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Fluorescence Quenching and Enhancement by H-bonding Interactions in Some Nitrogen Containing Fluorophores

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The benzo[*de*]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (1) shows solvent dependent fluorescence emission. The compound shows quenching of fluorescence emission on interaction with polyhydroxy compounds such as 1,3-dihydroxybenzene, 1,4-dihydroxybenzene. The result on fluorescence quenching is attributed to the hydrogen bonding interactions. Similar observation of fluorescence quenching by protic solvent is observed with isoindolo[2,1-a] perimidin-12-one (2). In the case of 2-(2-amino-phenyl)-isoindole-1,3-dione (3) enhancement of fluorescence emission in methanol solution is observed over benzene solution. This is explained on the basis of intermolecular hydrogen bonding. The crystal structure of adduct of 1 with 1,3-dihydroxybenzene, 1,4-dihydroxybenzene respectively and 3 are reported.

Keywords: Fluorescence; Quenching; H-bonding; Solvatochromicity

INTRODUCTION

There is a definite need for understanding enhancement or quenching of fluorescence emission of a fluorophore by externally added substrate/s [1,2]. Extensive literature is available on the fluorescence properties of naphthalimide derivatives [3–9]. Several such studies are devoted to identify on and off fluorescence states in these derivatives [10–13]. However, there are limited studies on understanding fixed geometry responsible for quenching or enhancement of fluorescence emission. This is predominantly because of the fact that such studies are generally performed in solution. In solution the molecules are relatively loosely bound, and this makes it difficult to explicitly demonstrate all the weak interactions such as $\pi-\pi$ or hydrogen bonding interactions [14]. On the other hand in solid state the difficulty is to identify an organized state that would serve as a model. Recently, it is pointed out that in solution $\pi-\pi$ interaction between aromatic rings leads to enhancing of electronic communication between the two subsystems and such effect is reflected in fluorescence emission of the interacting system [15,16]. Moreover, the naphthalimide derivatives have biological importance and in analogous molecules it was reported that $\pi-\pi$ interactions play a decisive role in fluorescence emission [16]. We felt that if suitable motifs are identified and their properties in solid state are studied, it will add real value in determining motifs responsible for fluorescence quenching or enhancement. Thus, we have studied the fluorescence properties of a few substrates (**1**–**7**; Fig. 1) with an aim to understand the role of hydrogen bonding in fluorescence emission in these compounds.

RESULTS AND DISCUSSION

It is observed that the position and intensity of fluorescence emission ($\lambda_{ex} = 450$ nm) of benzo[*de*]-benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (**1**) is solvent dependent. The fluorescence properties of this compound were reported earlier [17] but the effect of hydrogen bonding on fluorescence emission was not studied. The compound **1** on excitation at 450 nm in methanol shows emission at 507 nm whereas it shows emission at 485 nm in benzene (Fig. 2). When the intensity of fluorescence emission of samples with identical concentrations of **1** in methanol is compared with a solution of benzene it is found that there is a considerable amount of

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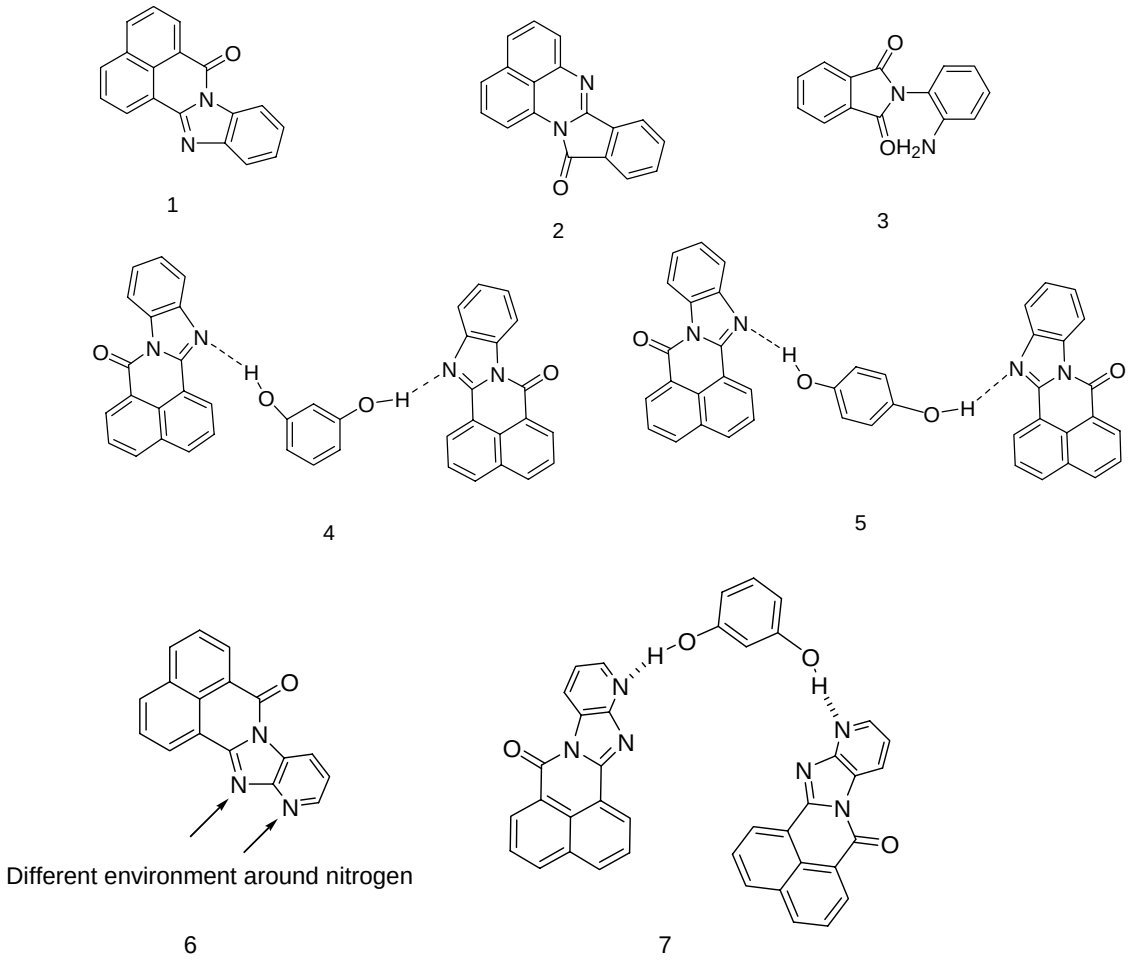

FIGURE 1 Nitrogen containing Flourophores and their adduct with dihydroxybenzenes.

reduction in intensity of emission in methanol over a benzene solution. Thus, a protic solvent reduces the intensity of fluorescence emission of **1** and also takes emission towards a higher wavelength. To establish this fact we have prepared two hydrogen bonded adduct of **1**, namely **4** with 1,3-dihydroxybenzene and **5** with 1,4-dihydroxybenzene and determined the crystal structures of these two adducts. The benzo[*de*]benzo[4,5]Imidazo[2,1-a]isoquinolin-7-one (**1**) forms 2:1 adducts **4** with 1,3-dihydroxybenzene and **5** with 1,4-dihydroxybenzene respectively (Fig. 1). The structure of the adduct **4** has several interesting features. In the adduct **4** the H-bonding takes place between two nitrogen atoms of two molecules of **1** with the hydroxy groups of one molecule of 1,3-dihydroxybenzene to form a U-shaped structure (Fig. 3a). The adduct is formed by weak hydrogen bonding interaction between the nitrogen atom and the hydroxyl groups. For the N···H—O interaction the donor–acceptor bond distance and bond angles participating in hydrogen bonding in this adduct are 2.884 Å and 173.96° respectively. The N···H and H—O distances are 1.958 Å and 0.93 Å, respectively. In the crystal lattice these interactions allow two molecules of **1** to appear above each other as stacks (Fig. 3b). In this orderly arrangement the hinges are provided by 1,3-dihydroxybenzenes. From the top view it can be seen that the molecular arrangement in the lattice is symmetric to a 90° rotation followed by a translation if each pair is considered to be an object to be rotated. There are two types of π-separations between the aromatic rings in the crystal lattice of the adduct **4**. The two separations between the aromatic layers are shown in the packing of the crystal lattice as **X** and **Y** (Fig. 3b) are 3.581 Å and 3.621 Å. These distances are slightly higher than the limit 3.5 Å that is conventionally found in molecules having π−π interaction [14,18,19]. Thus, one can say that in this system the π−π interaction has lesser significance.

Similarly, the adduct **5** formed by benzo[*de*]benzo [4,5]imidazo[2,1-a]isoquinolin-7-one with 1,4-dihyroxybenzene has the nitrogen atom of the benzo[*de*] benzo[2,1-a]isoquinolin-7-one bound to a hydroxyl group of 1,4-dihydroxybenzene. The other hydroxyl group of 1,4-dihydroxybenzene holds another nitrogen atom of benzo[*de*]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one. In the N···H—O interactions the d_{D-A} bond distance and < D—H···A angle is 2.884 Å and 75.75°, respectively (Fig. 4).

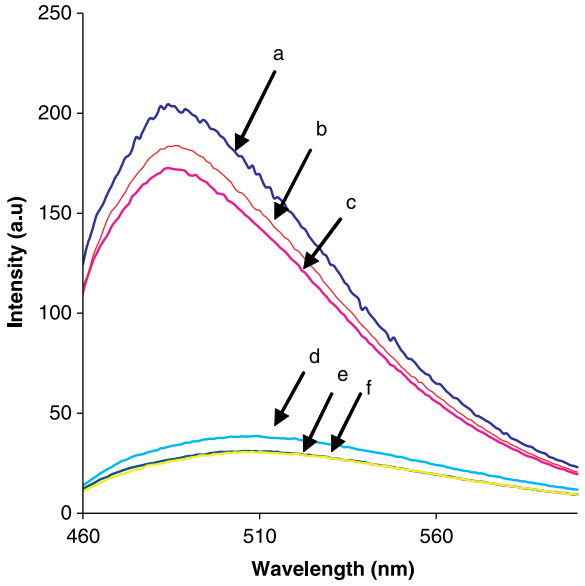

FIGURE 2 Emission spectra on excitation at 450 nm of (a) **1** in benzene, (b) **5** in benzene, (c) **4** in benezene, (d) 1 in methanol, (e) 4 in methanol with 1,4-dihydroxybenzene, and (f) 5 in methanol with 1,3-dihydroxybenzene (0.01 mmol in 5 ml in each case).

The fluorescence emission spectra of the compounds **1**, **4** and **5** in solid state were measured by exciting at 450 nm. In the solid state the parent compound **1** on excitation at 450 nm has a fluorescence emission at 493 nm with a shoulder at 550 nm. Whereas, the adduct **4** has a very feeble fluorescence emission at 530 nm (Fig. 5) (λ_{ex} = 450 nm). The adduct **5** also shows a very weak fluorescence emission at 535 nm on excitation at 450 nm. From crystallographic study it is evident that there are no $\pi-\pi$ interactions among the parent fluorophores. So, it may be suggested that by formation of H-bonded adducts, the inter-motif interactions that would have originally been present in the fluorophore are changed. This results in the modification of the energy states, which lowers the fluorescence intensity. We also examined the concentration dependent ^{1}HNMR spectra of the compound **1** in acetonitrile (please refer to supplementary material). No significant changes in the chemical shifts or coupling pattern of the ^{1}HNMR signals on change of concentration except broadening of the signals due to dipolar interactions was observed. This indicates no significant $\pi-\pi$ interactions among the molecules of **1** in solution also. Alternately, acetonitrile does not change the electronic environment of the molecule **1**, and this result also adds to the fact that it does not quench fluorescence of **1** but behaves in a manner similar to that of benzene.

The compound isoindolo[2,1-a] perimidin-12-one (**2**) is a structural isomer of **1** but has a different heterocyclic ring due to a difference in the position of the nitrogen atoms and carbonyl groups in the ring. The fluorescence emission of **2** on excitation at

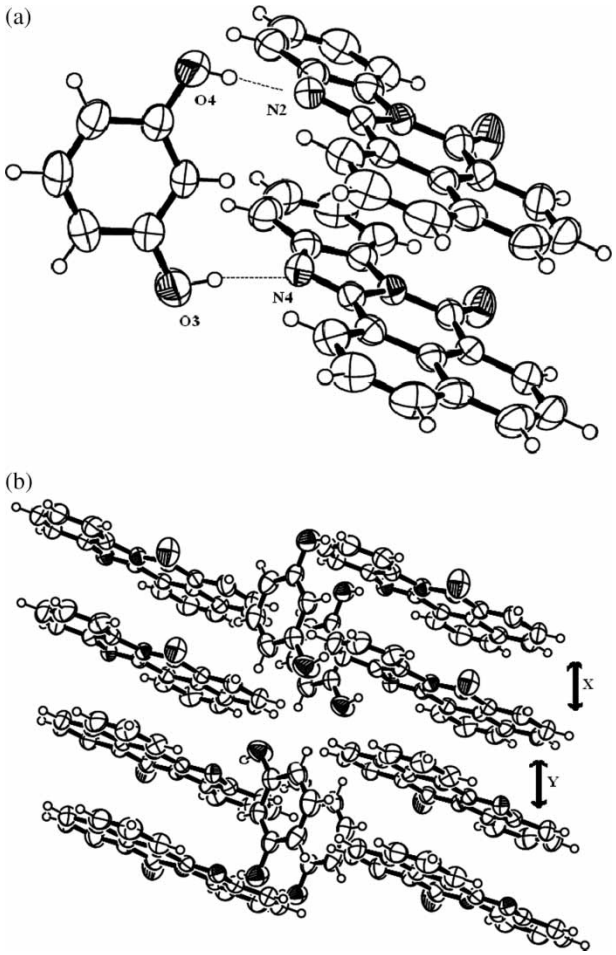

FIGURE 3 (a) The structure of **4** in solid state (50% thermal ellipsoid) and (b) packing of the adduct to show the arrangement of rings.

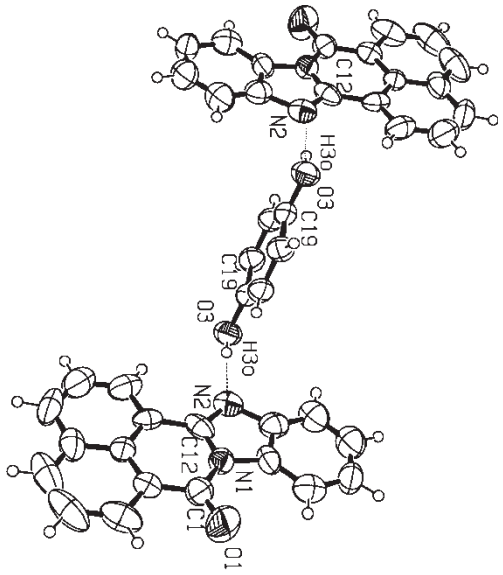

FIGURE 4 Structure of **5** (ORTEP with 50% thermal ellipsoid).

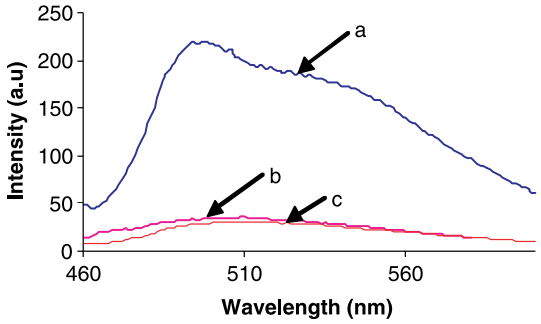

FIGURE 5 Fluorescence emission spectra of (a) **1**, (b) **4**, and (c) **5** on excitation at 450 nm in solid state.

540 nm is sensitive to solvent. For example, in methanol it shows poor fluorescence emission (Fig. 6) whereas, a solution of **2** in benzene (identical concentration) shows emission at 592 nm, which is about 12-fold higher in intensity than that of methanolic solution. The emission of an acetonitrile solution has an intermediate effect on the intensity of emission. Thus, the solvent capable of H-bonding such as methanol reduces the intensity of emission drastically. To check the possibility of identifying the type of interactions among the molecules of **2** in different solvents the concentration dependent UV–visible spectra were recorded in three different solvents namely benzene, methanol and acetonitrile. It was found that the slopes and trends of variation of concentration versus absorbance are different for each solvent. This suggests that the intermolecular solute solvent interactions causes changes in the spectra and such effects are well documented in the literature [20]. In case of a protic solvent the hydrogen bonded structure changes the original intermotif interactions and one can see the quenching of fluorescence due to modification of the ground state.

To further strengthen our observations, we studied another related molecule 2-(2-aminophenyl)-isoindole-1,3-dione **(3)** that has a phthalimide ring as well as an amino group. The position of the amino group allows it to have conjugation over the two rings. The protonation of the amino group of this molecule affects the intermolecular hydrogen bonding. We studied the visible spectroscopic and fluorescence emission spectra of this compound (**3**) in different solvents. It was found that the compound has different trends in the concentration dependent profiles (Figs. 7 and 8) in the UV-spectra in different solvents. In this case the protic solvent enhances the absorption intensity and shifts the absorption to a higher wavelength. The concentration dependent UV-spectra shows that in methanol the concentration versus absorbance has a regular growth as expected from Beer's Lambert law (Fig. 7, inset) but in the case of benzene as a solvent there is deviation from the straight line that would pass through the origin (Fig. 8, inset). This may be due to the fact that a protic medium disrupts the intermolecular hydrogen bonding among the individual molecules whereas benzene being a non-protic solvent allows intermolecular hydrogen bonding between the molecules of 2-(2-aminophenyl)-isoindole-1,3-dione. The effect is reflected in the fluorescence emission spectra of the compound (**3**) in different solvents (λ_{ex} = 435 nm) also. In methanol the compound shows emission at 505 nm, in acetonitrile it emits at 487 nm, whereas it emits at 471 nm in benzene (Fig. 9). The observed intensity of emission in different solvents are in the order methanol > acetonitrile > benzene. This indicates that the solvent polarity as well as hydrogen bonding may be responsible for such a process. Methanol forms hydrogen bonds with the amino group, thus changing the magnitude of intermotif interactions. To distinguish the effect of protonation from H-bonding interactions, we recorded the visible spectra of **3** in the presence of hydrochloric acid in methanol. The addition of acid to the methanolic solution of the compound immediately showed a new absorption peak at 456 nm with an intensity comparable to the absorption of the parent compound. The effect of addition of acid is also reflected in the fluorescence emission.

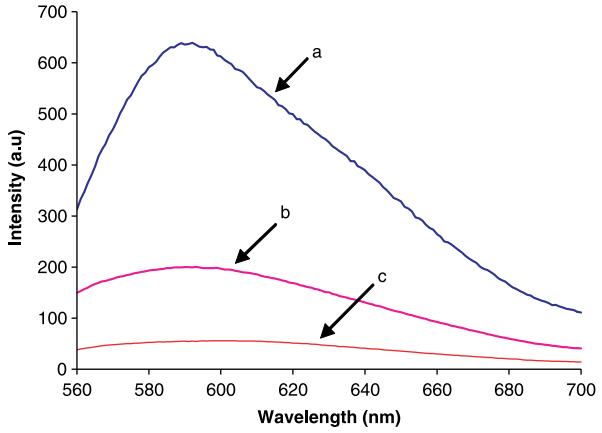

FIGURE 6 Fluorescence emission on excitation at 540 nm of **2** in (a) benzene, (b) acetonitrile, and (c) methanol (0.02 mmol in 5 ml solvent in each case).

On excitation of an acidic solution of **3** in methanol at 450 nm it showed altogether a new but very low intensity emission at 572 nm. These results clearly indicates that protonation of the amine quenches the emission in the case of **3**. However, the observation on enhancement of intensity of fluorescence by methanol in the parent compound shows that the role of an acid and a protic solvent are totally independent. It may be concluded that hydrogen-bonding with the $-NH_2$ group with methanol causes disruption of intermolecular hydrogen bonding in compound **3** but does not generate a protic state. The structure of the molecule **3** in solid state has intermolecular hydrogen bonding between $-NH_2$

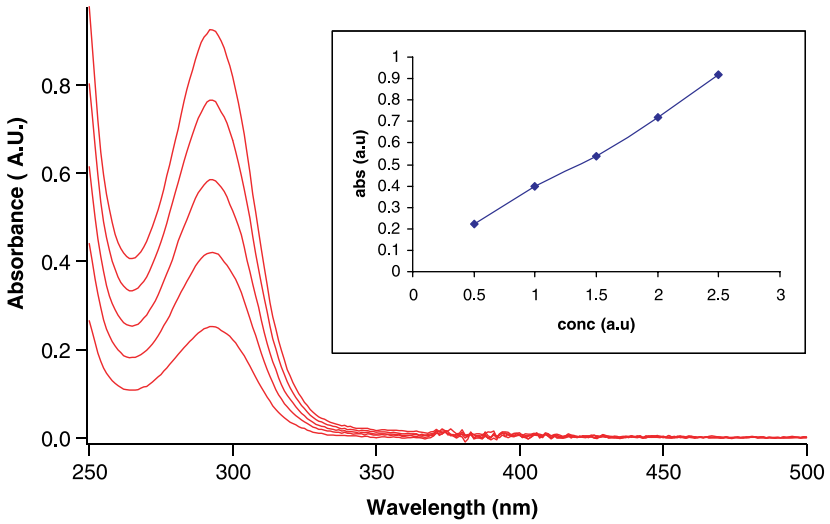

FIGURE 7 Changes in absorbance with the concentration of **3** in methanol (initial concentration 5×10^{-5} M (3 ml) with equal increments in concentration by adding 25 μl of stock solution to the parent solution after volume correction. Inset: plot of concentration versus absorbance).

groups with the carbonyl group of other molecules. The IR spectra in solid state clearly suggest the presence of intermolecular hydrogen bonding. In the IR spectra of **3** two very sharp absorptions at 3462 cm^{-1} and 3385 cm^{-1} due to intermolecular hydrogen bonding are observed. The effect can be explained by the scheme shown in Fig. 10a. Methanol being a protic solvent cause disruption of such hydrogen bonding and this leads to fluorescence enhancement. This suggests that the intermolecular hydrogen bonding among **3** is favoured in the case of benzene. The disruption of H-bonding makes the nitrogen atom more electron rich to pump in electron density to the aromatic ring which causes enhancement of intensity. The ability of water to exchange with the NH_2 group of **3** is revealed from the concentration dependent ^1H NMR of the compound **3**. We have recorded the ^1H NMR of the compound **3** in CD_3CN at a different concentration and found that the residual water in the acetonitrile could be distinguished from NH_2 group at low concentration (refer to supplementary data). The position of the NH_2 group was further ascertained by recording its ^{1}HNMR spectra in $CDCl_3$. At higher concentrations it was found that the residual water and the NH_2 signals cannot be distinguished as they appear as a broad signal. This shows that rapid exchange of NH_2 protons and water protons takes place at higher concentration, whereas at low concentration the exchange is less. This is obvious as the probability of interaction between two solute components in a dilute solution decreases. Although

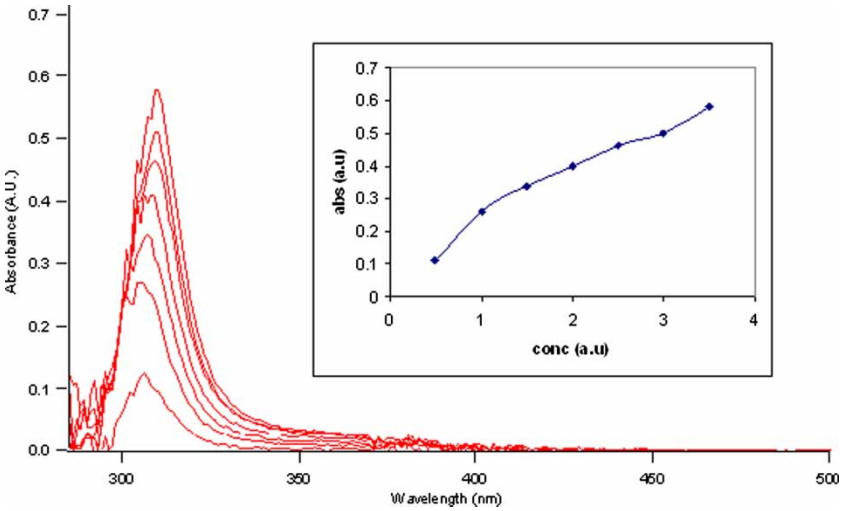

FIGURE 8 Changes in absorbance with the concentration of **3** in benzene (initial concentration 5×10^{-5} M (3 ml) with equal increments in concentration by adding 25 μl of stock solution to the parent solution after volume correction. Inset: plot of concentration versus absorbance).

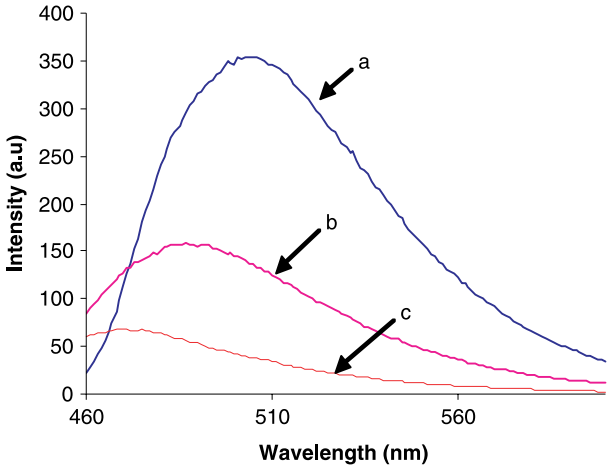

FIGURE 9 Fluorescence emissions on excitation at 435 nm of **3** in (a) methanol, (b) acetonitrile, and (c) benzene (0.02 mmol in 5 ml of each solvent).

this result is not conclusive to depict intermolecular hydrogen bonding among the molecules of **3**, it does tell us that the compound **3** prefers hydrogen bond formation with water. The fluorescence lifetime of the excited state of **3** was determined in methanol and benzene. It has a lifetime of $\Gamma = 45$ ns and $\Gamma = 27$ ns, respectively. Thus, the effect may be purely due to the hydrogen-bonding effect where the excited state is stabilised by hydrogen-bonding as the methanol has a longer lifetime. It is interesting to note that Licchelli *et al*. [21] had observer fluorescence quenching and enhancement of 1,8-naphthalimide-tethered iminopyridine ligands by adding copper(II) and zinc(II) ions respectively. The results were explained in terms of intramolecular excimer species, however, a careful look at the structure reveals that there is C = O···Cu interactions in the crystal structure whereas the zinc complex is devoid of such interactions. The compound **3** possesses C = O···H—N interactions which may be compared to the case of copper complex [21] where the electron density of the ring was drawn by this interaction and in our case such an effect is caused by an intermolecular hydrogen bonding.

Further support to our observations on the effect of hydrogen-bonding in enhancement on fluorescence comes from the compound **6** which shows slight enhancement of fluorescence at 481 nm (χ_{ex}, 450 nm) on addition of 1,3 dihydroxybenzene in acetonitrile solution. This effect is the reverse of the effect of 1,3-dihydroxybenzene on the fluorescence property of **1**.

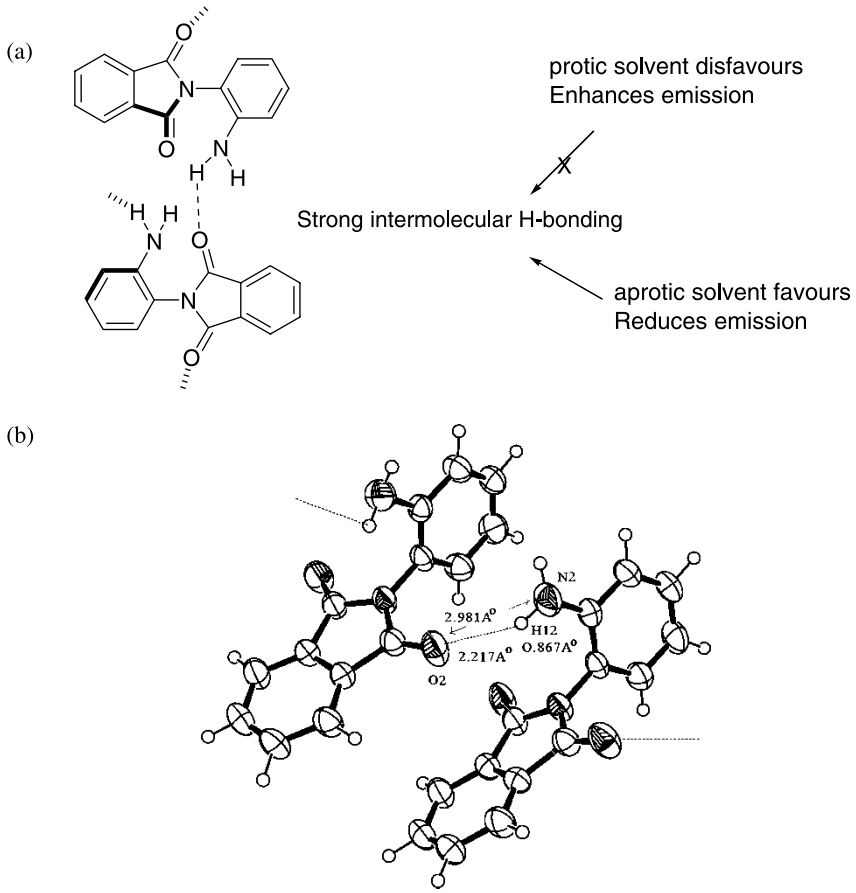

FIGURE 10 (a) Schematic representations of H-bonding in **3**, and (b) the crystal structure showing the intermolecular H-bonding interactions in **3**.

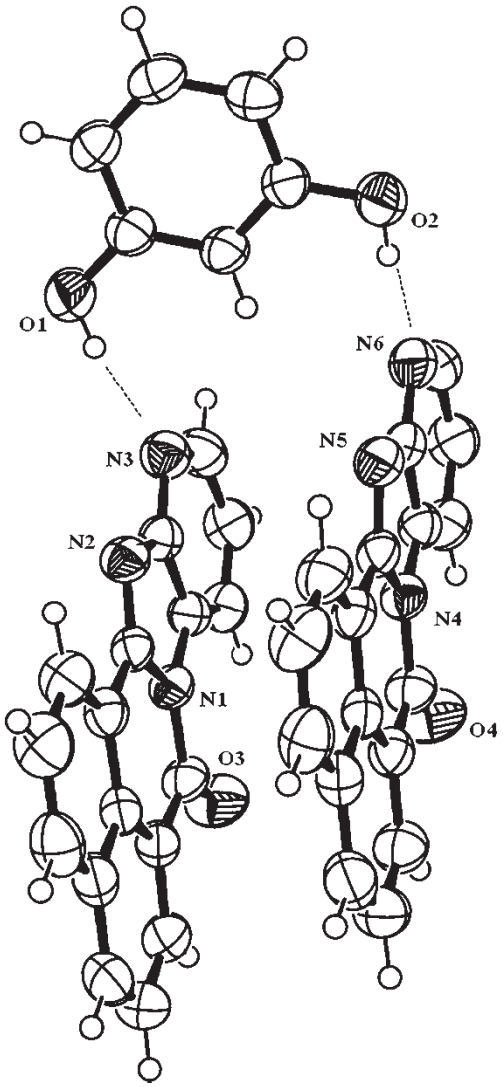

FIGURE 11 Structure of **7** (ORTEP with 50% thermal ellipsoid).

To further understand this effect, the crystal structure of the adduct was determined, and showed that the adduct of **6** with 1,3-dihydroxybenzene shows hydrogen bonding with the nitrogen of the pyridine ring rather than the nitrogen in the five-member ring as shown in Fig. 11. Thus, it is obvious that the hydrogen bond formation on the nitrogen atom of the pyridine ring makes the ring electron deficient thereby causing distinguishable delocalization in each case, namely in **4** and **7** resulting in a change in the fluorescence properties in the opposite manner. This is further supported by the fact that one equivalent of acetic acid in an acetonitrile solution of **6** enhances fluorescence emission whereas above one equivalent acetic acid shows a decrease in the intensity. This suggests that protonation of the nitrogen atom of pyridine ring of **6** enhances fluorescence whereas the protonation of imidazole nitrogen atom of the same compound causes a decrease in the intensity of fluorescence emission.

CONCLUSION

In conclusion, it has been shown that the site for hydrogen bonding in a fluorophore decides whether fluorescence enhancement or quenching will be observed on hydrogen bonding. In compound **1**, quenching of fluorescence is due to hydrogen bonding by 1,3-dihydoxybenzene to the nitrogen atom of the five-membered ring, whereas the opposite effect occurs in the case of **6** where the hydrogen bonding with 1,3-dihydoxybenzene preferably takes place at the nitrogen atom of the pyridine ring. The intermolecular hydrogen bonding in compound **3** causes lowering of fluorescence intensity. It has also been shown that the hydrogen bonding or protonation of **3** has a clear difference in terms of effecting the fluorescence emission. These results prove that the location of the heteroatom or functional group contributing to the hydrogen bonding of a fluorophore decides the enhancement or quenching of fluorescence and provides a greater understanding to control the fluorescence properties.

EXPERIMENTAL

All the chemicals were obtained from Sigma Aldrich Chemical Co and were used as obtained. The fluorescence spectra were recorded by a Cary Eclipse fluorescence spectrometer. For solid state fluorescence emission measurements, finely ground powder (50 mg) of each of the compounds were taken in a solid sample holder and was adjusted to an optimum position and excited at the wavelength as mentioned in the text. The fluorescence emissions in solutions were made by dissolving the substrate in suitable solvents and then exciting at the wavelength as mentioned. The IR spectra were recorded on a Nicolet DSP 450 spectrometer and the UV–visible spectra were recorded using a Hitachi U-3200 spectrophotometer. The X-ray diffraction data were collected using a Bruker 3-circle SMART Apex diffractometer with a CCD area detector, using graphite monochromated Mo–Kα; radiation from a 60 W microfocus Bede Microsource® with glass polycapillary optics. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software by direct methods. All data collection was carried out at room temperature.

Synthesis of Benzo[*de*]benzo[4,5]imidazo [2,1-a]isoquinolin-7-one (1)

Imidazole (340 mg, 5 mmol) was added to a solution of 1,8-naphthalic anhydride (396 mg, 2 mmol) and 1,2-phenylenediamine (216 mg, 2 mmol) in toluene

(15 ml). The solution was refluxed for 8hrs at 110°C, and a yellow coloured precipitate was formed. After removal of the solvent the precipitate was washed with water (20 ml) and the crude product obtained was purified by column chromatography. Yield: 90%. IR(KBr, cm^{-1}) 3058 (w), 1696(s), 1588(s), 1547(s), 1445(s), 1363(s), 1322(s), 1235(w), 1143(s), 1015 (w), 764(s). ^{1}HNMR ($CDCl_3$) 8.8 (dd, J = 7.2, 7.2 Hz, 2 H), 8.55 (t, J = 4.8 Hz, 1 H), 8.27 (d, J = 8 Hz, 1 H), 8.15 (d, J = 8 Hz, 1 H), 7.88 (t, J = 4 Hz, 1 H), 7.80 (q, J = 7.6 Hz, 2 H), 7.40 (d, J = 9.2 Hz, 2H) ^{13}CNMR ($CDCl_3$):160.37, 143.58, 135.0, 133.18, 131.64, 131.43, 127.26, 127.17, 126.96, 126.7, 125.61, 125.25, 119.81, 115.75. Elemental anal calcd. $C_{18}H_{10}N_2O$ for C, 80.00 H, 3.70, N,10.37 found C, 80.21 H, 3.74 N, 10.32.

Synthesis of Isoindolo[2,1-a]perimidin-12-one (2)

Imidazole (340 mg, 5 mmol) was added to a solution of 1,8-naphthalenediamine (790 mg, 5 mmol) and phthalic anhydride (740 mg, 5 mmol) in dry tetrahydrofuran (15 ml), and the reaction mixture was stirred at 65°C for 6hrs. Red coloured precipitate formed, the solvent was removed under reduced pressure and the precipitate obtained was washed with water (20 ml) and dried in open air. The compound was further purified by sublimation at 125°C. Yield: 85%. IR (KBr, cm^{-1}) 3063(w), 2925(w), 1726(s), 1660(s), 1588(s), 1465(w), 1414(s), 1337(s), 1214(w), 1173(w), 1102(w), 917(w), 835(s), 774(s), 707(s). ^{1}HNMR ($CDCl_3$) 8.48 (d, J = 7.2 Hz, 1 H), 8.1 (d, J = 6.8 Hz, 1 H), 7.77 (t, J = 7.6 Hz, 2 H), 7.51 (d, J = 10 Hz, 1 H), 7.55 (m, 2 H), 7.46 (m, 2 H). ^{13}CNMR ($CDCl_3$): 186.8, 139.0, 134.0, 133.2, 132.5, 130.3, 127.8, 127.6, 125.5, 123.6, 122.8, 122.3, 121.8, 109.5. Elemental anal calcd for $C_{18}H_{10}N_2O$ C, 82.5, H, 3.75, N, 8.75; found C, 82.26, H, 3.55, N, 8.35.

Synthesis of 2-(2-aminophenyl)-isoindole-1,3-dione (3)

A solution of phthalic anhydride (0.74 g, 5 mmol) and 1,2-phenylenediamine (0.54 g, 5 mmol) and imidazole (0.34 g, 5 mmol) was prepared in dry tetrahydrofuran (15 ml). The solution was refluxed for six hours at 65°C. The solvent was removed under reduced pressure and the residue obtained was washed with water (20 ml). The compound was recrystallized from benzene to obtain the desired compound **3** with a 92% yield. IR (KBr, cm^{-1}) 3462(s), 3380(s), 1706(s), 1634(s), 1511(s), 1460(w), 1378(s), 1271(w), 1112(w), 871(s), 769(s), 707(s). ^{1}HNMR ($CDCl_3$) 7.9 (m, 4H), 7.27 (d, J = 15.6 Hz, 1 H), 7.1 (d, J = 7.6 Hz, 1 H), 6.9 (t, J = 7.6, 2 H), 2.0 (broad s, 2H). ^{13}CNMR ($CDCl_3$): 167.0, 143.0, 134.2, 131.9, 130.0, 129.07, 123.7, 119.25, 118.02, 117.76. Elemental anal calcd for $C_{14}H_{10}N_2O_2$ C, 70.5, H, 4.20, N, 11.76; found C, 70.31, H, 3.95, N, 11.39. Crystal parameters of **3**: monoclinic, space group P2(1)/c, a = 11.420(3), b = 13.885(4), c = 7.3538(17)Å, α° = 90.00, β° = 101.656(5), γ° = 90.00, V = 1142.1(5)Å^3, Z = 4, T = 296K, gof, 0.996, WR = 0.1497, R_{all} = 0.1452.

Synthesis of 4

The benzo[*de*]benzo[4,5]imidazo[2,1-a]isoquinolin-7-one (0.27 g, 1 mmol) and 1,3-dihydroxybenzene (0.55 g, 0.5 mmol) were mixed together in acetonitrile (10 ml). The solution was left undisturbed for two days, and light yellow coloured crystals were formed. Yield: 95%. IR (KBr, cm^{-1}) 3452(w), 3073(w), 2919(w), 1706(s), 1547(s), 1455(s), 1322(s), 1281(w), 1224(s), 1183(w), 1148(w), 927(w), 851(s), 764(s), 697(w). ^{1}HNMR ($CDCl_3$) 8.75 (dd, J = 7.6, 7.2 Hz, 2 H), 8.46 (t, J = 3.6 Hz, 1 H), 8.2 (d, J = 8 Hz, 1 H), 8.05 (d, J = 8 Hz, 1 H), 7.8 (t, J = 5.2 Hz, 1 H), 7.77 (t, J = 7.6 Hz, 1 H), 7.69 (t, J = 7.6 Hz, 1 H), 7.40 (d, J = 2.4, 9.2 Hz, 2 H), 7.0 (t, J = 8.4 Hz, 1 H), 6.5 (s, 1 H), 6.4 (d, J = 8 Hz, 2 H),1.8 (b, 2 H). Elemental anal calcd for $C_{24}H_{16}N_2O_3$: C, 75.78, H, 4.20, N, 7.36; found C, 75.56, H, 4.29, N, 7.34. Crystal parameters of **4**: triclinic, space group P-1, a = 9.4814(12), b = 11.0842(14), c = 14.9069(19)Å, α° = 97.688(8), β° = 94.382(8), γ° = 97.959(8), V = 530.38 Å^3, Z = 3, T = 296K, gof, 1.149, WR = 0.1639, R_{all} = 0.0876.

Synthesis of 5

A similar procedure to that of **4** was employed but the 1,4-dihydroxybenzene was used. Yield: 90%. IR(KBr, cm^{-1}) 3391(w), 2925(w), 2858(w), 1690(s), 1516(s), 1465(s), 1363(s), 1332(s), 1255(s), 835(s), 758(s), 605(w). ^{1}HNMR($CDCl_3$) 8.96 (d, J = 7.6 Hz, 1 H), 8.76 (d, J = 7.2 Hz, 1 H), 8.50 (t, J = 8 Hz, 1 H), 8.3 (d, J = 8 Hz, 1 H), 8.18 (t, J = 8.4 Hz, 1 H), 7.90 (t, J = 6.8 Hz, 1 H), 7.8 (m, J = 5.2, 4.4 Hz, 2 H), 7.5 (d, J = 9.2 Hz, 2 H), 6.78 (s, 2 H), 6.72 (s, 4 H), 2.0 (b, 2 H). Elemental anal calcd for $C_{24}H_{16}N_2O_3$, C, 75.78, H, 4.20, N, 7.36; found C, 75.45, H, 4.18, N, 7.42. Crystal parameters for **5**: triclinic, space group P-1, a = 7.6551(3), b = 9.2749(4), c = 11.7109(5)Å, α° = 95.877(3), β° = 94.139(3), γ° = 111.295(3), V = 765.251Å^3, Z = 2, T = 296K, gof, 1.034, WR = 0.3513, R_{all} = 0.1562.

Synthesis of 6

The compound **6** was prepared by reacting 2,3-diaminopyridine with 1,8 naphthalic anhydride (1:1 molar ratio) in molten imidazole at 120°C for 2hrs. The compound was obtained in pure form by washing the reaction mixture with excess water. Yield: 94%. ^{1}HNMR ($CDCl_3$) 8.98 (d, J = 8.4 Hz, 1 H), 8.75 (dd, J = 8.4, 4.3 Hz, 2 H), 8.33 (d, J = 8.4 Hz, 1 H), 8.20 (d, J = 8.4 Hz, 1 H), 7.84(t, J = 8.4 Hz, 2

H), 7.40 (dd, J = 8.4, 4.3 Hz, 1 H). IR(KBr, cm^{-1}) 1702(s), 1591(s), 1542(s), 1387(s), 1278(s), 1225(m), 1117(w), 886(w), 777(s). Adduct **7** was prepared by co-crystallizing from a solution containing a 2: 1 molar ratio of **6** with 1,3-dihydroxybenzene in methanol. The identity of the adduct **7** was ascertained by X-ray crystallography.

Supplementary materials

Supplementary data on the crystal structures has CCDC numbers 282010, 291150, 277075 and 600510. The concentration dependent ^{1}HNMR spectra of **1** and **3**, the concentration dependent UV–visible spectra of **1** and **2** in different solvents, changes in visible and fluorescence emission spectra of **3** during titration with hydrochloric acid are available as supplementary materials.

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