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Research paper

Dipolar state assisted aggregation induced optical behavior of push-pull Salen-type Schiff base (BIHyDE) in solution

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1. Introduction

Organic chromophores are a class of functional π -electron rich systems, which have established themselves as attractive molecules in modern organic electronics [1-5]. Due to tunable optoelectronic properties of organic chromophores, these organic chromophores are widely applied for designing light-emitting diodes, [6-8] bioimaging probes, [9-10] and photoelectric emitting devices, [11-13] particularly in the visible region. To design efficient full-color emitting materials, the organic chromophores are designed on the basis of underlying mechanisms, including intramolecular charge-transfer (ICT), [14-15] twisted intramolecular charge-transfer (TICT), [16-17] excimer, [18] excited-state intramolecular proton transfer (ESIPT), [19] and photoinduced electron transfer (PET) [20]. Above strategies provide useful information to design novel and efficient full-color luminescent molecules. In recent, push-pull organic molecules play a crucial role on aggregation behavior and their application in organic electronics based on ICT state [21-22].

Further, aggregation behavior of organic chromophores can also influence on optical properties and device applications. Depending upon nature of molecular orientation, *J*-aggregate and H-aggregate are formed in solution. The *J*-aggregate has shown a red-shifted absorption compared to monomer band and enhanced fluorescence with a very small Stokes shift [23-26]. The *J*-aggregates are

ABSTRACT

Aggregation behavior of push-pull salen-type schiff base (BIHyDE) in different solvents at ground and excited state, has been investigated. At ground state, lower energy absorption band is suppressed during concentration dependent UV-Vis study in CHCl₃ solution. The broadening of lower energy emission band is observed during concentration dependent fluorescent study in CHCl₃ solution. Interestingly, fluorescence life time of BIHyDE in solution is also altered during concentration dependent fluorescence study in CHCl₃ solution. Solvent. Similar aggregation is also observed at ground and excited state in ACN solvent. Dipolar state and intermolecular dipolar interaction of BIHyDE molecule highly influence towards strong aggregation process and orientation of molecule in solution. Ground state and excited state optical properties are highly influenced by concentration of push-pull salen-type schiff base (BIHyDE) in different solvents.

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useful as photosensitizers, [27] light-harvesting systems [26,28-29] and nonlinear optical (NLO) materials. [30-31] H-type aggregates display a blue-shifted absorption band with a low molar extinction coefficient [32-33] and nonfluorescent behavior [23-26]. The quenching properties of H-type aggregates have been theoretically explained through the coupled oscillator model [34-35]. H-aggregates have shown third order nonlinear susceptibility [36-37] and used to measure the photocurrent in photovoltaic cells [38]. Generally, H-type aggregated molecules are nonfluorescent but remarkably large Stokes shift in fluorescent spectra in solution. [39] Nature of self-association is also influenced by structure of organic chromophores, concentration, solvent polarity, pH, ionic strength, and temperature [40-43].

Recently, Xiang et al. have reported that malonitrile-based salen ligand can be used as a photoisomerization induced colorimetric and fluorescent pH and Cu²⁺ probes. [44] Previously, reported UV-Vis spectra of push-pull Salen-Type Schiff Base (BIHyDE) has shown different absorption properties with respect to molar extinction coefficient, which is totally different from our experimental results. [45]

For details and clear understanding of the photophysical behavior salen-type schiff Base molecule (BIHyDE, chart 1), we have studied aggregation behaviors, intramolecular charge-transfer (ICT) and excited-state proton transfer (ESIPT) moieties in solution using UV-vis, and fluorescence spectroscopy (steady state and time resolved). Further, role of intramolecular interaction and nature of aggregation at ground state and excited state in solution has been investigated on the basis of experimental results.







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Chart 1. Structural Formula and Abbreviations of Investigated molecule.

2. Experimental section

2.1. Chemicals and synthesis

All starting materials were procured from Sigma Aldrich and are of analytical grade. Ultrapure water, acetonitrile, and dichloromethane, ethanol, DMSO, and other solvents were procured from Sigma Aldrich. CDCl₃ (Sigma-Aldrich) was used as received for NMR studies.

2.2. Synthesis and characterization of BIHyDE



2,3-diaminomaleonitrile (1 mmol) and 4-(diethylamino)-2-hydroxybenzaldehyde (2.5 mmol) were taken in a round bottom flask with catalytic amount of conc. H₂SO₄ and was heated in an oil bath at 60 °C for 3 hrs till the completion of the reaction. After completion of the reaction, crude mixture was washed with water (3 × 10 mL) followed by ethanol (3 × 10 mL), dried in high vacuum to afford NMR pure product. State: Solid; Colour: Black; MP.: 193 °C; Yield: 95 %; ¹H-NMR (300MHz, CDCl₃): δ (ppm) 11.64 (s, 2H), 9.48 (s, 2H), 7.27 (s, 2H), 6.26 (d, *J* = 7.5 Hz, 2H), 6.06 (s, 2H), 3.41 (q, *J* = 7.0 Hz, 4H), 1.21 (t, *J* = 4.2 Hz, 6H); ¹³C-NMR (75 MHz, CDCl₃): δ (ppm) 191.9, 164.3, 154.3, 135.3, 111.3, 104.3, 96.4, 44.0, 12.7.

2.3. NMR spectroscopy

¹H and ¹³C-NMR spectra are recorded on NMR (Bruker) spectrometers operating at 300 and 75 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) using the residual solvent peaks as reference relative to TMS. '*J*' values are given in Hz.

2.4. Steady state UV-Vis and fluorescence measurement

Steady state UV-Vis and fluorescence spectral measurements were measured in different solvents. The steady state absorption spectra were recorded on Hitachi UV-vis U-3501 spectrophotometer. The fluorescence spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer equipped with a 10 mm quartz cell and a thermostat bath.

2.5. Time-resolved fluorescence measurement

Fluorescence lifetimes were measured from time-resolved intensity decay by the method of time-correlated single-photon counting (TCSPC) technique by FluoroCube-01-NL spectrometer



Fig. 1. Normalized UV-Vis spectra of BIHyDE in different solvents.

(Horiba Jobin Yovon IBH Ltd.) using a nano LED light source at 340 nm, and the signals were collected at the magic angle (54.7°) polarization. The IRF of detector is (fwhm) = 750 ps. DAS6 software was used to deconvolute the fluorescence decays. The relative contribution of each component was obtained from the biexponential fitting and finally expressed by the following equation.

$$a_n = \frac{B_n}{\sum B_i}$$

 B_i is the pre-exponential factor. The mean fluorescence lifetimes for the decay curves were calculated from the decay times and the relative contribution of the components using the following equation.

$$\langle \tau \rangle = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i}$$

 τ_i and a_i are the fluorescence lifetime and its coefficient of the ith component, respectively.

3. Results and discussion

3.1. Steady-state absorption and fluorescence measurements

The UV-Vis spectra of BIHyDE are recorded in different solvents and presented in Fig. 1. From experimental absorption spectra, BI-HvDE molecule exhibits three different absorption bands at 562 nm, 433 nm and 344 nm in ACN solvent respectively. The absorption bands at 562 nm and 433 nm are weak and broaden but strong absorption band is observed at 344 nm in ACN. Intesity of weak absorption band at 433 nmand 562 nm is altered depending upon nature and polarity of solvents. Broaden lower energy absorption band (~562 nm) with low intensity is observed in polar protic solvents. But in polar aprotic solvents, intesity of lower energy absorption (~562 nm) is relatively higher compared to polar protic solvents. From UV-Vis studies, lower energy absorption band is shifted from 549 nm (n-hexane) to 582 nm (DMSO) in solution due to relative polarity of solvents. The shifting of lower energy absorption band (549 nm to 582 nm) is due to enhancement of solute-solvent interact from nonpolar to polar solvents (Fig. 1 and Table 1). Intensity of lower energy absorption band also changes from nonpolar to polar solvents. Relative intensity of lower absorption band is relatively higher in polar aprotic solvents compared to polar protic solvents (Fig. 1).

From our experimental results, it can be concluded that the dicyano group in BIHyDE plays an important role on electronic property and solute-solvent interaction in solution. So, electronic and

Table 1

Spectroscopic parameters from absorption and emission spectra.

Solvent	UV-Vis (λ_{max}^{Abs})	Fluorescence (λ_{max}^{Fl})	
n-hexane	549 nm	577 nm	
THF	550 nm	604 nm	
CHCl ₃	569 nm	600 nm	
ACN	562 nm	611 nm	
DMSO	581 nm	635 nm	
THF	566 nm	608 nm	
EtOH	565 nm	611 nm	
H_2O	581 nm	620 nm	



Fig. 2. Effect of aq KOH on UV-Vis spectra of BIHyDE in ACN solvent.

solvatochromic properties of BIHyDE are significantly influenced by the polarity of solvents at room temperature.

Further, alternation of optical properties of BIHyDE is also investigated in basic condition. For this purpose, diluted aq KOH solution is added to ACN solvent containing BIHyDE (Fig. 2). From UV-Vis spectra, it is observed that higher energy absorption band at 344 nm is not shifted at all but spectral broadening is also observed with increasing aq KOH concentration. Interesting factor is that the lower energy absorption band (at 562 nm) is unaltered at lower aq KOH concentration but prominent affect is observed at higher concentration of aq KOH solution. At high conc of aq KOH solution, the lower energy absorption band is shifted from 562 nm to 595 nm in ACN (Fig. 2). The influence of KOH on optical behavior in chloroform and DMSO solvents has been investigated and similar results are also obtained.

In presence of aq KOH, deprotonation of –OH group is taken place and electron density of core benzene moiety is also enhanced, result the higher degree of dipolar state lowering the energy levels and enhanced the aggregation in solution.

Further, steady state emission spectra of BIHyDE are recorded in different solvents by exciting at 530 nm and shown in Fig. 3 and Table 1. Since BIHyDE contains both the intramolecular charge transfer (ICT; Push-pull) and proton transfer moieties, there are the possibilities of observing ICT, ESIPT and local emission (LE) bands. But different emission processes like ICT state, ESIPT and LE bands are suppressed by aggregated emission from concentration dependent study.

BIHyDE has shown strong emission peaks at 577 nm in nhexane (nonpolar) and at 635 nm in DMSO (polar) solvent (Fig. 3). With increasing polarity of solvents, the nature of the emission band shifted from 577 nm to 635 nm from n-hexane (nonpolar) to DMSO (polar) solvent (Fig. 3). Remarkably, in every case, single gaussian shaped fluorescence spectrum is observed for BIHyDE molecule in polar and nonpolar solvents.



Fig. 3. Normalized fluorescence spectra of BIHyDE in different solvents ($\lambda_{ex} = 530 \text{ nm}$).



Fig. 4. Concentration dependent UV-Vis spectra of BIHyDE in CHCl₃ solvent.

Emission band from ICT state and ESIPT process may expect from ICT state (Push-pull system) and keto-enol (ESIPT process) but separately, emission band is not observed from ICT state and ESIPT process. Single emission band is only observed for BIHyDE in different solvents from fluorescence study.

3.2. Concentration dependent absorption and fluorescence measurement

The concentration dependent UV-Vis spectra of BIHyDE is recorded in CHCl₃ and presented in Fig. 4. From experimental absorption spectrum, BIHyDE has exhibited absorption bands at 344 nm (very strong), 433 nm (weak) and 562 nm (strong) in CHCl₃ solvent. At very low concentration, intensity of absorption band at 562 nm is higher than absorption band at 344 nm. With increase in concentration of BIHyDE, intensity of absorption band at 344 nm is started dominating over the absoptionband at 562 nm in CHCl₃ (Fig. 4). Others band at 433 nm is not altered significantly in same absorption spectra (Fig. 4).

Further, concentration dependent UV-Vis spectra of BIHyDE in CHCl₃ solvent is also normalized at 345 nm and presented in Fig. 5. It is observed that lower energy absorption band at 569 nm is decreasing with increasing concentration of BIHyDE keeping the absorption band constant at 345 nm. From Fig. 4 and 5, it is clear that the with increasing concentration of BIHyDE, change of absorption intensity is linear and it provides the aggregation behaviour via lower energy state. This aggregation at lower energy state is to be considered as *J*-type aggregation. So, BIHyDE shows the *J*-type



Fig. 5. Normalized UV-Vis spectra of BIHyDE @ 345 nm in \mbox{CHCl}_3 during concentration dependent Study.



Fig. 6. Normalized concentration dependent fluorescence spectra of BIHyDE in $\mbox{CHCl}_3.$

aggregation in CHCl₃ solvent. Similar aggregation is also observed in polar aprotic slovents like ACN and DMSO solvent. The *J*-type aggregation is observed due to presence of strong intermolecular dipole-dipole interaction among molecules. Intermolecular dipoledipole interaction among molecules plays important role on decreasing absorbance at 569 nm (Fig. 5) but increasing absorbance at 345 nm (normalized at 569 nm) with increasing concentration of BIHyDE in solution.

Further, steady state fluorescence spectra of BIHyDE with different concentration in $CHCl_3$ are also measured and shown in Fig. 6. The fluorescence maxima of BIHyDE at 600 nm is remained unaltered with different concentration of BIHyDE in $CHCl_3$. But emission band broadening is observed even at very low concentration (~10⁻⁶ (M)) and indicates that strong intermolecular interaction is present at excited state of BIHyDE in $CHCl_3$ (Fig. 6 and Figure S2).

From concentration dependent fluorescence spectra, it is clear that the emission is only appeared from *J*-type aggregated BIHyDE. *J*-type aggregated BIHyDE has shown unique lower energy emission band during concentration dependent fluorescence study. Excited state aggregation is occurred even at lower energy compared to nonaggregated form of BIHyDE molecule in CHCl₃. In presence of strong intermolecular dipole-dipole interaction among BIHyDE molecules, *J*-type aggregation is observed in CHCl₃ solution. Similar observation is also observed in ACN solvent (Figure S2). Intermolecular dipole-dipole interaction among molecules plays important role on broadening the fluorescence spectra (normalized at 600 nm) with increasing concentration (Fig. 6).



Fig. 7. Concentration dependent life time decay profile of BIHyDE in CHCl₃.

 Table 2

 Time resolved fluoresence parameters for BIHyDE in different solvents.

Solvent	τ_1 (ns)	τ_2 (ns)	a ₁	a ₂	$\langle \tau \rangle$ (ns)	χ²	
Concentration @2.4 \times 10 ⁻⁶ (M)							
CHCl ₃	2.06	3.86	0.77	0.23	2.47	1.18	
EtOH	1.06	1.89	0.15	0.85	1.91	1.14	
Concentration @4.8 \times 10 ⁻⁶ (M)							
CHCl₃	2.09	-	1	-	2.09	1.03	
EtOH	1.99	-	1	-	1.99	1.19	

3.3. Time-resolved fluorescence measurements

Fluorescence lifetimes have been measured to further investigate the excited state behavior of BIHyDE in solution (Fig. 7 and Table 2). All decay curves have been well fitted with mono and biexponential decay pattern having acceptable χ^2 values. Timeresolved data are presented in Table 2. Time-resolved data reveals that BIHyDE has shown mono and biexponential decay curves, depending upon nature of solvent and its concentration. At very low concentration (2.4 \times 10 $^{-6}$ (M)) in CHCl3, biexponential decay components is observed and the two species contribute different percentage (23% and 77%). But at high concentration (@ 4.8 \times 10⁻⁶ (M)) monoexponential decay components are observed and the one species contributes 100% (Table 2). Similarly, at very low concentration (@2.4 \times 10⁻⁶ (M)) in EtOH, biexponential decay components is observed and the two species contribute in different percentage (15% and 85%). But at high concentration (@ 4.8×10^{-6} (M)), monoexponential decay components are observed and the one species contributes 100% (ESI-Fig. 2: Table 2).

When monitoring life time at very low concentation, significant contribution arises from monomer of BIHyDE but at higher concentration, significant contribution comes from aggregated form of BIHyDE due to presence of the intermolecular H-bonding interaction and dipolar-dipolar interactions.

Here, value of τ_1 and τ_2 has been changed significantly with variation of solvents and concentration of solute. It is observed that τ_1 always predominates over τ_2 in polar protic and aprotic solvents. But τ_1 component fully is dominated by concentration of BIHyDE in polar aprotic and protic solvents. Polar aprotic solvent influences the life time of BIHyDE significantly. At lower to higher concentarion of BIHyDE in polar aprotic solvents, the life time is decreased and shows the change from biexpontial to monoexponential decay profile (Fig. 7 and Table 2). Overall, average fluorescence life time (τ_{av}) is also altered depending upon concentration of BIHyDE in solution. Change of average life time from 1.91 ns to 1.99 ns is observed in EtOH during change of concentration from



Fig. 8. Schematic presentation of aggregation of BIHyDE in solvent.

 $2.4x10^{-6}$ (M) to $4.8x10^{-6}$ (M). At similar concentration range, and average life time is also altered from 2.47 ns to 2.09 ns in CHCl₃.

Therefore, we conclude that at lower concentation $(2.4 \times 10^{-6} \text{ M})$ in polar aprotic and protic solvents, there is significant contribution of monomer (~23%) and aggregate (~77%) form of BIHyDE. Where as, at higher concentation (4.8 × 10⁻⁶ M) in polar aprotic and protic solvents, only aggregate form (100%) of BIHyDE contributes.

It is clear that H-bonding solvents can influence the photophysical properies of BIHyDE in solution. Intermolecular H-bonding interaction and dipolar-dipolar interactions may enhance the nonradiative path and responsible for shorter fluorescence life time. At very low concentration, monomer is observed in polar aprotic solvents to polar protic solvent. But at higher concentration, only molecular aggregate is formed and observed in both polar protic and aprotic solvents.

From these observations, it is clear that at lower concetration of BIHyDE, absorption and emission are solely occurred from nonaggregate (monomer) species but at relatively higher concentration, different absorption and emission are observed from aggregated species of BIHyDE in solution. Intermolecular dipolar state assisted aggregation is taking place in solution. Schematic concentration dependent aggregation and optical properties of BIHyDE in solution has been presented in Fig. 8.

4. Conclusion

Aggregation behavior of push-pull salen-type schiff base (BI-HyDE) at ground and excited state, has been investigated in different solvents. At ground state, lower energy band is suppressed in concentration dependent UV-Vis spectra but emission band broadening is observed in concentration dependent fluorescence spectra in solution. Interestingly, fluorescence life time of BIHyDE is also altered during concentration dependent fluorescence study in solution. From time resolved fluorescence spectra, it is observed that average life time is altered depending upon concentration of BIHyDE. With increasing concentration, average fluorescence life time is decreased. At low concentration (< 2.4 \times 10⁻⁶ M), average life time is contributed from monomer but at higher concentration (> 4.8 \times 10⁻⁶ M), average fluorescence life time is contributed from only J-type aggregated molecule. The variation of average life time with concentration indicates that non-radiative process plays important role on supramolecular self-assemble process in solvents. Dipolar state and intermolecular dipolar interaction may highly influence towards strong aggregation process and orientation of molecule in solution. The π -electron of benzene ring may take part an important role on *J*-type aggregation process at ground state and excited state. Aggregation is observed at ground and excited state in polar protic and aprotic solvents. Detailed aggregation mechanism is under process and will be helpful for wide application in material chemistry.

Declaration of Competing Interest

None.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2021.130140.

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