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Aggregation induced emission enhancement of 4,4′-bis(diethylamino) benzophenone with an exceptionally large blue shift and its potential use as glucose sensor

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Abstract:

Optical emission from a luminogen in solid state is generally red shifted with respect to its solution phase emission. But in our present study we report exceptionally large blue shifted enhanced emission from aggregated hydrosol of 4,4′-bis(diethylamino)benzophenone (BZP) compare to its solution phase emission in any good solvent. This exceptional blue emission from aggregated structure of BZP arises from its locally excited states with the concomitant suppression of twisted intramolecular charge transfer (TICT) motion. This is known as aggregation induced locally excited (AILE) state emission. A broad red shifted emission is also observed in case of larger aggregated structure of BZP and it originates from the excited intramolecular charge transfer (ICT) state of planar BZP. Morphology of the aggregated BZP is also studied by scanning electron and optical microscopic study. This AILE emission of the luminogen is used for sensing glucose in aqueous solution at very low concentration. The quenching of AILE in presence of glucose has been explained due to hydrogen bonded complexation between glucose and BZP molecule present at the surface of the aggregated structure and is responsible for crystal softening *i.e.* loosening of crystal packing.

1. Introduction:

Intensive effort have been devoted to synthesize efficient solid state organic luminogen materials due to their optical response in various application fields such as, organic light emitting diode (OLED)[1-3], organic photovoltaic (OPV)[4,5], organic field effect transistor (OFET)[6,7] and sensors[8-10] in condensed phase. Many luminogenic organic emitters are highly emissive in their dilute solution phase but their emissive property disappeared abruptly in aggregated form[11, 12]. This phenomenon is notoriously known as Aggregation Caused Quenching (ACQ) effect which has become a thorny obstacle to the fabrication of organic light emitting device. Various approaches have been taken in order to hamper chromophore aggregation and to moderate ACQ effect but only a few get successes.

Instead of passively fighting against the natural processes of chromophore aggregation, scientists were trying to utilize this property in a constructive way. Then this major problem was solved by Tang[13] and Park[14] *et al.* in 2001 by developing new organic luminescent which exhibit stronger emission property in solid state than their solution phase and this property is known as “Aggregation induced emission enhancement” (AIEE) effect. A variety of luminogens and their derivatives have successfully shown their fluorescence efficiency utilizing this effect, but the most common feature observed in all AIEE active molecules is that they contain multiaromatic ring with free rotating part[15-21]. These molecules are classified in two different groups. In the first group, the molecules are non emissive in their good solvent but become highly luminescent in aggregated form thus behaving exactly opposite to the conventional ACQ effect. This emission is induced by aggregation and coined the term as “Aggregation induced emission” (AIE) [22]. In the second group, the molecules are feebly luminescent in solution state but their efficiency increases in their solid form. This is known as “Aggregation induced emission enhancement” (AIEE) [23].

The luminogen molecules with donor-acceptor (D-A) structure is one of the important materials now-a-days to get desired application in optoelectronic devices[24]. Due to facile manipulation of frontier orbital energy level, energy band gaps, carrier injection and transport balance of D-A molecules, the photoluminescence spectra can be easily shifted to the longer wavelengths[25-27]. In such intramolecular processes of a conjugated system with donor and acceptor subunits, the reaction product is usually called an intramolecular charge transfer (ICT) state. This fact greatly hinders the progress of D-A molecules to the short wavelength *i.e.* blue or ultraviolet region when they are used as active film in optoelectronic device. So the major challenge was to introduce a luminogen which prevents the most general red shifting but preserving the merits of D-A architecture.

AIE effect has been utilized in various purposes and much effort has been devoted in different application field such as organic light emitting diodes, optical devices, photo switches, and sensory systems etc[28-33]. Amongst the different sensory system such as toxic metal sensors[34-36], volatile organic compounds sensor[37], explosives sensors etc[38]. Detection of saccharide e.g., D-Glucose has been a great interest for long time due to its importance in medical diagnosis and bioprocessing. Though enzyme-based detection approaches are highly selective and effective but there are many limitations, including instability, difficult sterilization, slow sensor time lags and high cost[39]. An optical response is especially favored because it can be detected remotely. After a long research the best ligand identified for binding glucose in aqueous media is boronic acid[40-42]. Singaram's group developed a series of two-component sensing system[43], but these glucose sensing systems are not only involving very complicated procedures to synthesize, but also not easy to be fabricated into device application.

Herein, a new low dimensional D-A material from 4,4′-bis(diethylamino)benzophenone (BZP) in which, two donor diethyl phenyl amine units are bridged by the accepter keto group have been introduced (Scheme 1). Aggregated BZP molecule exhibits exceptional blue shifted PL spectra with a strong intense emission in its aggregated state than its dilute solution in any good solvent. This aggregation induced enhanced (AIE) blue emission are explained due to suppression of twisted intramolecular charge transfer (TICT) state in the aggregated structure and the blue shifted emission appears from the locally excited (LE) state of BZP in its aggregated structures. A broad red shifted emission band is also observed and it increases in intensity with increasing size of the aggregates. This broad emission originates from the excited intramolecular charge transfer (ICT) state of the relatively planar molecule present within the aggregated structures of BZP due to crystal softening. We have also used this aggregated material in fluorescence sensory probe and found its quenching efficiency in presence of D-Glucose. Quenching of blue emission from the aggregated structure has been explained due to the hydrogen bonding complexation between D-Glucose and BZP molecule present in the aggregated structures.

2. Experimental:

Materials: 4,4′-bis(diethylamino)benzophenone (BZP) and D-Glucose were purchased from Sigma-Aldrich Chemical Corp. Tetrahydrofuran (THF), Cyclohexane (CH), N, N dimethyl formamide (DMF) were purchased from E-Merck India Ltd. All the chemicals were of analytical grade and the purity were checked by UV-Vis spectroscopy. Triply distilled deionised water was used throughout the experiment.

Fluorogen Preparation: BZP aggregates were prepared through well known reprecipitation method. 0.01 M solution of BZP was prepared using THF as good solvent. Then different amount of the above solution (10µL for Sample A, 20µL for Sample B, 30µL for Sample C, 50µL for Sample D, 70µL for Sample E, 100µL for Sample F) were rapidly injected into 5 ml water and allowed to stir for 2 min. The final concentrations of BZP are 20µM, 40µM, 60µM, 100µM, 140µM and 200µM for sample A, B, C, D, E and F respectively. Clearness of the solutions gradually decreases and milky white color was appeared. The solutions were allowed to stand for 30 min.

Characterization: UV–Vis absorption spectroscopy was used to characterize the optical properties and was measured in a 1cm quartz cuvette with a Shimadzu UV-1800 spectrophotometer. The spectra were recorded at room temperature in the range between 270 to 600 nm. Steady state fluorescence spectra were recorded using Hitachi F-7000 Fluorescence Spectrophotometer. Time-resolved fluorescence measurements were carried out under ambient conditions using a time-correlated single-photon counting (TCSPC) spectrometer [a picoseconds diode laser (IBH, UK)]. All samples were excited using 280 nm picoseconds diode laser and the emission was collected at 339 and 460 nm. Lamp profiles were measured with a band-pass of 3 nm using Ludox as the scatterer. The decay parameters were recovered using a non-linear iterative fitting procedure based on the Marquardt algorithm[44]. The quality of fit was assessed over the entire decay, including the rising edge, and tested with a plot of weighted residuals and other statistical parameters *e.g.* the reduced χ^2 ratio[45]. The morphologies of the synthesized micro structures were studied using ZEISS EVO 18 scanning electron microscope (SEM) operated at an accelerating voltage of 10 kV. Before SEM study samples were vacuum dries on a glass plate and a thin layer of Au was deposited onto the samples to minimize sample charging. Optical microscopy images were taken using NIKON ECLIPSE LV100POL upright microscope equipped with a 12V-50W mercury lamp. The samples for optical microscopic study were prepared by placing a drop of colloidal solution onto a clean glass slide.

Computational Method: In the aggregated structures of molecules, where strong interaction between different atomic centers's of similar kind of molecule take place, a second-order local reactivity descriptor (LRD) called Fukui function[46-49] may be used instead of electronic density. Fukui function is defined in terms of the derivative of electronic charge density, $\boldsymbol{\rho(r)}$ with respect to total no. of electrons, N.

$$f(r)=\left[\frac{\partial\rho(r)}{\partial N}\right]_{v(r)} \text{............................} (1)$$

The function $\boldsymbol{f(r)}$ reflects the ability of a molecular site to accept or donate electrons. High values of $\boldsymbol{f(r)}$ are related to a high reactivity at point *r* [46]. Since the number of electrons 'N' is a discrete variable[50], right and left derivatives of $\boldsymbol{\rho(r)}$ with respect to 'N' have emerged. By applying a finite difference approximation to equation 1, two definitions of Fukui functions depending on total electronic densities are obtained:

$$f^+(r)=\left[\frac{\partial\rho(r)}{\partial N}\right]^+_{v(r)}=\rho_{N+1}(r)-\rho_N(r) \text{........................} (2)$$

$$f^-(r)=\left[\frac{\partial\rho(r)}{\partial N}\right]^-_{v(r)}=\rho_N(r)-\rho_{N-1}(r) \text{......................} (3)$$

Where $\boldsymbol{\rho}_{N+1}(r)$, $\boldsymbol{\rho}_{N}(r)$, *and* $\boldsymbol{\rho}_{N-1}(r)$ are the electronic densities at point '*r*' for the systems with N+1, N, and N-1 electrons, respectively. The first one, $\boldsymbol{f}^{+}(r)$, has been associated to reactivity for a nucleophilic attack so that it measures the intramolecular reactivity at site 'r' toward a nucleophilic reagent. The second one, $\boldsymbol{f}^{-}(r)$, has been associated to reactivity for electrophilic attack so that this function measures the intramolecular reactivity at site 'r' toward an electrophilic reagent[47].

Morell *et al.*[51-55] have proposed a local reactivity descriptor (LRD) which is called the dual descriptor (DD) $\boldsymbol{f}^{2}(r) \equiv \boldsymbol{\Delta f}(r)$. Morell and co-workers used the notation $\boldsymbol{\Delta f}(r)$, but currently it has been replaced by the modern notation $\boldsymbol{f}^{2}(r)$ in order to highlight the fact that this is a Fukui function of second order. Its physical meaning is to reveal nucleophilic and electrophilic sites on a molecular system at the same time. Mathematically, it is defined in terms of the derivative of the Fukui function, $\boldsymbol{f}(r)$[46], with respect to the number of electrons, N. Through a Maxwell relation, this LRD may be interpreted as the variation of $\boldsymbol{\eta}$ (the molecular hardness which measures the resistance to charge transfer[56]) with respect to $\boldsymbol{v}(r)$, the external potential. The definition of $\boldsymbol{f}^{2}(r)$ is shown below as indicated by Morell *et al.*[51,52]

$$f^{(2)}(r)=\left[\frac{\partial f(r)}{\partial N}\right]_{v(r)}=\left[\frac{\partial \eta}{\partial v(r)}\right]_{N} \quad \text{........................} \ (4)$$

As mentioned above, DD allows one to obtain simultaneously the preferable sites for nucleophilic attacks ($\boldsymbol{f}^{2}(r) > 0$) and the preferable sites for electrophilic attacks ($\boldsymbol{f}^{2}(r) < 0$) into the system at point '*r*'. Density Function Theory (DFT) based computation with hybrid functional (B3LYP) and 6-31G(d) basis set were used to compute the second order Fukui function, $\boldsymbol{f}^{2}(r)$. All the computations in this present study were carried out using Gaussian-09 package programs[57].

3. Results and Discussion:

UV-Vis study: Fig. 1a shows the absorption spectrum of 60µM BZP in different nonaqueous good solvents at room temperature. There are two distinct absorption band of BZP in good solvent. The higher energy band at ~300-330 nm is due to n-π^{*} transition and the lower energy band at ~340-360 nm is due to

π-π^* transition[58]. Both the shape and the peak positions are highly sensitive to the solvent polarity. With increasing dielectric constant of the medium from Cyclohexane (2.02) to DMF (38), a regular red shift of the π-π^* transition from 340 nm to 362 nm is observed (Fig. 1a). Deconvolution of UV-Vis absorption spectra in cyclohexane medium using multiple Gaussian peaks shows two bands centered at 308 nm and 340 nm respectively (Fig. 2). Gradual red shifts of UV-Vis absorption bands from 316 nm and 353 nm to 326 nm and 362 nm are observed as we increase the polarity of the medium from THF to DMF. In addition to that, width of these bands also increases with raising the polarity of medium. The solvent polarity sensitivity of absorption spectra of 60μM BZP is further verified using different ratio of cyclohexane and THF as solvent (Fig. 1b). The large bathochromic shift of the low energy band with increasing polarity of solvent suggest that the π-π^* band has charge transfer character. The UV-Vis absorption study of aggregated hydrosol of BZP shows that apart from n-π^* and π-π^* band at 311and 344 nm another red shifted absorption band is appeared, the intensity and broadening of this red shifted band increases with the increase of the aggregated structure (Fig. 1c). It is observed that the broad red shifted band is centered at 398 nm (Fig. 2) while deconvoluting the spectra using multi peak Gaussian functions. The band at 398 nm is assigned to the J-aggregates of BZP. In general, the J-aggregation band is distinctly red-shifted and appears as an intense narrow absorption band due to the motional narrowing[59, 60], but that of BZP aggregates in Fig. 1c is relatively broad. This result suggests that the molecules in aggregates may be oriented in a less optimal way of J-aggregation. Lattice disorder is considered as one of the possible reasons of this inhomogeneous broadening of spectra[61].

Emission study: Fluorescence spectra of BZP in different nonaqueous solvents were recorded with an excitation at 300 nm (Fig. 3a). A gradual bathochromic shift of emission band from 388 nm to 405 nm to 416 nm with decreasing intensity were observed as we increased the solvent polarity from cyclohexane (ε=2.02) to THF (ε=7.5) to DMF (ε=38). Polarity sensitive nature of emission spectra was further verified by using different volume ratio of cyclohexane / THF as solvent (Fig. 3b). Shift of emission maxima and emission intensity as a function of different volume ratio of cyclohexane / THF are shown in Fig. 3c. This broad and solvent polarity sensitive emission band originates from the polar twisted intramolecular charge transfer (TICT) state of BZP. Our DFT based computational study on both the ground and excited singlet state geometry of BZP show that the angle between two phenyl rings is ~45^0 in S_0 state and ~82^0 in the S_1 state and one of the diethyl amino group twisted about 26^0 in the S_1 state compare to S_0 state. Therefore, a highly polar TICT state is present in BZP which is further stabilized with increasing polarity of the medium. The decrease of emission intensity from TICT state with solvent polarity is due to the decreasing energy gap between ^{1}(TICT) and the low lying ^{3}(TICT) state. This decreasing energy gap open up the deactivation intersystem crossing (ISC) channel from ^{1}(TICT) to ^{3}(TICT) and thus decreases the emission intensity originating from ^{1}(TICT) state[62]. But the dramatic increase in photoluminescence (PL) intensity in its aggregated state compare to its molecular electronic state in good solvent under identical reaction condition inspires us to explore the aggregation induced emission enhancement (AIEE) effect. In order to verify the stability of the luminogen, PL spectra of BZP hydrosol (sample A) at different time interval after its preparation are shown in Fig. 4a. PL intensity increases with time and reaches the maximum after 30min. Initially the mechanical shear stress leads to the increasing chances of most probable collisions; thus a portion of BZP molecules clustered together to form tiny particles. The remaining portion of BZP molecules presents in the solvent mixture then gradually deposited onto the initially formed particle in recrystallization pattern to give highly emissive aggregated structure. So with increasing time, the system attains an ordered cluster which restricts the free rotation of diethyl aniline groups and as a result the enhanced emission of molecules appears. After 30 min a very small ~4% decrease is observed in the intensity of the spectra with increasing time. This may be due to the fluctuation of power of the excitation source after prolonged use.

PL spectra (Fig. 4b) of BZP in THF/water mixtures (<80% water) are basically flat lines (320-380 nm) parallel to the abscissa and the emission intensity at around 430 nm gradually decreases (the inset of Fig. 4b) as the water fraction (f_w) increases. However, when a large amount of water (99%) is added to the solution in THF, the peak at around 430 nm disappears and a structured emission band with maxima at 339 nm is appeared. The PL intensity around 339 nm rises 580-fold as the water fraction is increased from 0% to 99%, (Fig. 4c). Inset of Fig. 4c shows the emission color of BZP in THF and aggregated BZP hydrosol under UV light illumination. No visual detection of emission color for BZP in THF indicates that the emission intensity is too weak to be observed in the naked eyes. The intense blue emission from aggregated BZP hydrosol suggests that AIEE occurs in our present case. Tang and Park groups first discovered the AIE/ AIEE phenomenon in 2001[13, 14]. Most of the reported AIE-active molecules are propeller-like shapes with weak π-π stacking interactions. The restriction of intramolecular rotation processes is proposed as the main mechanism for AIE. According to this mechanism, PL is enhanced in the solid state with a slight red shifted band than its emission from molecular state in good solvent. This cannot explain the present exceptional blue shift in the emission spectra of aggregated BZP. Another interesting feature of PL spectra of BZP hydrosol is that, the intensity of 339 nm band increases with the increasing concentration of BZP (i.e. increased size of aggregated structures), reaches a maxima and then decreases with further increase of BZP concentration. On the other hand, when we change the concentration of BZP keeping the water percentage same, another interesting feature of the emission spectrum *i.e.* a new broad and red shifted band with peak around 460 nm is appeared (Fig. 4d). We also observed visual change of emission color when UV light is irradiated on THF/water solution containing 60μM and 200μM BZP in water (inset of Fig. 4d). Two distinct colors *i.e.* deep blue and sky blue emissions are observed from these hydrosols respectively. There two distinct emissions band *i.e.* one at 339 nm and the other one broad peak at 460 nm is due to two kind of conformer of BZP present within the aggregates. Ground state optimized geometry of BZP shows that the angle between the two phenyl rings is ~ 45^0. Though there is certain angle between the two phenyl rings of the BZP, they are not free to rotate even in the excited state due to restricted geometry in the aggregated structure. Since the Van der Waals force of attraction which is responsible for aggregation of BZP in water, diethyl aniline rings of BZP are almost twisted in low concentration, restricting its free rotation. Excitation of these BZP to its locally excited (LE) state results structured emission band with peak maxima at 339 nm. On the other hand at higher concentration of BZP, crystals get soften resulting lattice disordered. We presume that due to irregular packing of BZP in larger aggregates few molecules attain more planer geometry in their aggregates to allow the most feasible intramolecular charge transfer (ICT) process and the broad red shifted emission at 460 nm arises from the ICT state.

Time resolved Fluorescence Study: In order to understand the nature of emission spectra of aggregated BZP hydrosols and BZP in good solvent, we have carried out time resolved fluorescence study with excitation at 280 nm and emissions were measured at 405 nm for BZP in THF and at 339 and 460 nm for aggregated hydrosols. Decay profile of monomer and hydrosols with emission wavelength at 339 nm and 460 nm are shown in Fig. 5a & 5b respectively. Fluorescence lifetimes of the samples are measured by deconvoluting the response function from the decay curves. Fluorescence lifetime of diluted BZP in THF is 0.49 ns with very weak emission intensity. It took nearly 30 times more to get comparable emission intensity as that of its aggregated hydrosols. Fluorescence decay profiles of aggregated BZP hydrosols having reasonably higher emission intensity are fitted with single exponential decay. The observed components of lifetime of aggregated BZP hydrosol at 339 nm peak position are within ~1.4-1.5 ns and the components corresponding to the peak position at 460 nm have fluorescence lifetime ~0.9 ns. Fluorescence lifetime data as listed in table-1 illustrates that the fluorescence monitored at 339 nm has average lifetime ~1.5 ns and the broad emission band at 460 nm has average lifetime ~0.9ns. Since all samples showing emission at 339 nm and 460 nm have similar average fluorescence lifetime, we may conclude that the emission from hydrosol comes from two different excited states. The ~1.5ns component of 339 nm band is due to locally excited BZP and the ~0.9ns component of 460 nm band is from ICT state of the relatively planer BZP present within the aggregated BZP.

Mechanistic Discussion: A systematic DFT investigation of the optimized geometry of the ground (S_0) and lowest singlet excited (S_1) states were performed to understand this new AIEE phenomenon. Ground state geometry shows that the dihedral angle between two phenyl rings is 45.53^0. But in the excited singlet (S_1) state, this angle changes to 80.09^0 (Fig. 6a). These significant differences in the geometry changes from S_0 to S_1 may have a close relationship with the AIEE properties of the molecule. HOMO-LUMO electron distribution (Fig. 6b) in the ground state of the molecule suggests that the TICT state is responsible for weak emission of this molecule in good solvent. But in aggregated state, rotation around intramolecular axis is completely restricted and the molecule attains relatively planar aggregated geometry where energy loss due to TICT is hindered. Thus in aggregated structures excitation of BZP occurs to its high energy locally excited (LE) state which shows intense blue shifted emission with structured vibronic band. This is known as aggregation induced locally excited (AILE) emission.[63] In case of larger aggregated structure, crystal softening occurs and this results to attain a more planer geometry of BZP than the molecule present at the tightly packed aggregates. These planer BZP molecules upon photo excitation undergo charge transfer between the donor diethyl aniline group and acceptor keto group. The presence of two identical donor groups (diethyl aniline), further resonance stabilizes the intramolecular charge transfer (ICT) state. Vertical transition from the ICT state occurs to the repulsive part of the ground state potential energy surface resulting broad and structures less emission. Since crystal packing is strong in smaller aggregates, the emission from the LE state of BZP molecules *i.e.* at 339 nm is the only emissive state. This is further supported by our experimental observation, where we observed that the emission band centered at 339 nm is decreased in intensity with the increased size of aggregated BZP (BZP concentration > 60μM) structures. This increased size results crystal softening of the aggregates *i.e.* the loosening of aggregated BZP molecules and facilitate the internal charge transfer in planer geometry. It is observed that the emission intensity of LE band (339 nm) decreases and intensity of the broad red shifted band (460 nm) from ICT state increases (Fig. 4d) with the increasing size of aggregates. Since we have not been able to grow single crystal of BZP for X-ray study or no such data of this molecule is available in the literature, we have tried to understand the possible sites of interaction by computing second order Fukui parameter as local reactivity descriptors between the neighboring molecules in the crystalline form. Second order Fukui Parameter ($\boldsymbol{f}^{\,2}(r)$) as local reactivity descriptor for each atomic centre of BZP is listed in table 2. Since negative value of $f^2(r)$ is a preferable cites for electrophilic attack and positive $f^2(r)$ values are the possible sites for nucleophilic attack, table 2 illustrates that C_{11}, C_{20}, C_{14}, C_{39}, H_{17} are the most electrophilic center and N_{24}, C_3, C_5, C_{13}, C_{49} are most nucleophilic center. Thus N_{24} centre of one BZP molecule will be close enough to the C_{11} centre of another molecule through Van der Waals force of attraction. The possible arrangement of BZP in its aggregates state is shown in Scheme 2 and it helps to predict that BZP aggregates will prefer head to head slipped geometry in its aggregated structures.

SEM & Optical Microscopic study: SEM micrograph of sample-F is shown in Fig. 7. From this micrograph it is observed that particles have mostly rectangular and higher polygon like morphologies with equal thickness. It seems a two dimensional growth of particles take place with the increasing concentration of BZP in solution.

Fig. 8a shows the optical microscopic images of sample-F. The sizes of other samples are too small to be detected within the resolution of our optical microscope. The morphology of the microcrystals of sample-F though irregular but a clear two dimensional growth of crystals are noticeable. Fluorescence microscopic images of the crystals under UV excitation show distinct sky blue emission from the edges of crystals (Fig. 8b). Initially we thought this emission may be due to crystal induced phosphorescence from BZP.

But the time resolved fluorescence emission study of sample-F monitored at 460 nm is found to be ~0.94 ns and we presume that this faster fluorescence lifetime component is coming from other than triplet state of BZP. Now the deep blue emission from the crystal surface and distinct sky blue emission from the edges of crystals, it is clear that two types of emissive states are present within BZP aggregates. Our UV-Vis study reveals that lattice disorder may be responsible for the inhomogeneous broadening of the 398 nm bands and the BZP molecules are present in less optimal way *i.e.* more planar form in the disordered sites. Since BZP is a donor-acceptor (D-A) type of molecule, the intramolecular charge transfer (ICT) state will get stabilized in this planar geometry. During the two dimensional growth of aggregates, disordered sites are formed on the growing part *i.e.* edges of larger aggregates. Thus the sky blue emission from the growing edges of crystals is coming from the ICT state of BZP. On the other hand the strong blue emission from the crystal surface arises from locally excited (LE) state of BZP present in twisted form within the crystals. Dark field's view of this sample F using polarizer and analyzer assembly shows different colors depending on the direction of incident radiation and it reveals the anisotropic nature of the synthesized microcrystal (Fig. 8c).

4. Glucose Sensor:

AIEE luminogens are useful analytical tools and have been judiciously utilized as sensitive and selective chemosensors and bioprobes. Sugars play important roles in biological processes such as metabolism. There is great demand for the development of convenient methods for selective recognition of sugars in aqueous media due to their obvious clinical and therapeutic values. For example, monitoring glucose levels in biological fluids such as urine and blood is essential for the management of diabetes. So here we introduce the most interesting turn off glucose sensing property of this aggregated luminogen. BZP molecules are aggregated in solid state through Van der Waals force of attraction with the neighboring molecules. Glucose is a hexose sugar possessing six hydroxyl groups in its open chain structure. With the help of this -OH groups, it will offer strong hydrogen bonding interaction with the electronegative N and O centers of BZP within the aggregates. This will cause loosening of crystal packing of BZP in the aggregated luminogen.

This loosening of crystal packing as well as hydrogen bonding interaction of glucose with the surface BZP molecules causes quenching of LE state emission of BZP within the luminogen. The decrease of LE state (339 nm) emission intensity with increasing glucose concentration is shown in Fig. 9a. Small increase of emission intensity of 460 nm band with increasing glucose concentration is due to crystal softening as glucose is added to the hydrosol of BZP aggregates. We also introduce a calibration curve where the change of the ratio of emission intensity with respect to the concentration of glucose is shown (Fig. 9b). Our study shows that the minimum glucose concentration that can be detected using the above method is about 1.1 mM.

5. Conclusion:

In our present study, we have introduced conjugated D-A moiety which exhibits broad and structure less fluorescence spectra in different kinds of solvents but in aggregated state blue shifted structured emission band is observed and it has been termed as aggregation induced locally excited emission enhancement (AILEE). Apart from AILEE, another broad red shifted band appears in the hydrosol with the increasing concentration of BZP. Simultaneous appearances of these two kinds of emission band in the aggregated hydrosols are rare in literature. Our extensive photo physical study of the hydrosol revealed that two types of emissive state are present in the aggregated structures of BZP. But with increasing concentration, lattice disordered is introduced to the microcrystals and the crystal softening allow this molecule to attain a planer geometry in which ICT is more feasible. The broad red shifted band at 460 nm is appeared from the ICT state of the relatively larger aggregates. On the other hand intense blue emission from the aggregated hydrosols is coming from the locally excited (LE) states of the relatively twisted conformer of BZP present within the microcrystals. Our study also revealed that the AILEE band can be used for sensing glucose at a very concentration in aqueous solution. The strong quenching of AILEE emission in presence glucose is due to softening of aggregated structures of the luminogen.

Keywords: BZP, AIEE, Crystal softening, Intramolecular charge transfer state, TICT, Fukui parameter, glucose sensor.

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