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Aggregation induced emission enhancement (AIEE) of fluorenyl appended Schiff base : A turn on fluorescent probe for Al³⁺, and its photovoltaic effect

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ABSTRACT

Fluorenyl-diformyl phenol Schiff (HL) base is spectroscopically characterized and demonstrates aggregation induced emission enhancement (AIEE) upon addition of water to THF solution. Maximum intensity is observed at 90% of water addition at 570 nm. Al^{3+} induced turn-on fluorescence enhancement is observed at 600 nm and the limit of optical detection (LOD) is $6.22x10^{-9}$ M. Isolation of Al(III)complex and mass spectral measurement shows the formation of phenoxo-bridged dinuclear complex. Applicability for DSSC device fabrication of probe shows photovoltaic efficiency 0.021%. DFT computation of optimized geometry of HL has been used to explain the spectral and photovoltaic activity.

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 π -conjugated molecules show several advantageous properties such as light-emitting diodes (LEDs), organic lasers, organic thinfilm transistors (OTFTs), nonlinear optical (NLO) materials, optoelectronic devices etc [9,10]. Fluorene and its derivatives are good contenders to perform aggregation induced emission enhancement and are effective probe for ion induced turn-on fluorescence enhancing agent. π -Delocalized molecules show good electrochemical activity, high quantum yields in emission spectral studies [11,12] and have wide applications in organic light emitting devices (OLEDs) [13]. In this work, we have synthesized fluorenyl appended diformylphenol Schiff base (HL) and has been characterized by spectroscopic data. The probe, HL, shows AIEE at the near red region in presence of water and exhibits very high fluorescence sensor activity to Al³⁺ in the presence of large number of other cations such as K^+ , Mg^{2+} , Ba^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Pb^{2+} , Ni^{2+} , Fe^{2+} while Hg^{2+} and Cu^{2+} show minor sensitivity in THF-MeOH (1:1, v/v) mixture.

Aluminum is neurotoxic, water pollutant and causes Alzheimer's [14] and Parkinson's [15] diseases, and hampers protein transportation, softening of bone, anemia in living beings. It is the third most abundant metal in the earth's crust (8% of its mass); resists corrosion and is a useful structural component of electronic and electrical gadgets, building materials, packaging stuff etc. So, designing of high sensitive multi-signaling chemosensor for Al³⁺

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1. Introduction

Fluorophores are described according to their absorption and fluorescence properties, including the spectral profiles, wavelengths of maximum absorbance and emission, and the fluorescence intensity of the emitted light. One of the parameters to monitor the intensity of emission is the concentration of the fluorophore. With increasing concentration from very dilute solution the emission intensity commonly increases, but the emission of polyaromatic hydrocarbon (PAH), in general, shows dramatic decrease in intensity after a limiting concentration which is commonly known as aggregation-caused quenching (ACQ) due to the strong intermolecular stacking interactions [1,2]. However, Tang [3] and Park [4] in 2001 and 2002, respectively, showed some anti-ACO materials and were termed aggregation-induced emission (AIE) and aggregation-induced emission enhancement (AIEE) materials. Since then, AIE and AIEE materials have attracted considerable attention [5]. PAHs are π -delocalized planar rigid motifs to demonstrate $\pi - \pi$ aggregation and have been suitable for performing aggregation induced emission [6-8]. Fluorenyl attached







is very important [16–18]. Many fluorescent probes based on quinoline [14,19,20], bipyridyl [21,22], coumarin [23,24], pyrazoline [25,26], tripyrrins [22], BINOL [27], fluorescein [24,25], rhodamine [28,29], sulfonamides [30] are known in the literature for detection of aluminum at very low concentration window. To the best of our knowledge, this is the first example in the series of diformylphenol derivative of fluorene that is showing selective Al³⁺-sensitivity. The molecule is also used to investigate the applicability in fabrication of Dye Sensitized Solar Cell (DSSC). The current–voltage characteristic of the device is analyzed to interpret the performance of DSSC activity [31]. The spectroscopic properties have been supported by DFT computation of optimized structure of HL.

2. Experimental section

2.1. Materials

Analytical grade anhydrous aluminum chloride (AlCl₃) and other chemicals were purchased from Merck, India; solvents used were of spectroscopic grade and used as received. Milli-Q Milipore 18.2 $M\Omega$ cm⁻¹ water was used in aggregation induced emission study. 2-Amino fluorene was purchased from Sigma-Aldrich and 2-hydroxy-5-methylisophthalaldehyde was prepared from reported procedure [32].

2.2. Physical measurements

Microanalytical data (C, H, and N) were collected on Perkin-Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were obtained using the following instruments: UV-vis spectra by Perkin-Elmer UV-vis spectrophotometer model Lambda 25; FTIR spectra (KBr disk, 4000–400 cm⁻¹) by Perkin–Elmer FT-IR spectrophotometer model RX-1; the ¹H NMR spectra by Bruker (AC) 300 MHz FTNMR spectrometer. Emission was examined by LS 55 Perkin-Elmer spectrofluorimeter at room temperature (298 K) in THF solution under degassed condition. The fluorescence quantum yield of HL was determined using quinine sulfate as a reference with known Φ_f (0.546 in 1N H₂SO₄) in ethanol. HL and the reference dye were excited at same wavelength, maintaining nearly equal absorbance (\sim 0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield is calculated according to the following equation:

$$\frac{\Phi_{\rm S}}{\Phi_{\rm R}} = \frac{A_{\rm S}}{A_{\rm R}} \times \frac{(Abs)_{\rm R}}{(Abs)_{\rm S}} \times \frac{\eta_{\rm S}^2}{\eta_{\rm R}^2}$$

Here, Φ_S and Φ_R are the fluorescence quantum yield of the sample and reference, respectively. A_S and A_R are the area under the fluorescence spectra of the sample and the reference, respectively, $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvent used for the sample and reference.

TEM images were taken with a JEOL-JEM 2010 electron microscope using 200 kV electron source and a UHR-FEG-TEM, JEOL; JEM 2100 F model using 200 kV electron source. Specimens were prepared by dropping a drop of nanocrystal solution of sensor prepared from THF-water (1:4) on a carbon coated copper grid, and the grid was dried in air. TEM images on STEM (HAADF) mode were taken in the UHR-FEG-TEM.

2.3. Synthesis

2.3.1. 2,6-Bis((E)-((9H-fluorene-2-yl)imino)methyl)-4-methylphenol (HL)

To methanol solution (15 ml) of 2-aminofluorene (500 mg. 2.76 mmol) was added 2-hvdroxy-5-methylisophthalaldehyde (225 mg, 137 mmol) in drops in the same solvent (15 ml) for 10 min and was refluxed for 3 h at dark. Orange crystalline products were separated on cooling the reaction mixture; filtered and recrystallized from methanol-THF mixture (1:5, v/v). Yield, 475 mg (95%); M.P. 180 ± 2 °C. Elemental analysis, C₃₅H₂₆N₂O; Calcd. (%) : C, 85.69: H. 5.34: N. 5.71% and found: C. 85.82: H. 5.25: N. 5.60%. TOF MS ES⁺ spectral study of HL had shown intense one molecular ion peak at 491.34, (HL+H)⁺ (Supplementary materials, Fig. S1). In FTIR spectrum HL has shown ν (C=N) at 1649 cm⁻¹ and ν (OH) at 3237 cm⁻¹ (Supplementary materials, Fig. S2). ¹H NMR data (CDCl₃, δ, ppm, J (Hz)) : 11.56 (s, 1-OH), 7.85 (s, 3-H), 2.44 (s, 4-Me), 9.28 (s, 7-CH=N), 7.24 (d, 7.5 Hz, 10,10[/]-H), 7.64 (m, 4H, 11,11[/], 12,12[/]) -H), 7.28 (m, 13,13[/]H), 7.12 (m, 2H, 14,14[/]-H), 7.42 (d, 7.5 Hz, 15,15[/]-H), 4.48 (bs, 4H, 16,16[/]-H) (Supplementary materials, Fig. S3).

2.3.2. Preparation of $[Al_2Cl_5(L)]$

To dry THF solution (10 ml) of HL (100 mg, 0.20 mmol) anhydrous AlCl₃ (60 mg, 0.44 mmol) in super dry methanol (30 ml) was added and the reaction mixture was refluxed for 1 h. The solution turned to deep red and cooled to room temperature. Bright red crystals were separated, filtered and dried in vacuum. Yield, 120 mg (83%); M.P. 210 \pm 2 °C. Elemental analysis: C₃₅H₂₅Al₂Cl₅N₂O; calculated; C, 58.32; H, 3.50; N, 3.89 % and found; C, 58.55; H, 3.58; N, 3.81%. TOF MS ES⁺ metal complex appeared at 719.85 corresponding to molecular mass of the complex (Supplementary materials, Fig. S4). In FTIR spectrum the frequencies are ν (C=N) at 1634 cm⁻¹, ν (C–O), 1240 cm⁻¹. ¹H NMR data (DMSO-d₃), δ , ppm, J (Hz)) : 6.097 (s, 3-H), 2.31 (s, 4-Me), 8.93 (s, 7-CH=N), 7.62 (d, 7.5 Hz, 8.8[/],10,10[/]-H), 6.77 (d, 4H, j = 6.5 Hz, 11,11[/]-H), 7.45 (m, 4H, 12,12^{/.} 15,15[/]-H), 7.14 (m, 13,13[/],14,14^{/-} H), 3.30 (bs, 4H, 16,16^{/-}H) (Supplementary materials, Fig. S5).

2.4. Photovoltaic measurements

A thin film of HL was prepared as reported in the literature [33,34]. In a cleaned test tube, 1 g of PVA was mixed with 10 ml of double distilled water, warmed gently and stirred to make a transparent viscous solution of PVA. Also, 6 mg of HL was mixed with this solution. A solid electrolyte was prepared in a separate cleaned beaker by mixing PEO, LiClO₄-EC and PC. The complex of PEO-LiClO₄-EC-PC (30.60%-3.60%-19.60%-46.20% by weight) were mixed, stirred and heated around a temperature 60 °C for 4 h. This gel-like solid electrolyte was mixed with the previously made HL-PVA solution to form the blend. This blend was heated at 60 °C and stirred properly to mix them well for about 2 h. This viscous gel-like solution was then sandwiched between two electrodes. The electrodes were cleaned in chloroform solution and dried under vacuum about 2 h before use. The two electrical leads were taken out from the two ends of the electrodes. The complete cell was dried in vacuum for about 6 h at around 60 °C before the final measurement. The active area of the cell was 0.04 cm² (Supplementary material, Figs. S6, S7).

To measure the dark I–V characteristics, the cell was biased with a dc source with a series resistance of 56 K Ω . The current flowing through the device was estimated by measuring the voltage drop (measured by Agilent data acquisition unit, model no. 34970A) across this sensing resistance. For optical measurement, a tungsten lamp of 200 W was used. Incident light was allowed on the cell. By varying the intensity of incident radiation, voltage drops and hence the photocurrent across the sensing resistance

was measured. The intensity was measured by a calibrated lux meter (Kyoritsu Electrical Instruments Works Ltd. Tokyo, model 5200). Photocurrent is measured by varying the intensity of light. To estimate the power curve the current was drawn from the cell for a constant illumination.

2.5. DFT computation

Geometry optimization of HL was performed by DFT/B3LYP method using Gaussian 09 software [35–37]. 6-311G+(d, p) basis set were used for C, H, N, O [38–40]. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there are only positive eigen values. Theoretical UV–vis spectra were calculated by time-dependent-DFT/B3LYP method in methanol using conductor-like polarizable continuum model (CPCM) [41–43]. GAUSSSUM [44] was used to calculate the fractional contributions of various groups to each molecular orbital.

3. Results and discussion

3.1. Synthesis and formulation

2.6-Bis((E)-((9H-fluorene-2-vl)imino)methyl)-4-methylphenol (HL) has been synthesized by the condensation of 2aminofluorene and 2-hydroxy-5-methylisophthalaldehyde in methanol under refluxing condition. The characterization of HL has been done by microanalytical and spectroscopic (FT-IR, UVvis, ¹H NMR, Mass) data. Mass ion peak appears at 491.34 which corresponds to $(HL+H)^+$ (Supplementary material, Fig. S1); the IR spectrum shows $\nu(OH)$, 3227 cm⁻¹ and $\nu(C=N)$ at 1649 cm⁻¹ (Supplementary material, Fig. S2); the ¹H NMR spectrum observes sharp singlet at 9.28 ppm which is assigned to imine-H (-CH=N-)and phenolato $\delta(OH)$ is a singlet at 11.56 ppm; aromatic protons appear in 7.24–7.64 ppm and a characteristic broad peak appears at 4.48 ppm is corresponding to fluorenyl –CH₂– (Supplementary material, Fig. S3). Upon reaction with Al³⁺ an orange colored crystalline product has been isolated that is sparingly soluble in common organic solvents (alcohols, acetonitrile, chloroform, dichloromethane) and fairly soluble in THF, DMF, DMSO. The conductance measurement shows neutral character (Λ_{M} (DMF). 3.4 Ω^{-} cm⁻¹ mol⁻¹). Molecular composition is supported by mass spectral appearance of molecular ion peak at 719.85 (Supplementary mterials, Fig. S4). The FT-IR spectrum of the complex does not show any significant change and the characteristic observation is the elimination of broad band corresponding to ν (OH); the ν (C=N) appears at 1604 cm⁻¹ and is lowered by 45 cm⁻¹. Because of low solubility on CDCl₃ the ¹H NMR spectrum of the complex has been recorded in DMSO-d₆; the characteristic observation is the elimination of singlet at 11.56 ppm which indirectly supports the binding to phenolato-O to Al³⁺ and other protons of Schiff base show irregular shifting (Supplementary materials, Fig. S5); some of the protons are downfield shifted by 0.5–0.7 ppm while others are upfield shifted by 0.3–1.8 ppm data. We could not isolate single crystals of either ligand or its complex for single crystal X-ray structure determination.

3.2. Aggregation induced emission (AIE) of HL

The absorption spectrum of HL in THF shows two well defined intense absorption bands at region 340 nm and 390 nm and is believed to be characteristic of intramolecular charge transfer transitions. Upon addition of water in THF solution these bands are shifted to longer wavelength 372 and 428 nm (Supplementary



Fig. 1. AIEE of HL upon gradual addition of water; inset emission vs concentration of water plot.



Fig. 2. HR-TEM image of aggregated nano material upon addition of H₂O to THF solution (90% water).

material, Fig. S8). Solvatochromism of absorption spectra of HL are not significant.

THF solution of HL shows weak emission at 470 nm upon excitation at 390 nm. Upon addition of water the emission has been red shifted to 565 nm alongwith manyfold enhancement of emission intensity. This observation has been described as aggregation induced emission enhancement (AIEE) and the increment has been continued to addition of 90% water to THF solution (Fig. 1). This observation may attribute to stereo-chemical rigidity of imino-phenol H-bond network and the restricted intramolecular rotation (RIR) process operating in fluorenyl moiety. After an optimum level concentration of water its emission intensity drastically decreased due to complete molecular agglomeration (90% water addition to THF solution) and formation of aggregated nano material (Fig. 2). The quantum yield (Φ)



Relative metal ions sensitivity of HL



Change of emission intensity at 600 nm for single and triple ion sensitivity of sensor

Fig. 3. a. Relative metal ions sensitivity of HL b. Change of emission intensity at 600 nm for single and triple ion sensitivity of sensor.



Scheme 1. 2,6-Bis((E)-((9H-fluorene-2-yl)imino)methyl)-4-methylphenol (HL), aggregation cartoon in THF-water (1:9, v/v) and Al³⁺ complex, [Al₂Cl₅(L)].



Fig. 4. Fluorescence titration upon adding Al³⁺ to HL solution; inset (right) change of emission intensity with [Al³⁺].



Fig. 5. Tauc's plot and optical band gap.

enhancement of HL is observed from 0.0344 to 0.45 as a function of water concentration (percentage).

3.3. Al^{3+} sensing activity of HL

The luminophore (HL in dry methanol) shows intense red emission (600 nm) upon addition of Al³⁺ (prepared in THF) while other ions such as K^+ , Mg^{2+} , Ba^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Pb^{2+} , Ni^{2+} , Fe^{2+} (all ions in dry MeOH) do not show any emission enhancement except Hg^{2+} and Cu^{2+} those exhibit minor enhancement (Fig. 3). Emission may be associated with AIEE ; however aggregation induced emission is shown at 565 nm in aqueous medium and Al³⁺ is taken in THF which shows that the emission band shifts to longer wavelength (600 nm). Isolation of Al^{3+} complex and its Mass spectral analysis establish [Al₂Cl₅(L)] composition (Supplementary material, Fig. S4). Upon coordination of L⁻ with Al^{3+} may form O-bridging N,O,N- chelated moiety (Scheme 1) which may resist the torsional motions of fluorenyl rotors introducing RIR process in the system. The confirmation of the molar composition of the complex has been done by mass spectroscopy (Supplementary material, Fig. S4) and Job's plot in emission spectroscopy and (Supplementary material, Fig. S9). . The

spectrophotometric titration in 4.5 μ M THF (at 25 °C) using Tris-HCl buffered ligand solution on gradual addition of Al³⁺ ion reveals red shift (388 nm to 522 nm) with enhancement of intensity from 0.760 unit to 1001 unit (almost 1317 fold) Fig. 4. A plot of the emission intensity *vs* Al³⁺ ion concentration is obtained from which Al³⁺ ion concentration of an unknown sample can be easily measured by employing HL as an indicator (Supplementary material, Fig. S10). The apparent binding constant (*K*_a) of complex measured adopting Benesi–Hildebrand [45] equation is 3.125x10⁸ M⁻². The limit of optical detection (LOD) is 6.22 x 10⁻⁹ M (*R*², 0.985).

3.4. Photovoltaic activity of HL

Using absorption data the optical band gap of HL is measured with the help of Tauc's $(\alpha h \gamma)^2$ vs $h \gamma$ plots (Fig. 5) [46]. Where α is the absorption coefficient. The plot of current density vs. voltage plot of the DSSC is shown in Fig. 6 under incident photons (of power density 100 mW cm^{-2}). From these response curves the open circuit voltage (V_{oc}) is 0.83 V; short circuit current density (I_{sc}) is 36.8 μ Acm⁻²; maximum power (P_{max}) shows 20.66 μ Wcm⁻²; fill-factor (FF) is 0.68 and photo-irradianced efficiency (η) is calculated 0.021%. The charge transport mechanism of this device during illumination is illustrated in Fig. 7. The band gap of TiO₂ is considered as 3.2 eV with HOMO and LUMO energy level at -7.46 eV and -4.26 eV respectively [47]. The direct energy band gap of the ligand was calculated as 2.9 eV, which is quite supported by the theoretical band gap (3.1 eV) i.e. estimated from the theoretical estimation of HOMO (-5.33 eV) and LUMO (-2.23 eV) energy levels (Fig. 8).

3.5. Theoretical interpretation

DFT computation technique has been used to optimize the geometry of HL and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are shown in Fig. 8 (detail of other MOs are given in Supplementary material, Fig. S11). HL carries fluorenyl, diformylphenol and imine motifs. Both occupied and unoccupied MOs contain these three functional units in different percentage (Supplementary material, Table S1). The HOMO and HOMO-1 contain 65% and 56% fluorenyl motif while LUMO and LUMO+1 share 27% and 37% only. Diformylphenolato function appears < 50% in the occupied and unoccupied MOs. Imine function (-CH=N-) contributes 10–40% to the



Fig. 6. Current density vs voltage plot of the dye-sensitized solar cell.



Fig. 7. The energy band diagram and the charge transport mechanism.

function. The calculated absorption peaks are comparable with the experimentally observed peaks (Supplementary material, Table S2). The calculated transition HOMO \rightarrow LUMO is of high oscillator strength (f, 0.6244) and calculated wavelength is 435.30 nm while transition at 392.23 nm (f, 0.8033) is defined HOMO-1 \rightarrow LUMO. The calculated information desires pure fluorenyl transition at 180 nm (energy difference between HOMO-5 to LUMO+7 is

 $\sim 7 \text{ eV})$ which is of very high energy and may be responsible for photo-degradation.

The transitions below 300 nm correspond to the admixture of imine to fluorenyl charge transfer and inter-fluorenyl charge transfer whereas transitions above 300 nm correspond to inter-fluorenyl charge transfer. The molecular aggregation may be accounted through π - π interaction of fluorenyl units. DFT studies support that fluorenyl to imine charge transfer is energetically favorable transition (Fig. 7). Besides, the excitation of HL by light irradiation leading to population of higher energy LUMO who is also fluorenyl dominated may initiate inversion in charge density and is responsible for creation and transportation of positive hole and hence, photoelectric effect.

4. Conclusion

Fluorenyl appended diformyl Schiff base shows aggregated induced emission enhancement upon addition of water to THF solution (90% water). Aggregation has been substantiated by HR-TEM analysis. Light irradiation generates substantial quantity of photocurrent. Theoretical calculation has been employed to explain the spectral and photovoltaic properties. Schiff base shows selective sensitivity to Al^{3+} in the presence of large number cations and acts as fluorescence sensor. The limit of optical detection is substantially low (6.22 x 10^{-9} M).



Fig. 8. DFT computed HOMO and LUMO of HL.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jlumin.2016.07. 008.

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