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## Carbazole-benzimidazole based dyes for acid responsive ratiometric emissive switches

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Three carbazole based benzimidazole derivatives exhibit the effect of intramolecular charge transfer (ICT) caused by the donor-acceptor interaction between its carbazole and benzimidazole units were synthesized. Their photophysical properties were systematically investigated in various solvents with different polarities. Positive solvatofluorochromic effects were observed with change the solvent from non-polar to polar for all of the three dyes. The synthesized compounds, presented proton-induced absorptions as well as ratiometric emissions changes, indicating that these compounds might be used as proton sensors. The dyes in their solid state are also able to detect acid vapours. The optimized structures of the dyes and their protonated forms were calculated by density functional theory calculations.

#### Introduction

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Small organic molecules possessing bright fluorescence in both solid and solution states are gaining importance recently because of their wide-spread applications in the field of optoelectronic materials, sensor design, electroluminescent devices and fluorescence bioimaging.<sup>1</sup> In this regard, many strategies such as the aggregation-induced enhanced emission,<sup>2</sup> and intra-molecular charge transfer transition<sup>3</sup> have been developed to achieve intense emitters in the solid state. A number of organic dyes with strong fluorescence in the solution state have been reported. But most of them remain nonemissive in the solid state mainly because of the aggregation. Thus, the development of new organic dyes with intense fluorescence in solid state as well as in solution state is very important. On the other hand fluorogenic sensory devices which can detect selectively and specifically volatile acid and base (amine) vapours have gained considerable interest in recent years due to the practical application in the field of environmental and medicinal purpose.<sup>4</sup> There are many fluorescent compounds that are sensitive to changes in pH and can be used as chemical sensors to measure pH. Many fluorescent derivatives have been extensively employed as pH

fluorescent probes and they have important implications in biological chemistry.<sup>5</sup> Ratiometric proton-induced sensors are in high demand, because ratiometric sensors usually allow measuring the emission intensity at two different wavelengths which is beneficial for the evaluation of analytes with better accuracy. This is because of the independency of ratiometric probe on the local probe concentration, photo bleaching and experimental condition such as optical path length etc.

Solvatochromic probes have emerged as powerful tools for identifying and characterizing microenvironments created by macromolecules and molecular assemblies. In this regard, organic materials possessing extended  $\pi$ -conjugation have received immense attention in recent years owing to their unique photophysical and charge transport properties. One important factor involved in displaying such properties is the presence and nature of electron-donating and electronaccepting groups. In continuation of our work,<sup>6</sup> herein, we have synthesized and characterized three benzimidazole conjugated carbazole dyes for fluorescence ratiometric proton sensing. The first one without spacer (CBIM1), second one with p-styryl spacer (CBIM2) and the last one with intervening phenyl moiety between carbazole and benzimidazole system (CBIM3). All of them showed bright fluorescence in their solution as well as solid state. Based on the investigation of these compounds in mixed aqueous system, the trio exhibit acid-dependent absorption and emission properties and thus might be used as efficient proton sensors. These dyes also have been examined to observe the change of solvatofluorochromism with increase the solvent polarity from n-hexane to DMSO.

#### **Results and discussion**

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#### Synthesis of the dyes (CBIM1, CBIM2 and CBIM3)

The target compounds were prepared by adapting the synthetic route outlined in the scheme 1. N-butylation of carbazole, followed by mono formylation afforded CA1 (9-butyl-9Hcarbazole-3-carbaldehyde). Finally, the condensation of CA1 with o-phenylenediamine gives the probe CBIM1 [3-(1Hbenzo[d]imidazol-2-yl)-9-butyl-9H-carbazole] as a white solid. Upon Wittig condensation of CA1 with methyltriphenylphosphoniumbromide salt, the vinyl derivative (9-butyl-3-vinyl-9H-carbazole) was produced in 72% yield. The Heck cross coupling reaction of the vinyl derivative with pbromo benzaldehyde afforded CA2 [(E)-4-{2-(9-butyl-9Hcarbazole-3-yl)vinyl}benzaldehyde] with 80% yield. Finally, CBIM2 [(E)-3-{4-(1H-benzo[d]imidazol-2-yl)styryl}-9-butyl-9Hcarbazole] was obtained from the condensation reaction of CA2 with o-phenylenediamine as a yellow solid. CBIM3 [3-(4-(1Hbenzo[d]imidazol-2-yl)phenyl)-9-butyl-9H-carbazole] was synthesized from the Suzuki coupling of compound 5 with 4formylphenylboronic acid followed by the condensation with ophenylenediamine. The detailed synthetic procedures of the probes are given in supporting information. All the new compounds are characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS (Figure S10 – S30, Supporting Information).



#### X-ray crystallographic study

Compound 4, crystallizes in triclinic space group P-1 and consists two molecules (A and B) of each species in the asymmetric unit, with similar geometries as shown in Figure 1a. The molecules exist in the E configuration with respect to the





**Figure 1: (a)** The molecular structure of compound 4, showing 30% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme. Open bonds show the minor component. (b) The crystal packing of the major components of compound 4 viewed down the a-axis. H atoms not involved in the hydrogen bond interactions (dashed lines) have been omitted for clarity.

In the crystal, the two independent molecules are linked into pairs, viz. A-B, by intermolecular C24A-H24A-O1B hydrogen bonds (Table S7, ESI). These pairs are stacked along the a axis (Figure 1b) by way of weak aromatic  $\pi \cdots \pi$  stacking interactions benzene (C15B-C20B)/pyrrole between the (N1B/C3B/C4B/C9B/C10B) [centroid-centroid separation = 3.654(3) Å] and benzene(C15B-C20B)/benzene(C1B-C3B/C10B—C12B) [centroid-centroid separation = 3.631(3) Å] rings of adjacent molecules. The crystal structure is further stabilized by C—H··· $\pi$  and Van Der Waals interactions.

Compound 6 crystallizes in monoclinic space group P2<sub>1</sub>/c and it also consists of two molecules (A and B) of each species in the asymmetric unit, with comparable geometries. The molecular structure of compound 6 is depicted in Figure 2. In molecule A, the benzene ring deviates slightly from plane parallel to the carbazole ring system [r.m.s. deviation = 0.040 Å] with a dihedral angle of 18.25 (9)<sup>9</sup>. The corresponding r.m.s. deviation and dihedral angle for molecule B are 0.040 Å and 2.77 (6)<sup>9</sup>, respectively. Atoms C21 and C22 for molecules A and B are disordered over two sites with a refined occupancy ratio of 0.564(8): 0.436(8) and 0.785(7): 0.215(7), respectively. No

hydrogen-bonding interactions were observed for the structure compound 6.



Figure 2: ORTEP view of compound 6, showing 30% probability displacement ellipsoids for non-H atoms and the atom-numbering scheme. Open bonds show the minor component.



#### Solvatofluorochromic study

Figure 3: Solvent dependent emission spectra of (a) CBIM1, (b) CBIM2 and (c) CBIM3. Concentrations of all dyes were in the order of 1  $\times$  10 $^{5}$  M.

Owing to, having a push-pull motif, our probes are examined for solvatochromic effect and monitored the absorption and emission properties in different solvents with altered polarity. In case of CBIM2 a slight red shift of absorption maxima is observed in the polar (DMSO) solvent compared to the non-polar one (n-hexane). In the emission spectra, the solvatofluorochromic property of CBIM2 is more prominent than the other two. As shown in Figure 3b, from n-hexane to DMSO the emission maxima gradually red shifted with increasing the solvent polarity. Accordingly, the apparent fluorescence color change is observed from violet to blue to cyan and finally green (Figure 3b). A remarkable red shift (~ 54 nm) of emission maximum is also noticed from n-hexane (419

nm) to DMSO (473 nm). The above findings (solvatochromatic effects) could be attributed to solven® stabilization of the internal charge-transfer (ICT) in the excited state.<sup>7</sup> Noteworthy the polarized excited state with large dipole moment got stabilized by a solvent with high polarity keeping the ground state is relatively untouched. As a result, we get a positive solvatochromic effect (bathochromic shifts or red shift) in the emission spectra.<sup>8</sup>





(a) n-hexane, (b) toluene, (c) THF, (d) DCM,
(e) CH<sub>3</sub>CN, (f) DMSO

Figure 4: Solvent dependent emission photos of the (i) CBIM2 and (ii) CBIM3 solutions under UV light. Concentrations of all dyes were in the order of  $1\times10^{-5}$  M.

The result also indicates that the excited state of CBIM2 is consistent with higher dipole moment than its ground state and the intramolecular charge transfer (ICT) transition is the responsible factor for the red shift. CBIM3 also bears the same electron acceptor and donor group with a different linker site and shows charge transfer (CT) transition in excited state. The CT process is expected to strongly increase the dipole moment in the excited state, explaining the positive fluorescence solvatochromism in this compound. In here also using the above mentioned solvents the emission maxima exhibit a regular red shift with increasing solvent polarity (n-hexane to DMSO), consequently the fluorescence color changes from fluorescence 'off' to intense blue (Figure 4). A red shift of approximately 30 nm was observed (n-hexane: 393 nm and DMSO: 422 nm) (Figure 3c). CBIM1 also showed same type of solvatofluorochromism but the effect was not so prominent because of the absence of extended  $\pi$ -conjugation (Figure 3a).

#### Acid induced fluorescence study in solid state

In order to investigate the solid state emissive property of the probes, we recorded emission spectra using their solid powders. As shown in Figure 5, all the dyes CBIM1, CBIM2 and CBIM3 showed intense fluorescence in their solid form and exhibit excellent high contrast emission change after bubbling with TFA vapour (their protonated forms). CBIM1 displayed bluish-violet fluorescence with the emission maximum at 417 nm upon excitation at 350 nm. In case of CBIM2 the emission maximum appeared at 520 nm upon excitation at 390 nm and an intense green fluorescence was observed under the UV light. CBIM3 exhibits emission maximum centred at 475 nm upon excitation at 380 nm.

Presence of basic benzimidazole moieties in the probes, leads us to investigate their acidochromic as well as vapochromic behaviour in the solid state. Upon exposure to volatile acid vapours (TFA), a bathochromic shift in the emission maximum is observed. However, the probe once exposed with acid vapours, further gets exposed with volatile base (NH<sub>3</sub> or Et<sub>3</sub>N)

vapours restores the original emission and indicates a reversible sensing nature of the probes towards acid/base vapours. The original emission of CBIM1 is stimulated via TFA vapour from 417 nm to 428 nm with a concomitant fluorescence color change from bluish-violet to cyan. Whereas CBIM2 shows a prominent change in fluorescence color, a green emission becomes yellow upon exposure to fumed TFA. The third probe CBIM3 exhibits a red shift from 475 nm to 525 nm; accordingly a color change was noticed from cyan to bright green after bubbling with TFA vapour. The Stokes shifts for the dyes were found to be 11 nm, 55 nm (from 520 nm to 575 nm) and 50 nm for CBIM1, CBIM2 and CBIM3 respectively. The TFA vapours can cause such type of changes in a closed container within 30 seconds for all the cases.

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**Figure 5:** Solid state emission spectra of (a) CBIM1, (b) CBIM2 and (c) CBIM3 before and after exposure to TFA vapour. Inset: The corresponding photographs of CBIM1, CBIM2 and CBIM3 after exposure to TFA vapour, taken under UV-light ( $\lambda_{ex}$ = 365 nm).

(TFA) CBIM1, CBIM2 and CBIM3 get protonated Arighe their respective benzimidazole moieties (Schemel 2) 37He<sup>6</sup> MPO WMR titration experiments of the probes and their respective protonated forms also suggests the following mechanism takes place (ESI, Figure S31-S33). Consequently colours of the fluorescence of the solutions dramatically changed which are observable through naked eyes after illumination under UV light. CBIM1 solution turns colourless to purple, CBIM2 changes cyan to yellow and CBIM3 turns blue to green under UV light after protonation.



**Scheme 2:** Probable sensing mechanism of the dyes towards H<sup>+</sup> (acid) and their corresponding photograph after illumination under UV light ( $\lambda_{ex}$  = 365 nm).

All the dyes act as good reversible solid state sensors in their respective solid states; it was observed that after exposure in  $NH_3$  vapours, the protonated forms of the dyes revert back to their original spectrum suggesting that the transformation of the protonation and deprotonation could be completely reversible, and essentially non-destructive.

Carbazole systems are planer in nature, the restriction in rotation ultimately help the probe to emit in solid state. The compactness of the carbazole systems interrupt the rotational freedom along with the incorporation of imidazole groups restricts the intramolecular rotation. This restriction of intramolecular vibration suppresses radiationless excited state deactivation which may leads to exhibit a prominent fluorescence in solvents or/ and in the solid state.

## Acid-induced spectroscopic studies of the dyes in solution state

Interestingly, all the dyes (CBIM1, CBIM2 and CBIM3) are sensitive towards acid. With increasing proton concentration

The UV-vis titration experiment was exemplified by increasing acid concentration. The solution of the dyes were prepared in MeOH/H<sub>2</sub>O (1/1, v/v) solutions. CBIM1 (10 µM) itself exhibits a prominent peak at 302 nm, upon increasing concentration of TFA this peak gradually decreases and a new peak at 346 nm regularly increases with a well defined isosbestic point at 335 nm (Figure 6a). This spectral red-shift might be the result of protonation at the benzimidazol nitrogen (CBIM1-H<sup>+</sup>), thereby enhancing the intramolecular charge transfer (ICT). In case of CBIM2, the dye itself demonstrates a peak at 343 nm, which was gradually quenched with increasing amount of TFA (Figure 6b). Meanwhile, a new peak centred at 395 nm resultant to a red shift of 52 nm. This large stokes shift is indicative of the strong ICT with the formation of new chemical species (CBIM2-H<sup>+</sup>). An isosbestic point was found at 379 nm corresponding to change of color from colorless to light yellow. CBIM3 showed a peak at 333 nm in absence of any proton. In here also after addition of TFA, the peak at 333 nm decreases rapidly, whereas a new peak generated at 368 nm with an isosbestic point at 359 nm. A red shift about 35 nm was found after addition of TFA (Figure 6c).

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Figure 6: Acid-induced UV-vis absorption changes of (a) CBIM1, (b) CBIM2 and (c) CBIM3 in MeOH/H<sub>2</sub>O (1/1, v/v) solution. Concentrations of all the dyes were 10 μМ.

We have also elaborated the emission signalling behaviour of the probes upon addition of TFA. As shown in Figure 7, upon excitation at 330 nm, the free probe CBIM1 (10  $\mu$ M) shows a strong emission band centred at 384 nm. With increasing proton concentration the peak at 384 nm decreases, whereas a new peak gradually appeared at 440 nm which increased regularly and a good ratiometric spectrum is obtained with a well defined isoemission point at 410 nm (Figure 7a).



Figure 7: Acid-induced fluorescence changes of the dyes (a) CBIM1 ( $\lambda_{ex}$  = 330 nm), (b) CBIM2 ( $\lambda_{ex}$  = 390 nm) and (c) CBIM3 ( $\lambda_{ex}$  = 340 nm) in MeOH/water (1/1, v/v) solution. Concentrations of all the dyes were 10  $\mu$ M.

However, in case of CBIM2 (10  $\mu$ M), the probe itself exhibited a peak centered at 480 nm when excited at 390 nm. With addition

of TFA a new peak grew at 570 nm and it increased rapidly with incremental addition of TFA. Consequently,1039/Fatilonetric spectrum was obtained with an isoemmision point at 526 nm and a red-shift of emission maximum about 90 nm was noticed (Figure 7b). A clear fluorescence color change from cyan to yellow was observed, after illumination under UV light (Scheme 2). The same type of observation was found for CBIM3 also. This probe itself showed a peak at 440 nm after excitation at 340 nm. Proton induced emission titration of CBIM3 exhibited a beautiful ratiometric spectrum. The peak at 440 nm gradually decreased whereas a new one which appeared at 532 nm readily increases and the corresponding stokes shift of 92 nm was found with an isoemissive point at 509 nm (Figure 7c). In this case, the strong blue fluorescence turns to green after protonation.

#### Sensing of acid/base vapours using TLC plate

Efforts were made to examine the sensing of acid/amine vapours with the dyes CBIM1, CBIM2 and CBIM3 in the solid state (using TLC plates). It is a simple but important experiment because it gives instant qualitative information without resorting to the instrumental analysis. In order to perform this experiment, we prepared TLC plates which were immersed into the solution of the probes  $(1 \times 10^{-4} \text{ M})$  in methanol solution, and then dried the plates by evaporating the solvent in open air. The TLC plates were then exposed to trifluoroacetic acid (TFA) vapours for 1 minute and their photographs were taken (Figure 8). Again the TLC plates which were exposed with TFA vapors were further exposed to triethyl amine vapors and the restored color were observed in each case. This experiment evokes a real time monitoring and it is devoid of using any instrumental analysis. Just by naked-eye detection and use of TLC plates we can easily investigate a qualitative instant detection of acid / amine vapors.



Figure 8: TLC plates immersed with CBIM1 or CBIM2 or CBIM3 (a) and after exposure to TFA vapours (b). The photographs were taken under the hand-held UV light ( $\lambda_{ex}$  = 365 nm).

#### **Computational study**

A theoretical calculation is performed to clarify the sensing mechanism of the probes in the ground state as well as to look insight into the optimized geometries of the probes before and after protonation (Figure 9). The optimized geometries, HOMO and LUMO of CBIM1, CBIM2 and CBIM3 calculated by DFT/B3LYP/6-31+G(d) method are shown in Figure S1 - S9 (ESI). The HOMO-LUMO energy gap in the protonated species (CBIM1-H<sup>+</sup>, CBIM2-H<sup>+</sup> and CBIM3-H<sup>+</sup>) gets significantly reduced

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by 0.87 eV, 1.36 eV and 1.62 eV compared to the respective non-protonated neutral species CBIM1, CBIM2 and CBIM3. These significant changes in HOMO-LUMO energy gap are also reflected in the calculated electronic transitions by TDDFT/B3LYP method. The calculated HOMO to LUMO vertical electronic transition has been observed at 330, 407 and 358 nm for CBIM1, CBIM2 and CBIM3 respectively, which has been shifted to longer wavelengths at 372 nm, 451 nm and 454 nm in CBIM1-H<sup>+</sup>, CBIM2-H<sup>+</sup> and CBIM3-H<sup>+</sup> respectively (Table S4).



Figure 9: Energy diagrams of HOMO and LUMO orbitals of CBIM2 and CBIM2-H\* calculated at the DFT level using a B3LYP/6-31+G(d) basis set.

#### Fluorescence lifetime decay

In order to examine the excited state behaviour, nano second time-resolved fluorescence technique has been adapted for CBIM2 and CBIM2-H<sup>+</sup> (Figure 10). The fluorescence decay curves of compounds were fitted by utilizing the mono-exponential functions with the acceptable  $\varkappa^2$  values (Table S5). According to the equations  $\tau^{-1} = k_r + k_{nr}$ , where  $k_r = \Phi_f / \tau$ , the radiative rate constant  $k_r$  and the total non-radiative rate constant  $k_{nr}$  of CBIM2 and CBIM2-H<sup>+</sup> species were calculated. For CBIM2,  $\tau$  = 0.776 ns ( $\chi^2$  = 1.005) and CBIM2-H<sup>+</sup>,  $\tau$  = 2.036 ns ( $\chi^2$  = 1.123).



Figure 10: Life time decay profile of CBIM2 (•••) and CBIM2-H<sup>+</sup> (•••) in MeOH ( $\lambda_{e}$ ) = 370 nm).

#### Conclusions

In summary, we have designed and synthesised three carbazole-benzimidazole conjugated solid state emitters, which recognize the volatile acid vapours in the solid state with high sensitivity. The reversibility of the probes is also established upon exposure to volatile amine vapors. In addition, the dyes display significant spectroscopic responses when protonated, clearly suggesting that they can function as "naked-eye" dual mode probes for protons. DFT and TDDFT theoretical studies are conducted to support the experimental findings.

#### Experimental

#### General

Unless otherwise mentioned, materials were obtained from commercial suppliers and were used without further purification. Thin layer chromatography (TLC) was carried out using Merck 60 F<sub>254</sub> plates with a thickness of 0.25 mm. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL 400 MHz and 125 MHz instruments respectively. For NMR spectra, CDCl<sub>3</sub> and d<sub>6</sub>-DMSO were used as solvents using TMS as an internal standard. Chemical shifts are expressed in  $\delta$  units and <sup>1</sup>H–<sup>1</sup>H and <sup>1</sup>H–C coupling constants in Hz. UV-vis spectra were recorded on a JASCO V-630 spectrometer. Fluorescence spectra were recorded on Perkin Elmer LS 55 fluorescence spectrometer. Fluorescence lifetimes were measured using a time-resolved spectrofluorometer from IBH, UK. The instrument uses a picoseconds diode laser (NanoLed-07, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting. The goodness of fit was evaluated by  $\chi 2$ criterion and visual inspection of the residuals of the fitted function to the data.

#### General method of UV-vis and fluorescence titration UV-vis method

For UV-vis titrations, stock solution of the receptor (10 µM) was prepared in [(CH<sub>3</sub>OH / water), 1/1, v/v] (at 25°C) mixed aqueous solution. UV-vis spectra were recorded on a JASCO V-630

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spectrometer. Solutions of various concentrations containing the sensor and increasing concentrations of acid were prepared separately. The spectra of these solutions were recorded by means of UV-vis method.

#### Fluorescence method

For fluorescence titrations, stock solution of the sensor (10  $\mu$ M, CH<sub>3</sub>OH / water, 1/1, v/v, at 25°C) used was the same as that used for UV-vis titration. Fluorescence spectra were recorded on a Perkin Elmer LS 55 fluorescence spectrometer.

#### Determination of fluorescence quantum yield

To determine the quantum yields of the dyes and their protonated forms, we recorded their absorbance in methanol solution. The emission spectra were recorded using the maximal excitation wavelengths, and the integrated areas of the fluorescence-corrected spectra were measured. The quantum yields were then calculated by comparison with fluorescein ( $\Phi_s = 0.97$  in basic ethanol) as reference using the following equation:

#### $\mathcal{O}_x = \mathcal{O}_s \times (I_x/I_s) \times (A_s/A_x) \times (n_x/n_s)^2$

Where, x & s indicate the unknown and standard solutions respectively,  $\Phi$  is the quantum yield, I is the integrated area under the fluorescence spectra, A is the absorbance and n is the refractive index of the solvent.

#### Preparations of the compounds

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Synthetic method for the preparation of the dyes (CBIM1, CBIM2 and CBIM3)

#### Synthesis of 9-butyl-9H-carbazole-3-carbaldehyde (2)

To a stirred solution of DMF (4 ml, 51.9 mmol), POCl<sub>3</sub> (2 ml, 21.82 mmol) was added dropwise over five minutes at 0°C under N<sub>2</sub>-atmosphere. After complete addition, the reaction mixture was left to stir for 1 hour at room temperature. 9-butyl-9*H*-carbazole (0.5 g, 2.24 mmol) was added to the reaction mixture and then heated at 50°-60°C for 6 hours, when the TLC showed the full conversion of starting material to product. The whole reaction mixture was poured into ice-water (50 ml) and extracted the organic layer using dichlorometane (3 × 30 ml). The solvent was dried under reduced pressure and the crude was subjected to column chromatography using 10% EtOAc in petroleum ether as eluent to get the pure compound 2 as gummy liquid which solidified on standing. Yield = 0.48 g (87%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.95 (t, J = 4 Hz, 3H), 1.39 (m, 2H), 1.84 (m, 2H), 4.27 (t, J = 4 Hz, 2 H), 7.31 (t, J = 8 Hz, 1 H), 7.42 (m, 2H), 7.97 (d, J = 4 Hz, 1H), 8.12 (d, J = 8 Hz, 1 H), 8.56 (s, 1 H), 10.07 (s, 1H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.87, 20.54, 31.07, 43.17, 108.95, 109.45, 120.32, 120.75, 123.01, 123.07, 123.94, 126.74, 127.13, 128.53, 141.21, 144.08, 191.74

HRMS (ESI, positive): Calculated for  $C_{17}H_{18}NO (M + H)^+ (m/z)$ : 252.1388; found: 252.4609

Synthesis of 9-butyl-3-vinyl-9H-carbazole (3)

To a solution of methyltriphenylphosphonium bromide (3.5) g 9.79 mmol) in dry THF (20 ml) was added: BuOK9 (2:212; ),01936 mmol) at 0°C under N2-atmosphere. The resulting yellowishorange solution was stirred for 30 min at that temperature. THF (10 ml) solution of compound 2 (2 g, 7.96 mmol) was added to the reaction mixture and ice bath was removed to allow to warm to room temperature. After continuous stirring of 6 hours, the reaction mixture was quenched with the addition of saturated ammonium chloride solution. The organic layer was extracted with dichloromethane (3 × 30 ml) and the combined organic layer was dried over anhydrous sodium sulphate. After evaporation of the solvent under reduced pressure, the crude product was subjected to column chromatography (silica gel, 100-200 mesh) using 5% EtOAc in petroleum ether as eluent to get the title compound as colourless gummy liquid. Yield = 1.42 g (72 %).

<sup>1</sup>**H NMR (400 MHz, CDCI<sub>3</sub>):**  $\delta$  0.89 (t, J = 4Hz, 3H), 1.33 (m, 2H), 1.79 (m, 2H), 4.21 (t, J = 4 Hz, 2H), 5.17 (d, J = 8 Hz, 1H), 5.75 (d, J = 8 Hz, 1H), 6.89 (m, 1H), 7.19 (m, 1H), 7.29 (d, J = 4 Hz, 1H), 7.34 (d, J = 8 Hz, 1H), 7.42 (t, J = 8 Hz, 1H), 7.53 (d, J = 8 Hz, 1H), 8.07 (t, J = 8 Hz, 2H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.97, 20.58, 30.50, 42.99, 108.78, 108.93, 111.01, 118.54, 119.02, 120.50, 123.03, 123.11, 124.06, 125.82, 128.96, 137.70, 140.44, 140.96

**HRMS (ESI, positive):** Calculated for C<sub>18</sub>H<sub>20</sub>N (M + H)<sup>+</sup> (m/z): 250.1596; found: 250.5050.

#### Synthesis of (*E*)-4-{2-(9-butyl-9H-carbazole-3yl)vinyl}benzaldehyde (4)

A mixture of KOAc (0.59 g, 6.02 mmol) and n-Bu<sub>4</sub>NBr (1.5 g, 4.65 mmol) in DMF (15 ml) was stirred for 15 min in a double necked round-bottomed flask under nitrogen atmosphere at room temperature. To this reaction mixture, p-bromo benzaldehyde (0.75 g, 4.05 mmol), PPh<sub>3</sub> (0.1 g, 0.038 mmol) and 9-butyl-3-vinyl-9H-carbazole (1 g, 4.01 mmol) were added simultaneously and stirred for another 15 min. Catalytic amount of Pd(OAc)<sub>2</sub> (0.05 g) was added and heated for 12 hours at 80<sup>o</sup>-90<sup>o</sup>C. The mixture was cooled to room temperature and extracted with dichloromethane (50 ml). The organic layer was washed with water (3 × 10 ml), brine (10 ml), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed under reduced pressure and the crude product was purified through column chromatography (silica gel, 100-200 mesh) using 10% ethyl acetate in petroleum ether to yield compound 4 as yellow solid. Yield = 1.12 g, (80 %).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.96 (t, J = 4Hz, 3H), 1.41 (m, 2H), 1.87 (m, 2H), 4.31 (t, J = 4 Hz, 2H), 7.24 (m, 3H), 7.46 (m, 4H), 7.68 (d, J = 8 Hz, 3H), 7.87 (d, J = 8 Hz, 2H), 8.13 (d, J = 8 Hz, 1H), 8.26 (s, 1H), 9.99 (s, 1H)

 $^{13}\mathbf{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.99, 20.68, 31.28, 43.14, 108.63, 109.14, 109.18, 119.47, 120.44, 120.58, 121.13, 122.95, 124.88, 126.16, 126.93, 127.85, 129.87, 130.42, 133.50, 134.07, 134.97, 140.89, 141.08, 144.40, 191.91

**HRMS:** Calculated for  $C_{25}H_{23}NONa$  (M + Na)<sup>+</sup> (m/z): 376.1677; found: 376.1680.

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#### Synthesis of 3-(1H-benzo[d]imidazol-2-yl)-9-butyl-9Hcarbazole (CBIM1)

A mixture of 2 (0.1 g, 0.39 mmol) and o-phenylenediamine (0.1 g, 0.92 mmol) was dissolved in DMF (5 ml) solution and a catalytic amount of p-TSA (20 mg) was added to it. The whole reaction mixture was stirred under reflux for 5 hours at N<sub>2</sub>-atm. After cooling the reaction mixture to room temperature, it was poured into ice-water (20 ml) when an off-white precipitate formed which was filtered. Then the crude product was purified through column chromatography using neutral alumina and 20% EtOAc in petroleum ether as eluent to give the product as a white compound with 76% (0.98 g) yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.86 (t, J = 4 Hz, 3H), 1.18 (m, 2H), 1.73 (m, 2H), 4.16 (m, 2H), 7.14 (m, 3H), 7.34 (m, 3H), 7. 53 (m, 3H), 8.02 (dd, 2H), 8.71 (s, 1H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 13.71, 20.44, 31.02, 42.90, 109.01, 109.07, 114.54, 119.01, 119.39, 120.36, 120.45, 122.30, 122.81, 123.12, 124.50, 126.15, 139.06, 140.94, 141.42, 153.43.

**HRMS:** Calculated for  $C_{23}H_{22}N_3$  (M + H)<sup>+</sup> (m/z): 340.1814; found: 340.1820.

#### Synthesis of (*E*)-3-{4-(1H-benzo[d]imidazol-2-yl)styryl}-9butyl-9Hcarbazole (CBIM2)

To a stirred solution of 4 (0.1 g, 0.28 mmol) and ophenylenediamine (0.05 g, 0.46 mmol) in DMF (5 ml), p-TSA (20 mg) was added and the reaction mixture was refluxed under N<sub>2</sub>- atm for 8 hours. After cooling to room temperature, the mixture was poured into ice-water. A yellow precipitate separated out which was filtered and subjected to column chromatography using neutral alumina and chloroform as eluent to afford the pure product as a yellow solid with 58% (0.07 g) yield.

<sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO): δ 0.88 (t, J = 4 Hz, 3H), 1.31 (m, 2H), 1.76 (m, 2H), 4.40 (t, J = 4 Hz, 2H), 7.23 (m, 3H), 7.35 (d, J = 12 Hz, 1H), 7.46 (t, J = 8 Hz, 1H), 7.54 (t, J = 4 Hz, 2H), 7.65 (d, J = 8 Hz, 1H), 7.79 (t, J = 4 Hz, 3H), 8.19 (t, J = 8 Hz, 3H), 8.44 (s, 1H), 12.89 (s, 1H)

<sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO): δ 13.67, 19.73, 30.61, 42.10, 109.47, 109.56, 111.17, 118.71, 118.95, 120.31, 121.60, 122.07, 122.42, 124.78, 125.89, 126.46, 126.75, 127.94, 128.40, 130.71, 135.00, 139.16, 139.95, 140.44, 143.91, 151.12

**HRMS:** Calculated for  $C_{31}H_{28}N_3$  (M + H)<sup>+</sup> (m/z): 442.2283; found: 442.2287.

#### Synthesis of 4-(9-butyl-9H-carbazole-3-yl)benzaldehyde (6)

A mixture of 9-butyl-3-iodo-9*H*-carbazole (5) (0.2 g, 0.57 mmol) and 4-formylphenylboronic acid (0.1 g, 0.66 mmol) were dissolved in toluene (10 ml) under nitrogen atmosphere. Aqueous solution of  $K_2CO_3$  (2 ml, 2 M), tricaprylylmethyl ammoniumchloride (Aliquat<sup>®</sup> 336) (3 drops) and Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mg) was added to the mixture. The reaction mixture was heated at 90° C for 12 h. After being cooled to room temperature, distilled water (5 ml) was added and extracted with dichloromethane (3×10 ml). Organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under feduced pressure and the residue was puRHed<sup>0.10</sup>39996<sup>N</sup>COVMM chromatography using ethyl acetate/petroleum ether (1/9, v/v) as eluent afforded the compound 6 (0.12 g, 65%) as white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.97 (t, J = 7.4 Hz, 3H), 1.44 (m, 2H), 1.88 (m, 2H), 4.32 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.2 Hz, 1H), 7.50 (m, 3H), 7.75 (d, J = 6.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.96 (d, J = 8.0 Hz, 2H), 8.17 (d, J = 7.6 Hz, 1H), 8.38 (s, 1H), 10.06 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  13.98, 20.67, 31.25, 43.12, 109.15, 109.30, 119.38, 120.58, 122.99, 123.66, 125.24, 126.24, 127.61, 130.44, 130.57, 134.58, 140.75, 141.13, 148.33, 192.03. HRMS: Calculated for C<sub>23</sub>H<sub>22</sub>NO (M + H)<sup>+</sup> (m/z): 328.1701; found:328.2006.

#### Synthesis of 3-(4-(1*H*-benzo[*d*]imidazol-2-yl)phenyl)-9-butyl-9*H*-carbazole (CBIM3)

A mixture of compound 6 (0.1 g, 0.30 mmol) and ophenylenediamine (0.05 g, 0.46 mmol) was stirred in DMF (5 ml) solution. A catalytic amount of p-TSA (10 mg) was added to it and stirred in refluxing condition for 6 h under N<sub>2</sub>- atmosphere. After cooling to room temperature, the mixture was poured into ice-water. Yellow precipitate appeared which was filtered and subjected to column chromatography using neutral alumina and chloroform as eluent to afford the pure product as light yellow solid with 52% (0.07 g) yield.

<sup>1</sup>**H NMR (500 MHz, CDCl<sub>3</sub>):**  $\delta$  0.88 (t, *J* = 5.2 Hz, 3H), 1.32 (m, 2H), 1.78 (t, *J* = 7 Hz, 2H), 4.21 (t, *J* = 6.5 Hz, 2H), 7.16 (m, 4H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 8 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 3H), 8.06 (dd, *J*<sup>1</sup> = 7.5 Hz, *J*<sup>2</sup> = 8 Hz, 3H), 8.23 (s, 1H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 14.00, 20.69, 31.27, 43.10, 109.04, 109.17, 118.97, 119.21, 120.60, 123.07, 123.19, 123.57, 125.08, 126.06, 127.25, 127.78, 131.00, 140.44, 141.09, 144.19, 151.85. HRMS: Calculated for  $C_{29}H_{26}N_3$  (M + H)<sup>+</sup> (m/z): 416.2127; found: 416.2680.

#### **Computational details**

Full geometry optimizations were carried out using the density functional theory (DFT) method at the B3LYP <sup>9-11</sup> level for the compounds. All elements were assigned 6-31+G(d) basis set. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and there were only positive eigen values. Vertical electronic excitations based on B3LYP optimized geometries were computed using the time-dependent density functional theory (TDDFT) formalism<sup>12-14</sup> in methanol using conductor like polarizable continuum model (CPCM) <sup>15-17</sup>. All calculations were performed with Gaussian09 program package<sup>18</sup> with the aid of the GaussView visualization program.

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## **Graphical Abstract**

Three carbazole conjugated benzimidazole dyes has been synthesized and their acid/base induced photophysical properties has been studied.

