Pyridyl substituted 4-(1,3-Dioxo-1H,3H-benzo[de]isoquinolin-2-ylmethyl)-benzamides with aggregation enhanced emission and multi-stimuli-responsive properties

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1,8-Naphthalimide connected to benzoic acid chloride via methylene group was condensed separately with 3-amino pyridine and 4-amino pyridine and provided compounds 4-(1,3-Dioxo-2,3-dihydro-1H-phenalen-2-ylmethyl)-N-pyridin-3-yl-benzamide 1 and 4-(1,3-Dioxo-2,3-dihydro-1H-phenalen-2-ylmethyl)-N-pyridin-4-yl-benzamide 2. The compounds are characterized by spectral (IR, UV–Visible, 1H and 13C NMR) measurements and supported by their X-ray crystallography. Their photoelectron spectroscopy, SEM and TEM measurements are also made. They are found luminescent in DMF solution as well as in the solid state and form nano-aggregates with enhanced emission (AEE) in aqueous-DMF solution. Their AEE behavior depends on the polarity of the solvents. On grinding, crystalline solids 1 and 2 turn to amorphous and the process is reversible on annealing as supported by their powder X-ray diffraction (PXRD) measurements. Both compounds show mechanochromic properties and display multi-stimuli response. Density Functional Theory calculations rationalize their optical data.

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1. Introduction

The design and synthesis of organic materials which display luminescence in solid-state is a demanding area of research owing to their various applications [1]. However, unfavorable intermolecular interactions lead to quenching of the fluorescence in the solid state owing to non-radiative deactivation of the excited state [2]. These interfluorophore electronic interactions can be suppressed either by incorporation of bulky group or by the design of non-planar structure [3]. In this context, Tang et al. found several materials that are non luminescent in solution, displayed emission in the aggregate as nano particle suspensions in solvents or as thin films in solid state and introduced the concept of aggregation induced emission (AIE) [4,5]. Several naphthalimides find applications in fluorescent sensors, imaging agents, optoelectronic materials etc. [6]. Unfortunately, the applications may be limited because of the aggregation-caused quenching of fluorescence due to π–π stacking [7]. Therefore, the feasibility of converting naphthalimides to AIE-active molecules is considered a great development and. We recently, reported some compounds with bent shaped structures which showed interesting photophysical properties [8]. However, only a few naphthalimides based AIE-active molecules have been reported [9] till now and the fluorophores showed emission enhancement either with red shift or without red shift in their emission wavelengths. Intramolecular charge-transfer (ICT) [10,11] excimer formation [12] and excited-state intramolecular proton-transfer (ESIPT) [13] processes enable emission enhancement with red shift. In contrast, emission enhancement without red shift follows the restricted intramolecular rotation (RIR) process. The RIR does not change the electronic property of excited states of fluorophore whereas ICT, excimer formation and ESIPT alter it. In recent years, the latter approach is appealing to more researchers due to the good color stability and significant color change [14]. The molecules become mechanoresponsive owing to the presence of hetero atoms in their skeleton which facilitate the interactions such as hydrogen bonds, π–π stacking, and van der Waals forces between molecules [15–17]. Enthused by our preceding observations, we found worthwhile to tune the conformation of 1,8-naphthalimide...
structures were solved by direct methods using SHELXS-97 and libration was achieved by using KBr disks. The $1H$ NMR/$13C$ NMR spectra were recorded using a high resolution PAN analytical Empereyean spectrometer G9800A. Powder X-ray diffraction (PXRD) patterns were recorded using Cary Eclipse Fluorescence Spectrophotometer 59800A. Powder X-ray diffraction (PXRD) patterns were recorded using a high resolution PAN analytical Empereyean diffractometer, equipped with PIXcel3D detector employing Cu $K_{α}$ radiation ($λ=1.5418 Å$) over the range of $2θ=5–50°$. SEM micrograph of the samples were carried out using a Hitachi S-3700 M microscope (MIRA 3TESCAN). Geometry optimization was performed using Gaussian 09 suite of programs [27]. A hybrid version of Density Functional Theory (DFT) and Hartree–Fock (HF) methods was used, namely, B3LYP density functional theory method in which the exchange energy from Becke’s exchange function was combined with exact energy from Hartree–Fock theory [28,29]. Basis set 6-31G* has been used for all atoms of compound. In addition, we have also performed time-dependent density functional theory (TD-DFT) [30,31].

2.3. Synthetic procedure

2.3.1. Synthesis of 1 and 2

Compounds 1 and 2 were readily synthesized from 1,8-naphthalimide bearing benzoic chloride and amino pyridine in a single step reaction with fair yield. Synthetic details of 1 and 2 are given in S1. Methods of preparations of solutions of ppm level are provided in S2 along with detection procedures for ppm levels of OH$^-$ in S3. The Synthetic scheme of compounds are shown in Fig. S1. The $1H$ and $13C$ NMR spectra of 1 and 2 are provided in Figs. S2 and S3 respectively. The molecular characterizations of 1 and 2 were also carried out by X-ray photo-electron spectroscopy. This technique is ideal, as it permits high vertical resolution, giving information on the bonding states of the molecules [32]. It also allows estimation of the surface elemental composition, once the relevant atomic sensitivity factors have been taken into account. Fitted high-resolution C 1s peak, N 1s and O 1s XPS spectra in same solvent were recorded on Horiba Jobin Yvon Fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA-449 F3 instrument in the temperature range of 35–850 °C at a scan rate of 10 °C/min. The emission decay measurements were performed using a Horiba Jobin Yvon Nanollog Spectrofluorimeter. The excitation source was a pulsed Horiba Scientific Nanoleo at 285 nm wavelength, with a pulse duration less than 200 ps. The emission signal was dispersed with a iHR320 monochromator (equipped with a 1200 lines/mm grating, blazed at 500 nm). The decay curves were obtained using a Time-Correlated Single-Photon Counting Technique (TCSPC), with a Single Time Photon Correlating Unit (Horiba, Fluorohub). The decay times were obtained using a deconvolution procedure taking into account the shape of the exciting laser pulse (Horiba Software).

SEM samples were prepared by drop-casting of the $1×10^{-5}$ M solution in DMF/water (4:6 for 1 and 2) solution and evaporated to complete dry the sample. UV–Vis spectra in solid state were recorded using analytikjena SPECTROD 250 with a quartz cuvette (path length=1 cm, volume=3 mL) and their solid state emission were measured using Cary Eclipse Fluorescence Spectrophotometer 59800A. Powder X-ray diffraction (PXRD) patterns were recorded using a high resolution PAN analytical Empereyean diffractometer, equipped with PIXcel3D detector employing Cu $K_{α}$ radiation ($λ=1.5418 Å$) over the range of $2θ=5–50°$. SEM micrograph of the samples were carried out using a Hitachi S-3700 M microscope (MIRA 3TESCAN). Geometry optimization was performed using Gaussian 09 suite of programs [27]. A hybrid version of Density Functional Theory (DFT) and Hartree–Fock (HF) methods was used, namely, B3LYP density functional theory method in which the exchange energy from Becke’s exchange function was combined with exact energy from Hartree–Fock theory [28,29]. Basis set 6-31G* has been used for all atoms of compound. In addition, we have also performed time-dependent density functional theory (TD-DFT) [30,31].

2. Experimental

2.1. Materials

All reagents and solvents were obtained from commercial sources.

2.2. Instrumentations

The elemental analyses were performed on Carbo-Erba elemental analyzer 1108. The infrared spectra of the complexes were recorded on a Varian 3100 FT-IR spectrometer (4000–400 cm$^{-1}$) using KBr disks. The $1H$ NMR/$13C$ NMR spectra were recorded using a jeol 300 MHz instrument. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm). X-ray photoelectron spectra (XPS) were measured at 45° photoelectron take-off angle relative to the surface plane with a PHI 5600 Multi Technique System which gives good control of the electron take-off angle (base pressure of the main chamber $3×10^{-10}$ Torr) [20]. Spectra were excited with the Al-$K_{α}$ radiation. XPS peak intensities were obtained after Shirley background removal [21]. Spectra calibration was achieved by fixing the main C 1s peak at 285.0 eV. Experimental uncertainties in binding energies lie within ±0.4 eV. Spectral fitting was carried out with symmetrical Gaussian peaks after subtraction of the background. The residual or agreement factor R defined by $R=[\sum(\text{F}_{\text{obs}}-\text{F}_{\text{calc}})^2]/[\sum(\text{F}_{\text{obs}})^2]^{1/2}$ after minimization of the function $\Sigma(\text{F}_{\text{obs}}-\text{F}_{\text{calc}})^2$ converged to the values of 0.01–0.02 [22]. Single crystal X-ray diffraction data for compound 1 and 2 were collected on an Oxford Diffraction X-curilbur CCD diffractometer at 293 K using Mo $K_{α}$ radiation. The structures were solved by direct methods using SHELXS-97 and refined on $F^2$ by full matrix least squares technique using SHELXL-97 [23,24]. Drawings were carried out using MERCURY [25], and special computations were carried out with PLATON [26]. All non hydrogen atoms were refined anisotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition Nos. CCDC 989197 (1),

989198 (2). UV–Visible absorption spectra in DMF solution were recorded on Jasco V-630 at room temperature. The fluorescence spectra in same solvent were recorded on Horiba Jobin Yvon fluorescence spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA-449 F3 instrument in the temperature range of 35–850 °C at a scan rate of 10 °C/min. The emission decay measurements were performed using a Horiba Jobin Yvon Nanollog Spectrofluorimeter. The excitation source was a pulsed Horiba Scientific Nanoleo at 285 nm wavelength, with a pulse duration less than 200 ps. The emission signal was dispersed with a iHR320 monochromator (equipped with a 1200 lines/mm grating, blazed at 500 nm). The decay curves were obtained using a Time-Correlated Single-Photon Counting Technique (TCSPC), with a Single Time Photon Correlating Unit (Horiba, Fluorohub). The decay times were obtained using a deconvolution procedure taking into account the shape of the exciting laser pulse (Horiba Software).

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3. Results and discussion

3.1. Molecular structure of compounds

The compound 1 crystallizes in the monoclinic crystal system with \(\text{P2}_1\) space group while 2 crystallizes in the triclinic system with \(\text{P1}\) space group. Packing diagram of 1 and interplanar angle between amide and pyridyl plane are shown in Fig. 2(a) and (b) respectively. The interplanar angle between amide and pyridine planes in 1 of 29.68° facilitates intermolecular hydrogen bonding. Amide to amide hydrogen bond formation occurs only when the interplanar angle between pyridyl and amide plane is

![Fig. 2. (a) Packing diagram of 1 showing H-bonds (b) Interplanar angle between amide and pyridyl plane.](image)

<table>
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<tr>
<th>D–H–A</th>
<th>D–H</th>
<th>H–A</th>
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<td>1.98</td>
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<td>2.7021</td>
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<td>2.7315</td>
<td>112°</td>
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<td>H···(\pi_m)</td>
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<tr>
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<td>28.30</td>
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<td>3.106</td>
<td>124.82</td>
<td>23.35</td>
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</tbody>
</table>

Symmetry codes: \(a(x, 1+y, z)\) \(b(2-x, 1/2+y, 1-z)\). where, D=Donor, H=Hydrogen, A=acceptor.

![Fig. 3. C–H···π interactions in 1 (bond lengths are in Å and bond angles are in degree (°)).](image)

![Fig. 4. Electronic absorption spectra of 1 recorded in DMF-water solution containing different water fractions \((\lambda_{ex} = 330 \text{ nm})\).](image)
above 20° as in case of 1. Therefore in case of 2 (shown in Fig. S6 (a)) the angle of 4.36° restricts the formation of such hydrogen bond [33–35]. Compound 1 forms an infinite one dimensional chain owing to intermolecular amidic linkage between its monomer units, as shown in Fig. 2(a). This moiety consists of one classical and four non classical H-bonds and results in a 2D layered structure in which cores of benzene and pyridine rings are wrapped up by 1,8-naphthalimide ring from only one side as shown in Fig. 2(b). The compound 1 also shows two C–H⋯π interactions explicitly represented as C(2)–H(3)⋯πm and C(6)–H(1)⋯πm as shown in Fig. 3. It satisfies four parameters (C⋯πm ≤ 4.3 Å, H⋯πm ≤ 3.8 Å, C–H⋯πm ≥ 120°, C–πm–πn ≤ 30°) as accounted by Babu et al. [36] for non-canonical interactions. The weaker interactions and C–H⋯π interaction are listed in Table 1 for compound 1. The compound 2 shows one classical and five non classical H-bonds. The classical hydrogen bond is formed between amide nitrogen N(2)–H(10)⋯O(3) and one of the oxygen O(3) of the 1,8-naphthalimide ring whereas amidoo O(3) forms non classical hydrogen bond as C(25)–H(13)⋯O(3). The reverse amide linkages form 2D layered structures, as shown in Fig. S6(b). The core rings of benzene and pyridine are again wrapped by naphthalimide ring from both sides as observed in 2.

**Fig. 5.** Emission spectra of (a) 1 in DMF–water solution with different water fractions (λex=330 nm); (b) Plot of emission intensity vs. % of water fraction (fW). Photographs of 1 (c) and 2 (d) under UV illumination.

**Fig. 6.** (a) SEM; (b) and (c) are TEM images of 2 in DMF/water (4:6) (10 μM).
3.2. Photophysical properties of 1 and 2 in solution

The UV–Vis spectra of compound 1 and 2 recorded in pure DMF (1 × 10⁻⁵ M) are depicted in Figs. 4 and S7, respectively. They exhibited absorption bands at \( \lambda_{\text{max}} = 335 \) and 336 nm with a shoulder at longer wavelength \( \lambda_{\text{sh}} = 350 \) nm and 351 nm for compound 1 and 2, respectively and are assigned to \( \pi-\pi^* \) and \( n-\pi^* \) transitions. For preparing the aggregates, water (up to 90%) was added separately to the corresponding 1 × 10⁻⁵ M DMF solutions. Absorption spectra of 1 and 2 displayed a tail due to Mie scattering on the addition of water [37,38]. The emission from 1 displays peaks at \( \lambda_{\text{max}} = 365 \) and 374 nm, as shown in Fig. 5(a). The emission spectrum of 2 is depicted in Fig. S8. In the aggregated state, peaks from 1 shift to 375 and 390 nm with concomitant enhancement of the fluorescence intensity. A similar pattern was also observed on the aggregation of 2 (Fig. S8).

The fluorescence intensity from 1 and 2 were enhanced by 1.63 and 1.32 fold in DMF-water solutions as compared their intensity in DMF only. These changes were attributed to aggregation induced emission. A variation of intensity versus different water
fraction is displayed in Fig. 5(b). The photographs of samples with different fraction of water under UV-illumination are depicted in Fig. 5(c) and (d) for 1 and 2, respectively. The photographs clearly indicated that emission intensity maximises in DMF-water (40/60) mixtures. The aggregation enhanced emission (AEE) effect was also observed in acetone-water and THF-water solution as shown in Fig. 59. The many fold enhancement in these solvent mixtures support the polarity dependent characteristic of the AEE from both compounds [39]. The emission enhancement with the incremental addition of water in corresponding DMF solution can be attributed to molecular aggregation due to some intramolecular torsion motions that inhibit the nonradiative decay process thus enabling enhanced emission intensity [40].

3.3. Thermogravimetric analysis

The thermal stabilities of 1 and 2 were investigated by thermogravimetric analysis (TGA). 1 and 2 exhibit high thermal stability. The thermal decomposition temperature (T_d) at 367 °C corresponds to 3% and 16% weight loss for 1 and 2 respectively under nitrogen atmosphere (Fig. S10). It shows that 1 is thermally more stable than 2.

3.4. SEM and TEM analysis

The morphology and size of the nanoggregates of 1 and 2 in DMF-water (40/60) fraction were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurement. These images of compound 2 are shown in Fig. 6, whereas images for compound 1 are displayed in Fig. S11. It is noteworthy that all the fluorescent solutions are transparent and macroscopically homogeneous. The TEM images of 2 shows spherical nano particles of size 20 nm.

Using Kubelka-Munk function [41], the band gaps of 1 and 2 were estimated to be 3.10 eV and 2.89 eV, as depicted Fig. S12(a) and (b) respectively. Theoretically calculated band gaps for 1 and 2 were found as 3.50 eV and 3.87 eV, respectively.

3.5. Mechanochromic property of 1 and 2 in the solid state

The mechanochromic properties of 1 and 2 were evaluated from their solid state emissions (Fig. S13). The red-shift (with respect to solution measurements) observed in the spectra could be attributed to O–H···N bond interaction along with the bent structure [42,43]. In the pristine form, 1 and 2 showed indigo light emission at λ_max = 438 and 428 nm, respectively. Upon grinding using a pestle, the 1 and 2 solids showed a change in their emission behavior and exhibited super blue emission with maxima at 469 and 473 nm, (Fig. 7(a) and (b)), respectively. The mechanochromic property was found reversible by annealing the ground samples of 1 and 2 at 220 °C for 15 min. The bathochromic shift observed in emission owes to enhanced conjugation, can be attributed to the transformation of the twisted conformation in the pristine form to the comparatively planar conformation in the ground form.

The pristine, ground and annealed forms of 1 and 2 were characterized using PXRD (Fig. 8(a) and (b)). The diffraction patterns for pristine samples showed sharp peaks, which is the characteristic properties of the crystalline state. The pristine samples upon grinding showed diffuse peaks for 1 and 2.

Table 2

<table>
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<th>Various states</th>
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<th>Ground</th>
<th>Annealed</th>
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<td>τ_2 138</td>
<td>τ_1 7.6</td>
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<tr>
<td>Compound 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Compound 2</td>
<td>2.1</td>
<td>12</td>
<td>2.6</td>
</tr>
</tbody>
</table>

τ_1 and τ_2 are biexponential lifetimes of compounds in solid state.

Fig. 10. (a) Absorbance changes of 1 (10^-5 M, DMSO) (red) upon addition of input 2-26 ppm of OH^- in H_2O. The entire area under the peak or any wavelength in the 260-400 nm region can be utilized for “turn-on” response. (b) Plot of absorbance at λ_max = 337 nm (blue balls R^2 = 0.97) as a function of OH^- concentration (ppm) in water. Note: ‘turn on’ readout allows measurement of low concentration of the analyte and decreases the possibility of false positive signals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
indicating their amorphous nature. The ground samples after annealing restored the sharp peaks, thus suggesting the regeneration of the crystalline nature. The crystalline sample showed a uniform grain like morphology (Fig. 9(a)) while the amorphous sample evidences irregular shaped particles (Fig. 9(b)).

3.6. Time resolved fluorescence studies

The Fluorescence lifetime of compounds 1 and 2 was also recorded in pristine, ground and annealed state and the corresponding decay curves are shown in Fig. S14. All the emission decays are found bi-exponential, with a faster component and a shorter one. After a two exponential fit, the lifetimes for 1 and 2 in pristine, ground and annealed are shown in Table 2. In general, the lifetimes for the compound 2 are much shorter than those for the compound 1. The difference in the lifetimes of compounds 1 and 2 depends on their molecular structures, those, lead to different weaker and C-H⋯π interactions. The variation of the lifetimes for the same sample undergoing different treatments (grinding and heat annealing) is relevant.

3.7. Multi-stimuli responses of compound 1 and 2

Multi-stimuli-responsive properties of the compounds were studied using inputs viz. cations (Ca\(^{2+}\), Hg\(^{2+}\), Co\(^{2+}\), Zn\(^{2+}\), Pb\(^{2+}\), Mn\(^{2+}\), Cd\(^{2+}\), K\(^+\), Fe\(^{2+}\), Ni\(^{2+}\), Cr\(^{3+}\), Cr\(^{6+}\), Li\(^+\), Fe\(^{3+}\), Cu\(^{2+}\), Na\(^+\), Mg\(^{2+}\)) and anions (Cl\(^-\), F\(^-\), Br\(^-\), PF\(_6^-\), SO\(_4^{2-}\), I\(^-\), NO\(_3^-\), NO\(_2^-\), CN\(^-\), CH\(_3\)COO\(^-\), CO\(_3^{2-}\), HCO\(_3^-\), ClO\(_4^-\), and OH\(^-\)) in aqueous/non-aqueous media. Interestingly, 1 and 2 display significant modulation via UV-Vis mode on chemical stimulation with OH\(^-\) at ppm levels associated with turn-on readout in real time (~5 s). For instance, the processing of 1 (10\(^{-5}\) M, DMSO) via 26 ppm of OH\(^-\) (KO\(_7\)) in H\(_2\)O, as input, produces a hyperchromic shift (1.2 fold) at \(\lambda_{max}=337\) nm (Fig. 10(a)). Also the band at \(\lambda_{max}=339\) nm of 2 (10\(^{-5}\) M, DMSO) shows a hyperchromic shift (2.37 fold) upon addition of OH\(^-\) (30 ppm, H\(_2\)O) (Fig. S15(a)). These shifts evidence the interaction of OH\(^-\) with the NH group. The output signals were stationary for OH\(^-\) at 26 ppm and 30 ppm for 1 and 2, respectively and showed no deviation on triplicate the reaction time.

Moreover, in each case the OH\(^-\) additions shows linear responses (Fig. 10(b) and S15(b) [44]). These results allow selective monitoring of OH\(^-\) via differential responses at different wavelengths. These experiments were replicated in non-aqueous medium with similar efficiency (4-5% error) for compounds 1 and 2 as shown in Figs. S16 and S17, respectively. The repetitive action of a receptor is highly sought after for real applications.

In fact, the chemical information written on 1 and 2 by OH\(^-\) can be erased by H\(_2\)O. No significant variation was observed in absorption spectra of 1 (Fig. 11, red bars), upon addition of F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), CN\(^-\), CH\(_3\)COO\(^-\), CO\(_3^{2-}\), HCO\(_3^-\), NO\(_3^-\), NO\(_2^-\), PF\(_6^-\), SO\(_4^{2-}\), and ClO\(_4^-\) inputs. Selective detection of OH\(^-\) was also achieved in presence of other test anions (Fig. 11, blue bars). Moreover, similar outcomes (~4-5%, experimental error) were achieved for 2 (Fig. S18). It emerges that the output is input selective, as 1 and 2 brilliantly recognize OH\(^-\) in aqueous/non-aqueous media.

Time dependent absorption measurement for 1 at \(\lambda_{max}=337\) nm and for 2 at \(\lambda_{max}=339\) nm, at 298 K suggested that, in both cases, the reaction with OH\(^-\) is of pseudo first order (1-OH\(^-\) rate constant, \(k=1.11 \times 10^{-2}\) s\(^{-1}\), Fig. S19) (2-OH\(^-\) rate constant, \(k=1.17 \times 10^{-2}\) s\(^{-1}\), Fig. S20). Interestingly, high on/off ratios (on/off ratios: \(\lambda_{max}=337\) nm, 1.99 for 1 and \(\lambda_{max}=339\) nm, 2.37 for 2) combined with fast reaction rates allow a precise quantification of OH\(^-\) in the 260–400 nm optical window, instead of monitoring at a single wavelength as shown earlier in Figs. 10 and S19(a).

The processor was potentially sufficient to respond to OH\(^-\) in pool and tap water as demonstrated by proof-of-concept experiments. The absorbance changes at \(\lambda_{max}=337\) nm for 1 (Fig. S21)
and $\lambda_{\text{max}} = 339$ nm for 2 (Fig. S22) increase linearly as a function of the concentration of OH$^-$ (ppm) till the saturation limit. The detection limit [45] for OH$^-$ came out to be $2.35 \times 10^{-6}$ M for 1 and $2.96 \times 10^{-6}$ M for 2. Further, the binding constant obtained using the Benesi-Hildebrand method for OH$^-$ was $1.77 \times 10^3$ M$^{-1}$ for 1 (Fig. S23) and $2.54 \times 10^3$ M$^{-1}$ for 2 (Fig. S24) [46].

3.8. Theoretical studies

Fig. 12(a) and (b) show the optimized structures for 1 and 2. In both cases the HOMOs are located from pyridine to the benzene rings through the amide linkage while the LUMOs are located on the naphthalimide unit. The HOMO–LUMO energy levels and band gaps of 1 and 2 are similar. This result is in good agreement with their UV–Visible absorption spectral profiles.

TD-DFT energy (vertical excitation and oscillator strength) calculations on optimized ground-state structures were performed to simulate the UV–Visible absorption spectra. The TD-DFT-simulated absorption profiles of 1 and 2 obtained experimentally at 330 nm resemble to HOMO–2 → LUMO and HOMO–3 → LUMO transitions for 1 and HOMO–2 → LUMO and HOMO–1 → LUMO transition for 2, respectively (Tables S4 and S5).

In addition, the TD-DFT optimized first excited-state structures of compounds 1 and 2 do not show significant structural reorganizations compared with the corresponding optimized ground-state structures as shown in Fig. S25.

Insignificant structural reorganizations in the excited states are accompanied by negligible lowering of the HOMO–LUMO band gap (Table 3). These observations are also in agreement with the small Stokes shifts observed for 1 and 2.

To understand the nature of the interactions in dimers, ground state (B3LYP/6-31G(d), gaseous state) geometry optimizations of the model D1 (Fig. 12(e)) and D2 (Fig. 12(f)) systems were carried out. The stabilization energies for the formation of these dimeric structures were found as 26 and 39 kJ mol$^{-1}$ for 1 and 2, respectively.

As shown in Fig. 12(g) and (h), the HOMO of D1 is delocalized throughout the pyridine moiety and amide unit whereas its LUMO is localised on the naphthalimide unit of only one monomer. But in D2, they are localized in both monomers. This suggests that charge-transfer transitions may occur in the dimeric state. The HOMO–LUMO band gaps in the dimeric structural models D1 and D2 were found lower than those of the corresponding monomers (Table 3), which could be attributed to a combined effect of the destabilisation of the occupied MOs (i.e., HOMOs) and the weaker stabilization of the virtual unoccupied MOs (i.e., LUMOs). The lowering of the HOMO–LUMO band gaps in these model systems corroborates the red shift in the emission bands of 1 and 2 in their aggregated states.

4. Conclusions

In summary, we have synthesized and characterized two compounds 1 and 2, embedded with a 1,8-naphthalimide fluorophore and a pyridyl amido group, which tunes the optical properties of the resulting molecules. X-ray photo-electron spectroscopy provides information on the bonding states of the molecules. These molecules display polarity dependent aggregation enhanced emission (AEE). Their SEM and TEM micrographs show the formation of nano-aggregates. They also exhibit reversible mechanochromic property with a color contrast between indigo and super blue. The solid state emission and powder XRD studies revealed the transformation of the twisted crystalline state to the planar amorphous state. Outstandingly, our processors present label-free responses among matrix of analytes keeping uniqueness of information with no scope of mixing. They may pick up their molecular convenience towards analytes and unlock stimulating potential in the field of new generation molecular memory modules. Theoretical studies using DFT and TD-DFT calculations support the experimental data.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jlumin.2016.10.042.

References
