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Design, synthesis and structural optimization of two click modified butterfly molecules: Aggregation induced ratiometric fluorescence change and ICT associated hydrogen bonding effect in solvatochromic analysis



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1. Introduction

A new category of fluorescent organic materials with aggregation-induced emission (AIE) have attracted serious attention for their prospective applications in photo memory, optoelectronic devices, up-converted fluorescence, fluorescence sensors or bio-probes, solid-state lighting, and organic lasers [1]. However, the material itself containing AIE property is very limited and so why several groups have studied on the design and synthesis of new AIE active molecules, by investigating their aggregate morphologies and manipulating their luminescence [2].

Normally the unhindered AIE materials having intramolecular rotation in the free state leads to efficient non-radiative decay and fluorescence emission is quenched. To overcome such type of aggregation-caused quenching (ACQ) effect, the main fluorophore is attached with different bulky groups, branched chain and dendritic species covalently and the emission is greatly enhanced by the restriction of the intramolecular rotation and decrease in the non-radiative decay rate constant. Depending on the principle of the aggregation phenomenon various types of branching and crowding compounds such as silole [3], tetraphenylethene [4], cyano-biphenylethene [5], triphenylethelene [6], azobenzene [7], metallole [8] and triarylamine [9] derivatives have been synthesized. Beside the restriction of the intramolecular rotation of different molecules for the aggregation induced emission, the other mechanisms like J-aggregation, intramolecular planarization, dual mode of assembly, inhibition of photoisomerization, and photocyclization are also responsible for AIE [10]. The AIE method shows not only fluorescence enhancement of some substances by the aggregation but also in some cases, large shift of the emission wavelength [11]. The shifting of emission wavelength results the changes in electronic properties of the excited states that take place

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ABSTRACT

Two click modified butterfly molecules are designed and synthesized having presence and absence of the aggregative moiety to differ between aggregation induced ratiometric emission changes via excimer formation and ICT associated hydrogen bonding effect. These two distinct phenomena can be successfully employed in solvatochromic analysis. This is also supported by the theoretical study through the structural variation of the two butterfly molecules.

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in proceeding from the solution to the dense phase. All these changes have been classified as intramolecular charge-transfer (ICT) [12], excimer formation [13] and excited-state proton-transfer [14]. On the other hand the study of the photophysical properties of some aromatic condensed heterocyclic derivatives have the potential to down-regulate the oxidative stress at the preliminary stage of carcinogenesis [15], in various solvents having different polarity as well as the change of the hydrogen bonding ability due to the change in the solvent polarity. Solvatochromic behavior of different compounds can be explained by the combined effect of ICT and dye-solvent specific hydrogen bonding interaction. Herein our aim is to combine the two different solvatochromic effects by synthesizing two different phenomena (i) aggregation-induced emission (AIE) via excimer formation (**BBCP**) (ii) ICT associated

hydrogen bonding effect (BBCQ).

1.1. Synthesis of the targets BBCP and BBCQ

The synthesis of **BBCP** and **BBCQ** is given in Scheme 1. Vilsmeier-Haack formylation with DMF and POCl₃ of N-phenyldiethanolamine afforded **Compound 1. Compound 2** was produced by the reaction of 2-amino thiophenol with **Compound 1** in dry ethanol medium under refluxing condition. Azide displacement of chloride in **Compound 2** gave rise to **Compound 3**. Finally the receptors **BBCP** and **BBCQ** were prepared via click reaction between **Compound 3** with pyrene and quinoline modified triple bond respectively. In this investigation we have studied the solvatochromic effects of two butterfly like molecules, pyrene based **BBCP** and quinoline based **BBCQ** depending upon aggregation induced emission for **BBCP** and



Scheme 1. (a) (i) dry DMF, dry POCl₃, 0-5 °C, 5 h. (ii) resulting mixture, 60-80 °C, 8-10 h. (b) 2-amino thiophenol, Compound 1, KHSO₄, dry ethanol, reflux, 5 h. (c) Compound 2, NaN₃, dry DMF, 80 °C, overnight. (d) Compound 3, Compound 4, sodium ascorbate, copper sulphate, THF:H₂O (1:1), rt, 10 h. (e) Compound 3, Compound 5, sodium ascorbate, copper sulphate, THF:H₂O (1:1), rt, 10 h. (e) Compound 3, Compound 5, sodium ascorbate, copper sulphate, THF:H₂O (1:1), rt, 10 h. (e) Compound 3, Compound 5, sodium ascorbate, copper sulphate, THF:H₂O (1:1), rt, 8 h.

ICT associated hydrogen bonding effect in BBCQ.

2. Results and discussion

2.1. Solvatochromic analysis of BBCP and BBCQ by fluorescence spectra

At first we have investigated the solvatochromic effect of **BBCP** and it has been shown that due to the presence of π -excessive pyrene moiety the polarity changes of the solvent causes monomer and excimer induced aggregation emission in different solvent systems. The monomer and aggregation induced emission of **BBCP** depending on the solvent polarity and solubility have been shown in Scheme 2. In order to investigate the monomer and aggregation induced excimer emission, we have studied the emission spectra of **BBCP** ($c = 1 \times 10^{-5}$ M) by using different organic solvents and water.

Only in CH₃CN **BBCP** shows an intense peak at 417 nm which corresponds to blue fluorescence and in water at 472 nm results white green fluorescence. On gradual increase of the (v/v) fraction of CH₃CN in the H₂O–CH₃CN solutions of **BBCP** from 0 to 90%, the receptor peak at 472 nm corresponds to pure H₂O which gradually falls down and ratiometrically (isoemission point at ~ 442 nm) a new blue shifted ($\Delta\lambda = 55$ nm) intense peak arises at 417 nm (Fig. 1) and similarly the vice-versa occurs increasing the (v/v) fraction of H₂O in the H₂O–CH₃CN solutions of **BBCP**.

The emission intensity at 417 nm in CH₃CN is greater (quantum yields, $\Phi_F = 0.75$) than the intensity at 472 nm in H₂O (quantum vields, $\Phi_F = 0.69$) (Fig. S9). At the same time **BBCP** shows sharp emission peak at 417 nm in different organic solvents giving blue color (in hexane the emission blue color intensity is low) like CH₃CN and the red shifted peak at 472 nm in H₂O (Fig. 2). All the emission color changes in click modified **BBCP** moiety by using pyrene fluorophore can be explained by the excellent properties of pyrene (strong UV-vis absorption spectra, strong emission spectra, high quantum yield and expanded π -electron delocalisation). Pyrene monomer molecules ($\lambda em = 350-400$ nm) are known to form intramolecular or intermolecular excimers ($\lambda em = 450 - 500 \text{ nm}$) due to aggregation into close proximity by the several external factors. Here the various solvents play the external role for showing the different properties of **BBCP**. In pure organic solvent **BBCP** shows intense peak at 417 nm giving blue emission color due to the strong ICT (mainly from tri-podal nitrogen to fluorophore benzothiazole moiety) within the molecule. But in protic polar solvent H₂O due to high strong hydrogen bonding ability as well as better solvation of the nitrogen lone pair in water molecule, the ICT is prohibited followed by the aggregation via $\pi - \pi$ stacking forces of pyrene rings.

The photophysical properties of all the parent backbone of **BBCP** and **BBCQ** (aminophenylbenzothiazol, pyrene and quinoline) [16] has already been reported. The intermolecular nature of π - π



Fig. 1. (a) Changes of emission spectra of **BBCP** in pure H_2O solutions containing CH₃CN fractions (v/v) in the range of 0–90%. (b) Solvent dependent ratiometric changes of emission intensities of **BBCP** at I_{472} nm and I_{417} nm.

stacking interactions of the pyrene rings favours intermolecular aggregation rather than showing intramolecular $\pi - \pi$ stacking interactions between the pyrene rings in presence of water which is also supported by DFT calculations . Furthermore, from the structural orientation of **BBCP**, the intramolecular excimer formation between two pyrene rings is somehow difficult for the steric hindrance due to the presence of two triazole rings on the two wings of **BBCP**. Thus, aggregation favoured by intermolecular pyrene $\pi - \pi$ interactions leads to fluorescence color changes in different solvents in presence of water due to excimer formation in aggregated association from monomer. Thus the aggregation induced emission (AIE) in the excited state, ICT and the hydrogen bonding effects operate on the same molecule of **BBCP** changing the different solvents and playing the different indicator site for showing the different emission color. On the other hand the solubility factors are also responsible for this different emission color in organic and H₂O



Scheme 2. Schematic diagram showing monomer and aggregation induced excimer emission by changing the solvent polarity.



Fig. 2. Top: Fluorescence changes of **BBCP** in different solvent systems. **Bottom:** Normalized emission intensity of **BBCP**($c = 1 \times 10^{-5}$ M) in different organic solvents and H₂O.

media. In the organic solvents with good solubility and moderate polarity (MeOH, CH₃CN, DMSO, DMF, EtOAc, THF, DCM, CHCl₃, Tol), **BBCP** shows monomer emission ($\lambda em = 417$ nm, blue color). In the organic solvent with no polarity (hexane) the same monomer emission is observable but the intensity is quite low with respect to the other organic solvents having high solubility of **BBCP** due to the insolubility of **BBCP** in hexane. On the other hand, in highly polar protic solvent H₂O, due to the very much insolubility of **BBCP**, it aggregates in water medium giving AIE induced white green fluorescence ($\lambda em = 472 \text{ nm}$). Thus, we see that in **BBCP** the click modified pyrene moiety is responsible for the aggregation and the benzothiazole moiety is for ICT and these two different phenomena are opended up in two different solvent systems. Now if we compare **BBCP** with **BBCQ** in which the aggregation active pyrene moiety is replaced by the non-aggregative quinoline moiety, then the aggregation effect is vanished in high protic polar H₂O media. In pure organic solvent, BBCQ shows the same emission peak at 417 nm for the strong ICT from tri-podal nitrogen to the benzothiazole moiety.

On gradual addition of H₂O to the CH₃CN solution of **BBCQ** ($c = 1 \times 10^{-5}$ M), the emission peak at 417 nm gradually falls down due to the inhibition of ICT for the strong hydrogen boding effect and solvation of nitrogen lone pair with the H₂O molecule (Fig. 3). As a result the blue color intensity gradually vanishes but there is no more peak appearance at 472 nm in water (Fig. 4). In less polar solvents (EtOAc, THF, DCM, CHCl₃, Tol) the emission maximum occurs at λ_{max} - 400 nm but in more polar solvents (H₂O, MeOH, CH₃CN, DMSO, DMF) the emission peak at 400 nm is red shifted to 410 nm - 420 nm (Fig. 4). Thus in two butterfly molecules **BBCP** and **BBCQ**, we see that if the body of the butterfly remained fix but with the changing of the substituents in the wings, it shows different properties like it moves anywhere by moving the wings.

2.2. Absorption study

In both the probes **BBCP** and **BBCQ**, there are no significant changes observable to the various solvent systems in the UV–vis spectra except the low intensity of the absorption spectra in hexane due to the insolubility factor (Fig. 5).



Fig. 3. (a) Emission spectra of **BBCQ** in pure CH₃CN solutions containing H₂O fractions (v/v) in the range of 0–90%. (b) Normalized emission intensity of **BBCQ** ($c = 1 \times 10^{-5}$ M) in different organic solvents and H₂O.



Fig. 4. Top: Fluorescence changes of BBCQ in different solvent systems. Bottom: The comparison emission spectra of BBCQ in different solvents.

2.3. Practical application

To investigate the practical application of this solvatochromic

effect of **BBCP** and **BBCQ** in organic and aqueous solvent, the test strips are prepared by immersing the TLC plates into the organic (CH₃CN) and aqueous solution of **BBCP** ($c = 1 \times 10^{-5}$ M) and **BBCQ** separately. The emission color of **BBCP** in the test strips immersing in organic solvent shows blue fluorescence and the strips in aqueous solvent shows white green fluorescence in solid phase. But in case of **BBCQ** the blue emission color in the test strips of organic solvent is totally vanished in the test strips of aqueous solution of **BBCQ** (Fig. 6). Thus the development of such dipsticks is useful as instant qualitative information may be obtained without resorting to the time consuming instrumental analysis.

2.4. Theoretical study

The possible structures have been optimized by using DFT(B3LYP) [17] method and 6-31 + g(d,p) as basis set on the basis of the optimized excited state geometry, the emission spectral properties in both CH₃CN and H₂O medium has been calculated by time-dependent density functional theory (TDDFT) associated with the conductor-like polarizable continuum model (CPCM). We have computed the lowest 40 triplet – triplet transition and results of the TD calculations were qualitatively very similar with the experimental results. All the calculations were performed with the Gaussian 09W software package [18].

2.5. Geometry optimization and electronic structure

The optimized geometries of BBCP and BBCQ are shown in



Fig. 5. UV-vis absorption spectra of (a) BBCP and (b) BBCQ in various solvents.



Fig. 6. Visualized emission color changes in test strips (solid phase) by immersing TLC sticks to in organic and aqueous solution **BBCP** (Top panel) and **BBCQ** (Bottom panel) separately.

Fig. 7. However, the displacement of pyrene moiety from the corresponding least-squares of body of BBCP (benzothiazolyl-benzenamine part) planes are 1.741-3.445 Å, suggesting that the pyrene moiety lies significantly tilted away from the concerning mean plane (Fig. S10). Similarly, butterfly views are observed in **BBCO** but the two wings are not so much away from the body of **BBCQ** (benzothiazolyl-benzenamine part) by the distance 7.315–7.788 Å like **BBCP**. In that case, the displacement of methyl quinoline moiety from the corresponding least-squares of body of BBCO (benzothiazolyl-benzenamine part) planes are 1.638–3.314 Å, suggesting that the pyrene moiety lies significantly tilted away from the concerning mean plane (Fig. S11).

The **BBCP** and **BBCQ** have C1 point group. In case of **BBCP**, the molecular structure adopts the butterfly views with tri-podal nitrogen flanked by triazole containing two pyrene rings like two flying wings (Fig. S12, bottom).

Two wings are away from the body of **BBCP** (benzothiazolylbenzenamine part) by the distance 7.776–8.476 Å. Similarly, a butterfly view is observed in **BBCQ** but the two wings are not so much away from the body of **BBCQ** (benzothiazolyl-benzenamine part) by the distance 7.315–7.788 Å like **BBCP**. The fluorescence spectra of the **BBCP** and **BBCQ**, used in the present work were studied at room temperature in CH₃CN and H₂O medium. The **BBCP** shows well resolved peak at 417 and 472 nm whereas the **BBCQ** exhibits the peak at 400 and 420 nm in CH₃CN and H₂O solvent respectively. These bands are assigned to S₀→S₂₀ and S₀→S₁₆ for **BBCP**; S₀→S₂₄ and S₀→S₂₂ electronic transitions for **BBCQ**, respectively (Figs. 8 and 9). The emission energies associated with their oscillator strengths are given in Tables 1 and 2.

In case of **BBCP**, in the excited state, the electron density resides mainly on HOMO and HOMO–3 and LUMO orbitals occurs at the pyrene ring attached to pyrazolyl ether moiety, whereas the same for LUMO+8 orbital remains at body of BBCP (benzothiazolylbenzenamine part) with an energy gap between HOMO and LUMO of 1.722eV (Fig. 10). In case of **BBCQ**, HOMO and LUMO orbital mainly originates from the contribution of methyl quinoline moiety and LUMO+2, LUMO+3 from pyrazolyl moiety with an energy gap between HOMO and LUMO of 1.739eV (Fig. 10).

The Dipole moment of BBCP in CH_3CN is 5.5095D and in H_2O 5.5192D. In case of BBCQ, the dipolemoment in CH_3CN is 13.4528D and in H_2O 13.5364D. There is no such difference of dipole moment is observed in various solvents for both of the ligands.



Fig. 7. Top: The geometry optimized molecular structure of BBCP. Bottom: The geometry optimized molecular structure of BBCQ.



Fig. 8. Frontier molecular orbitals involved in the fluorescence transitions of the BBCP in CH₃CN and aqueous solvent.



Fig. 9. Frontier molecular orbitals involved in the fluorescence transitions of the BBCQ in CH₃CN and aqueous solvent.

Table 1

The comparable calculated fluorescence transitions with experimental values for the BBCP.

Electronic transition	Solvent	Composition	Excitation energy	Oscillator strength(f)	CI	Fl. intensity (λ_{exp}) (nm)
$\begin{array}{l} S_0 \rightarrow S_{20} \\ S_0 \rightarrow S_{16} \end{array}$	CH ₃ CN	HOMO →LUMO + 8	2.9681 eV(417.73 nm)	0.0355	0.99740	417
	water	HOMO 3→LUMO	2.5749 eV(481.51 nm)	0.0268	0.99969	472

Table 2

The comparable calculated fluorescence transitions with experimental values for the BBCQ.

Electronic Transition	Solvent	Composition	Excitation energy	Oscillator strength(f)	CI	Fl. Intensity (λ_{exp}) (nm)
$S_0 \to S_{24}$	CH ₃ CN	$\begin{array}{l} HOMO \rightarrow LUMO + 2 \\ HOMO \rightarrow LUMO + 3 \end{array}$	2.9875eV (412.25 nm)	0.0094	0.60099 0.79883	400
$S_0 \rightarrow S_{22}$	water	$HOMO \rightarrow LUMO$	2.3788 eV (429.12 nm)	0.1207	0.99958	420

2.6. Experimental section

2.6.1. General

Unless otherwise mentioned, chemicals and solvents were purchased from Sigma-Aldrich chemicals Private Limited and were used without further purification. ¹H NMR spectra were recorded on Brucker 300 MHz instrument. For NMR spectra, CDCl₃ was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ¹H–¹H and ¹H–C coupling constants in Hz. UV–vis titration experiments were performed on a JASCO UV–V530 spectrophotometer and fluorescence experiment was done using PerkinElmer LS 55 fluorescence spectrophotometer using a fluorescence cell of 10 mm path.

2.7. Experimental procedure

2.7.1. Synthesis of compound 1 and compound 2

Compound 1 was synthesized by the reported procedure [19].

2-aminothiophenol (800 mg, 6.39 mmol) and compound 1 (1573 mg, 6.39 mmol) were refluxed in dry ethanol (30 mL) by using catalytic amount of KHSO₄ for 10 h. The excess ethanol was removed under high vacuum and the residue was extracted in organic layer and dried over anhydrous Na₂SO₄. The crude product **compound 2** was purified by a short column using silica gel (100-200 mesh) by using 10% Ethyl acetate in petroleum ether as eluent to give a white solid (1500 mg, 67%).

¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.994 (t, 3H, J = 6.3 Hz), 7.858 (d, 1H), 7.454 (t, 1H), 7.312 (m, 1H), 6.725 (m, 2H), 3.673 (t, 4H, J = 6 Hz), 3.561 (d, 4H, J = 5.7 Hz).

MS (ESI-TOF): (m/z, %): M + Calculated for $C_{17}H_{16}Cl_2N_2S$ is 350.0411; Found: 351.24 (M + H)⁺;

2.7.2. Synthesis of compound 3

Compound 2 (1000 mg, 2.84 mmol) was taken in a 100 ml r.b and it was dissolved in 10 ml dry DMF at 80 °C under nitrogen atmosphere. After stirring for half an hour at 80 °C, excess sodium



Fig. 10. The comparable energy difference between involved frontier molecular orbital of BBCP as well as BBCQ.

azide was added to the reaction mixture and the reaction mixture was kept stirring at the same temperature for 5 h. After completion of the reaction (monitored by TLC), the whole mixture was poured onto the ice cold water and a solid was precipitated out. After filtration of the precipitate, the solid product **compound 3** (800 mg, 77%) was purified by column chromatography by using 15% Ethyl acetate in petroleum ether as solvent.

¹H NMR (CDCl₃, 300 MHz): δ (ppm): 8.012 (t, 3H, J = 6.9 Hz), 7.859 (d, 1H), 7.463 (t, 1H), 7.338 (t, 1H), 6.761 (d, 2H, J = 8.4 Hz), 3.829 (t, 4H, J = 6.9 Hz), 3.675 (m, 4H).

MS (ESI-TOF): (m/z, %): M + Calculated for $C_{17}H_{16}N_8S$ is 364.1219; Found: 365.15 (M + H)⁺;

2.7.3. Synthesis of BBCP

To a mixture of **compound 3** (500 mg, 1.37 mmol) and **compound 4** (740 mg, 2.74 mmol) in a solution of water and THF (v/v = 1:1, 8 mL), a catalytic amount of sodium ascorbate (4 equiv.) was added followed by a catalytic amount of copper (II) sulphate pentahydrate (2 equiv.). The heterogeneous mixture was stirred vigorously overnight in the dark at room temperature. The completion of the reaction was checked by TLC and the solvent was removed under reduced pressure and extracted by DCM and water several times; the combined organic part was evaporated to give crude product which was then purified by column chromatography by 1% MeOH in CHCl₃ to yield the desired product **BBCP** (500 mg, 40%) as a white solid.

¹H NMR (DMSO-*d*₆, 300 MHz): δ (ppm): 8.277 (d, 6H, J = 9 Hz), 8.176 (d, 6H, J = 7.8 Hz), 8.116 (d, 3H, J = 6 Hz), 8.032 (d, 9H, J = 7.8 Hz), 7.453 (d, 1H), 7.354 (d, 1H), 6.804 (s, 2H), 5.134 (s, 4H), 4.677 (s, 4H), 4.538 (d, 4H), 3.778 (s, 4H).

MS (ESI-TOF): (m/z, %): M + Calculated for $C_{57}H_{44}N_8O_2S$ is 904.3308; Found: 905.40 (M + H)⁺.

Elemental analysis: Calculated value: C, 75.64; H, 4.90; N, 12.38; Observed value: C, 75.68; H, 4.88; N, 12.36.

2.7.4. Synthesis of BBCQ

The compound **BBCQ** (500 mg, 48%) was prepared by the similar procedure by using **compound 3** (500 mg, 1.37 mmol) and **compound 5** (540 mg, 2.74 mmol).

¹H NMR (CDCl₃, 300 MHz): δ (ppm): 7.969 (q, 3H, J = 12.9 Hz), 7.819 (d, 2H, J = 6.9 Hz), 7.675 (q, 2H, J = 12.6 Hz), 7.427 (t, 5H, J = 11.4 Hz), 7.308 (t, 3H, J = 12.6 Hz), 7.187 (m, 3H), 6.244 (s, 2H), 4.178 (d, 4H, J = 5.4 Hz), 3.268 (d, 4H, J = 5.4 Hz), 2.708 (d, 6H, J = 12.9 Hz), 2.027 (s, 4H).

MS (ESI-TOF): (m/z, %): M + Calculated for $C_{43}H_{38}N_{10}O_2S$ is 758.2900; Found: 759.2974 (M + H)⁺.

Elemental analysis: Calculated value: C, 68.05; H, 5.05; N, 18.46; Observed value: C, 68.02; H, 5.06; N, 18.48.

3. Conclusions

In summary, we have developed two click modified butterfly molecules **BBCP** and **BBCQ** for the solvatochromic study depending on aggregation induced excimer emission and ICT induced strong hydrogen bonding effect. To our belief this is a rare example of such click modified butter fly molecule having pyrene moiety which shows ratiometric emission in solvatochromic analysis in H₂O and organic solvents which has been successfully supported by DFT and TD-DFT study. The test strips based on **BBCP** and **BBCQ** in solvatochromic analysis are fabricated, which can act as a convenient and efficient test kits for the detection of various fluorescence changes in solid phase without remedying for the time consuming instrumental analysis.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2018.12.079.

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