —NH(3) proton of compound L (N(2)—H(3)···O(5) with distance 2.147 Å) and oxygen atom (O4) of DMSO is also involved in H-bonding with hydrogen atom (H9) of carboxylic group of compound L (S(1)=O(4)···H(9) distance 1.753 Å). Water of crystallization acts as a bridge between two molecules of compound L. Here H(11) of water molecule formed H-bonding with O(3) of carboxylic group of compound L (C(12)—O(3)···H(11) distance 2.147 Å) and H(12) formed H-bonding with O(1) of compound L (C(4)—O(1)···H(12) distance 1.932 Å) (S3). The packing diagram of compound L showed helical type of network along crystallographic *c* axis (S4). In this structure, DMSO molecules were embedded between two chains of compound molecules.

Naked eye detection and ESI-MS studies

Changes in colour were studied in a first step in DMSO by addition of 5 equiv. $(5 \times 10^{-3} \text{ M})$ of the corresponding anion



Fig. 2. Colour changes of L (2×10^{-3} M, DMSO) with the addition of tetrabutylammonium salts (from left to right: free L, 5 equiv. F⁻, Cl⁻, Br⁻and l⁻ in DMSO).



Fig. 3. ESI–MS spectrum of complex $(M + H)^+$ in acetonitrile/dmso (9:1 v/v) solution.

(F⁻, Cl⁻, Br⁻ and I⁻) separately as tetrabutylammonium salts to solutions of compound L (1×10^{-3} M) in DMSO. The most selective colour change occurred in the presence of fluoride anion from white to yellow colour (Fig. 2). An image of visual colour changes with increasing concentration of fluoride ions is given as S5. In interference experiment, we can say that in presence of excess of other halides like Cl⁻, Br⁻ and I⁻ did not show any visual changes in compound–fluoride complex colouration with the persistence of pale yellow colour (S6).

ESI–MS as depicted in Fig. 3, supported the formation of $[L-TBA^+F^-]$ and $[L-F^-]$ complexes showing corresponding peaks at m/z 720 and 479 respectively.

Absorption spectral response for anions

UV–vis spectra of the solution of L $(1.0 \times 10^{-5} \text{ M})$ recorded upon the incremental addition of F⁻ is shown in Fig. 4. Upon addition of F⁻, the intensity of the absorption peak of L observed at λ 315 nm was found to be decreasing and peak position also shifted at λ 319 nm. However, the absorbance of its peak observed at λ 275 nm was increasing. The resulting titrations showed isosbestic point at λ 285 nm. Observation of isosbestic point showed that a stable complex of definite stoichiometry between L and anion was formed. Interestingly, addition of other halide ions like Cl⁻, Br⁻ and I⁻ did not bring out any observable change in the



Fig. 4. Absorption spectra of L = $(10^{-5} \text{ M}, \text{DMSO})$ in absence (a) and in the presence of increasing amounts of F⁻ = $(1-10) \times 10^{-6} \text{ M}$ (in DMSO) at room temperature. Inset: (a) change of absorbance at 574 nm and (b) absorbance changes upon increasing F⁻ concentrations.



Fig. 5. Emission spectra of $L = (10^{-5} \text{ M}, \text{DMSO})$ in absence (a) and in the presence of increasing amounts of $F^- = (1-10) \times 10^{-6} \text{ M}$ (in DMSO) at room temperature. Inset: emission intensity changes upon increasing F^- concentrations.

absorption spectrum of L (S7) at this wavelength. The selective binding with of F^- as compared to Cl^- , Br^- and l^- may be attributed to its higher basicity [41].

Colour changes occur most probably due to formation of hydrogen bonds between the amido groups and fluoride ions. The formation of these hydrogen bonds affects the electronic properties of the chromophore resulting in a colour change with a subsequent new charge-transfer interaction between the fluoride-bound amido group and the electron deficient 4-carboxyphenyl group [42]. It was supported by the appearance of a new peak at λ 574 nm upon addition of fluoride solution. The value of association constant (K_a) of fluoride binding was found as 1×10^5 . This was further supported by Job's plot (S8) and ESI-MS analysis. Electronic spectra for L remained unchanged even in the presence of excess (20 mol equivalents) of other halide salts like Cl⁻, Br⁻ and I⁻. For these anions, the absence of any change in absorption spectral pattern suggested either no interaction with L or the interaction of corresponding anions with L is too weak to perturb the energies of the frontier orbitals of the compound molecule. The observed changes in solution (DMSO) of L upon addition of 5.0 M equivalents of tetrabutyl ammonium salts of respective anions are shown in Fig. 2. This clearly showed that except F^- , no colorimetric response was observed on addition of any other anions in DMSO solution of L in comparable concentration. In interference experiment, λ_{max} of ligand (L) appeared at 315 nm but after addition of fluoride salt it shifted to 319 nm. However, addition of excess salt like chloride, bromide and iodide in same solution show little perturbation (~1 nm) in UV-vis spectra (S9).

Flourescence response from anions

Fluorescence from compound L $(1.0 \times 10^{-5} \text{ M})$ in the absence and presence of fluoride anions, in DMSO medium was recorded keeping tetrabutylammonium (TBA) cation constant in each case. A weak emission band at λ_{max} 351 nm was displayed from free compound L, which was attributed to the intrinsic emission from phenyl group and a strong luminescent band observed at λ_{max} 556 nm was attributed to the excimer emission [43] resulting from the intramolecular excimer formation by $\pi - \pi^*$ stacking between two phenyl rings (Fig. 5). Owing to the involvement of non-bonding electron of NH group in H-bonding with F⁻ anion, $n \to \pi^*$ transition which normally masks the $\pi \to \pi^*$ transition



Fig. 6. The emission spectra of L (2×10^{-5} M, DMSO) in absence or presence of a 5 mol ratio of F⁻ and 20 mol ratio of anions Cl⁻, Br⁻ and l⁻ anions (in DMSO) at room temperature.



Fig. 7. ¹H NMR spectra of L(1 mM) in DMSO- d_6 in the presence of increasing amounts of F⁻ at 25 °C.

(responsible for the emission behaviour), its fluorescence intensity is enhanced [44]. Upon addition of Cl⁻, Br⁻ and l⁻ anions as their TBA salts in a 20-fold excess, no change in their emission was observed. However, a strong fluorescence enhancement was observed in the presence of a small amount of F⁻ anion as shown in Fig. 6. Moreover, the fluorescence "switch on" rather than "switch off" upon recognition is preferred in order to notice a greater signal output and could be of interest in sensing processes. The binding constant K_s is determined from the changes in fluorescence intensity resulting from the titration of dilute solutions (10⁻⁵ M) of L against F⁻ anion solutions. The linear fit of the fluorescence intensity data at a particular wavelength for 1:1 complexation was obtained [45] by applying the following equation:

$$I_{F}^{'}/(I_{F} - I_{F}^{'}) = [a/(b-a)][1/K_{s}[M] + 1]$$
(2)

where I_{F}° and I_{F} are the fluorescence intensities of the free L and L-anion complex, respectively; [*M*] is the concentration of the anion added for the complexation. The K_{s} is obtained as intercept/slope ratio from the plot of $I_{F}^{\circ}/(I_{F} - I_{F}^{\circ})$ against [*M*]⁻¹. The results of the systematic analysis of fluorescence titrations (Fig. 6) also supported

the binding stoichiometry of 1:1 with a binding constant of $1\times 10^5\,M^{-1}.$

¹H NMR titration

¹H NMR titration of L at its fixed concentration (10^{-3} M) with guest (fluoride anions) of concentration (10^{-2} M) was performed. Initially, —NH peak appeared at δ 12.44 ppm shifted to δ 12.59 ppm on addition of 0.50 equivalent of fluoride ions in a solution of L. Further addition of 0.25 equivalent of fluoride ions shifted the NH— peak at δ 12.75 ppm (Fig. 7). Finally, at 1.0 equivalent of fluoride ions, NH— peak appeared at δ 13.02 ppm. The deshielding of NH protons supported their involvement in H-bonding with fluoride ions. Upon addition of 10.0 equivalent of fluoride ions in the solution of L, formation of HF₂⁻ was considered since a peak appeared at δ 15.80 ppm was found in consistence with the earlier report for HF₂⁻ anion [46]. As a consequence of deshielding of NH protons, imino protons (CH=N) were also deshielded from δ 8.81 ppm to δ 8.82 ppm. Thus, NMR titrations demonstrated 1:1 binding ratio between compound L and F⁻ ions as no further



Fig. 8. Optimized structures (top view) of compound L and compound L + X⁻(X = F, Cl and Br).



Fig. 9. Optimized structures (side view) of compound L and compound L + X⁻(X = F, Cl and Br).

changes in either NH or CH=N protons could be observed even upto 3.0 equivalent ration of F⁻ ions as compared to L. This observation supported that binding site of F⁻ ion is most likely with NH groups and its charge is counter balanced by TBA ion as evidenced by its peak observed at δ 0.89–1.54 ppm. However, addition of other TBA halides separately even in 20-fold excess to a solution of L brought no significant change in peak position of either NH or CH=N protons.

FT-IR analysis

The electronic rearrangement of compound $L+F^-$ is demonstrated also by IR spectra (S10 and S11). In particular, stretching band of >CONH and -CH=N groups observed at 3463 and 1609 cm⁻¹ respectively in compound L, shifted to 3418 and 1654 cm⁻¹ in the spectrum of compound $L+F^-$. This indicated weakening of N-H bond and strengthening of -CH=N bond and supported co-operativity of amide and imine groups in H-bonding. [47].

DFT calculations

DFT calculations were performed to optimize the structures as shown in Fig. 8. The energy of optimized structure of compound L and its adduct with F⁻, Cl⁻ and Br⁻ ions were found as -43860.9811 eV, -46584.6394 eV, -56389.2885 eV and -113846.0214 respectively. The relevant frontier molecular orbitals of the compound L and of its adduct with X⁻(X = F, Cl and Br) ion are depicted in (S12 and S13). The HOMO distribution of compound L is concentrated only on both arms of L where as LUMO distribution is concentrated on whole molecule including pyridine ring. Some useful optimized parameters of compound L and L + X⁻ (X = F, Cl and Br) are given in Table 1. The optimized structure of L + F⁻ shows that hydrogen bonding interactions exist within the

Table 1Some useful optimized parameters of compound L and L + $X^-(X = F, Cl, Br)$.

Compound	$H - X^{-}(A)$	N2—H3 (A)	N2—X ⁻	$H - X^{-} - H(^{\circ})$
L		1.01		
L + F ⁻	1.63	1.05	2.66	100
$L + Cl^{-}$	2.40	1.02	3.37	75
$L + Br^{-}$	2.49	1.02	3.47	71

acceptable donor–acceptor distances [48]. Side view of optimized geometry shows fluorine atom fits in plane of compound L whereas chlorine and bromine are out of plane as depicted in Fig. 9. The en-



Fig. 10. Energy level diagram of HOMO and LUMO orbitals of compound L and compound $L + F^-$ complex.

Table 2	
Summary of electronic transition of compound L and compound L + F-	complex.

	Electronic	TDDFT//B3LYP/6-31G (d,p)/631 + G (d,p)			
	Transition		ſ ^b	Composition ^c	CI ^d
Compound L	$\begin{array}{l} S_0 \rightarrow S_1 \\ \\ S_0 \rightarrow S_4 \end{array}$	3.6162 eV 342.86 nm 3.7633ev/ 329 (nm)	0.6362 1.2778	$\begin{array}{l} H\text{-}1 \rightarrow L\text{+}1\\ H \rightarrow L\\ H\text{-}1 \rightarrow L\text{+}1\\ H \rightarrow L\text{+}1 \end{array}$	0.35287 0.60309 0.36767 0.59270
Compound L + F ⁻	$S_0 \rightarrow S_1$ $S_0 \rightarrow S_2$ $S_0 \rightarrow S_4$	3.3743 eV 367(nm) 3.4756 eV/ 356 nm 3.5611 eV/ 348 nm	0.5354 0.6576 0.8765	$H-1 \rightarrow L+1$ $H \rightarrow L$ $H-1 \rightarrow L+1$ $H \rightarrow L+1$	0.23503 0.66095 0.69848 0.69524

^a Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength.

^b Oscillator strength (only the f > 0.2 was considered).

^c H stands for HOMO and L stands for LUMO.

^d The CI coefficients are in absolute values.

Table 3Mulliken charges on compound L and L + F⁻.

Compound L		Compound L +	- F ⁻
Atom	Charges	Atom	Charges
N1	-0.635	N1	-0.032
C3	0.254	C3	-0.014
C4	0.605	C4	0.346
01	-0.542	01	-0.652
N2	-0.406	N2	-0.646
H3	-0.305	H3	0.452
N3	-0.265	N3	0.229
C5	0.113	C5	-0.147
H4	0.119	H4	0.168
C6	0.091	C6	0.244
C12	0.561	C12	0.910
03	-0.512	03	0.500
02	-0.501	02	0.553
H9	0.347	H9	0.412

ergy gap (ΔE) of compound L and its fluoride complex are shown in Fig. 10. Addition of F⁻ ions to N2H2 moiety through H-bonding decreased the HOMO–LUMO energy gap from $\Delta E = 4.0583 \text{ eV}$ to ΔE = 3.8248 eV and consequently made the colorimetric recognition of F⁻ ions energetically easier [49]. In the case of compound L TD-DFT calculations provide a calculated absorption band at 329 nm belonging to the $S_0 \rightarrow S_4$ energy state (Table 2). This is consistent with the absorbance band at 315 nm obtained experimen- $HOMO-1 \rightarrow LUMO$ transitions tally. The of and HOMO \rightarrow LUMO + 1 contribute 72% and 26% of S₀ \rightarrow S₄ energy state, respectively. Similarly TD-DFT calculation for compound L + F⁻ complex provide a calculated absorption band at 367, 356 and 348 nm belonging to the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_4$ energy state respectively (Table S1). The transitions of HOMO $-1 \rightarrow LU$ -MO + 1 and HOMO \rightarrow LUMO contribute 11% and 87% respectively of $S_0 \rightarrow S_1$ energy state whereas HOMO-1 \rightarrow LUMO contribute 98% to $S_0 \rightarrow S_2$ energy state transition from $S_0 \rightarrow S_4$ belongs to HOMO \rightarrow LUMO + 1(97%). Relevant frontier molecular orbitals of compound L and its fluoride complex which are involved in electronic transition are shown in (S14 and S15).

Mulliken charges on atoms of L and its adduct with F^- ion are shown in Table 3. Moreover, in the compound L, Mulliken charge on two N2H3 increased significantly (from -0.305 to 0.452) after complexation with fluoride ion suggesting the formation of N-H···F⁻ hydrogen bond as F⁻ ion can abstract the H-atom of the N-H moiety as H⁺ to form the H-bond. This is supported by ¹H NMR titrations. Interestingly, the results obtained the theoretical study corroborated well with the experimental findings.

Conclusion

Compound bis[N'-(4-carboxybenzylidene)]-pyridine-2,6-dicarbohydrazide (L) is synthesized and characterized using spectroscopic and X-ray diffraction techniques. Compound L detects F^- ions (5 × 10⁻³ M) selectively by naked eye as colour of L changes from white to intense yellow. Changes in optical signals (absorption and emission spectra) also demonstrate the selective recognition of F^- ions by L up to 1 × 10⁻⁵ M concentration. ¹H NMR titrations support that NH protons of L are bonded with F^- ions (NH···F⁻···HN) whereas TBA cation remains as counter ion. Theoretical study performed in DMSO medium support this observation.

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Appendix A. Supplementary material

CCDC reference numbers 760554 contains the supplimentary crystallographic data for L. This data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk). The experimental details (Absorption, fluorescence, NMR, ESI-MS, X-ray and computational studies) of ligand can be found in online version.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.07.045.

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