

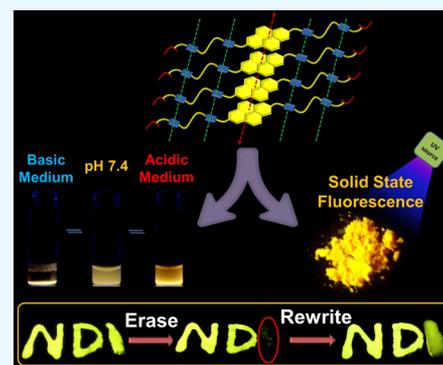
# Luminescent Naphthalene Diimide-Based Peptide in Aqueous Medium and in Solid State: Rewritable Fluorescent Color Code

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## Supporting Information

**ABSTRACT:** This study convincingly demonstrates a unique example of the self-assembly of a naphthalene diimide (NDI)-appended peptide into a fluorescent J-aggregate in aqueous media. Moreover, this aggregated species shows a remarkable yellow fluorescence in solid state, an unusual phenomenon for NDI-based compounds. The aggregated species has been characterized using transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy, X-ray diffraction, time-correlated single proton counting (TCSPC), UV–vis, and photoluminescence studies. TEM images reveal cross-linked nanofibrillar morphology of this aggregated species in water (pH 7.4). TCSPC study clearly indicates that the aggregated species in water has a higher average lifetime compared to that of the non-aggregated species. Interestingly, this NDI-based peptide shows H<sup>+</sup> ion concentration-dependent change in the emission property in water. The fluorescence output is erased completely in the presence of an alkali, and it reappears in the presence of an acid, indicating its erasing and rewritable property. This indicates its probable use in authentication tools for security purposes as a rewritable fluorescence color code. This NDI-appended peptide-based molecule can be used for encryption of information due to erasing and rewritable property of the molecule in the aggregated state in aqueous medium.



the corresponding fluorescence quenching.<sup>34</sup> Generally, water molecules can serve as good electron acceptors, which could facilitate aggregation-caused quenching phenomenon. Although there are some examples of aggregation of rylene dyes in water, the aggregation of NDI-based molecular systems is not significantly emissive in aqueous medium.<sup>35–39</sup> Moreover, they have a high tendency to form nonfluorescent species in solid state as well.<sup>33</sup> Thus, obtaining a solid-state fluorescence derived from rylene dyes still remains a real challenge.<sup>40–43</sup> A few attempts have been made to explore the assembly of NDI/peptide-conjugated soft materials in aqueous medium.<sup>44–47</sup> In our previous study on the self-assembly of NDI-based peptide PI (Figure 1a), it has been shown that the peptide upon self-association forms a fluorescent gel in organic medium, exhibiting aggregation-induced emission phenomenon.<sup>48</sup> The next challenge associated with NDI derivative is whether it can be made soluble to water medium. If at all it is soluble in water medium, will it be fluorescent? Therefore, it is interesting to make NDI-based water-soluble soft materials that exhibit significant fluorescence in water as well as in solid state for optoelectronic device fabrication. There are only a few examples of rylene-based peptide molecules showing pH-dependent fluorescence in aqueous medium.<sup>49–55</sup> Thus, there is a genuine need to make NDI-appended peptide-based

## INTRODUCTION

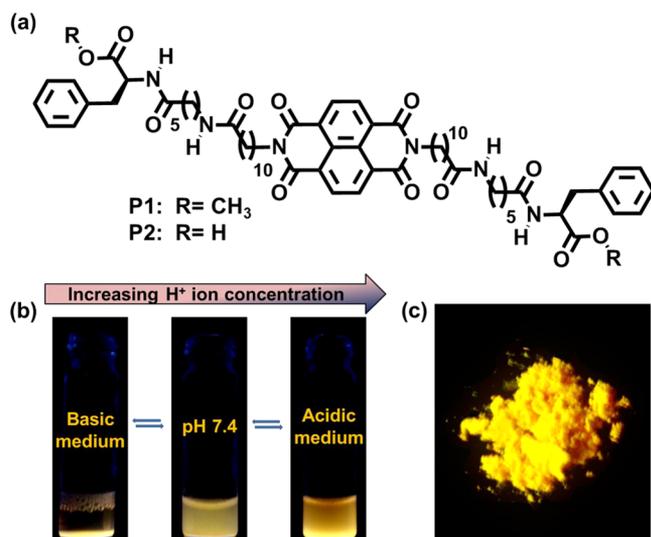
Supramolecular soft materials<sup>1–6</sup> consisting of organic  $\pi$ -conjugated molecules<sup>7–13</sup> are attracting enormous interest due to their successful applications in organic electronics. The interesting photophysical properties, high  $\pi$ -acidity, and redox behavior of naphthalene diimide (NDI) make it an excellent candidate for various applications.<sup>14–19</sup> Moreover, this moiety offers better solubility, and it is relatively easier to synthesize compared to its higher analogues such as perylene, terrylene, and quaterrylene. The incorporation of a peptide unit into the NDI system affords the expansion of the library of NDI-based molecules with structural diversity and functional variability in response to the external stimuli.<sup>20–25</sup> Although NDIs are good candidates for supramolecular chemistry, the very weak fluorescent behavior of NDIs makes them unsuitable for fluorescent applications in optoelectronics.<sup>26</sup> However, a few attempts have been made to obtain fluorescent NDI nanoaggregates in solution state by developing aggregation-induced emission enhancement (AIEE)<sup>27–31</sup> effect through the incorporation of peptide or other moieties in the imide position and by attaching bulky substituent(s) in the aromatic core of the NDI moiety.<sup>32</sup> NDI-based molecules generally show nonfluorescent behavior in water due to the aggregation-caused quenching phenomenon.<sup>33</sup> The high polarity nature of water molecules generally facilitates the charge separation (intramolecular charge transfer) in the chromophoric moieties, lowers the energy of the first singlet excited state, and thereby alleviates the transition of the molecule into a triplet state with

the corresponding fluorescence quenching.<sup>34</sup> Generally, water molecules can serve as good electron acceptors, which could facilitate aggregation-caused quenching phenomenon. Although there are some examples of aggregation of rylene dyes in water, the aggregation of NDI-based molecular systems is not significantly emissive in aqueous medium.<sup>35–39</sup> Moreover, they have a high tendency to form nonfluorescent species in solid state as well.<sup>33</sup> Thus, obtaining a solid-state fluorescence derived from rylene dyes still remains a real challenge.<sup>40–43</sup> A few attempts have been made to explore the assembly of NDI/peptide-conjugated soft materials in aqueous medium.<sup>44–47</sup> In our previous study on the self-assembly of NDI-based peptide PI (Figure 1a), it has been shown that the peptide upon self-association forms a fluorescent gel in organic medium, exhibiting aggregation-induced emission phenomenon.<sup>48</sup> The next challenge associated with NDI derivative is whether it can be made soluble to water medium. If at all it is soluble in water medium, will it be fluorescent? Therefore, it is interesting to make NDI-based water-soluble soft materials that exhibit significant fluorescence in water as well as in solid state for optoelectronic device fabrication. There are only a few examples of rylene-based peptide molecules showing pH-dependent fluorescence in aqueous medium.<sup>49–55</sup> Thus, there is a genuine need to make NDI-appended peptide-based

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**Figure 1.** (a) Chemical structure of compounds **P1** and **P2**. (b) Photographs of compound **P2** dissolved in phosphate buffer solution of pH 7.4, under acidic and basic conditions (at 2 mM concentration) under UV lamp (365 nm). (c) Solid sample obtained from the same buffer solution under UV lamp (365 nm).

molecules that not only will exhibit fluorescence in aqueous medium, but also can change fluorescence behavior significantly depending on the  $H^+$  ion concentration of the medium.

Over the past few years, a wide variety of anticounterfeiting and security technologies has been developed against counterfeiting. These methods include water markers, holograms, fluorescent materials, and others.<sup>56</sup> Erasing and rewritable properties are unique properties of smart materials that can be used as authentication tools and devices for security purpose. There are some examples of rewritable materials based on inorganic materials, carbon dots, organic materials, hybrid materials, and others.<sup>57–61</sup> However, to the best of our knowledge, none of the above-mentioned examples of rewritable invisible ink include the NDI-based luminescent soft material in aqueous medium, and the water-based operations are more desirable from an eco-friendly perspective. Due to low processing cost, good photostability and stimuli responsiveness, and easily modifiable characteristics, self-assembling organic materials like rylene dyes can be good candidates for this purpose. Thus, it is interesting to make an NDI-based fluorescent soft aggregate in aqueous medium that can be used as an invisible security ink as well as for write–erase–rewrite purposes. An NDI-based amphiphilic peptide molecule **P2** has been made, and it has been shown to form a soluble aggregate in buffer and also in solid state, exhibiting a bright yellow fluorescence (Figure 1). Interestingly, in the acidic medium, this NDI-appended peptide fluorescence is enhanced, and in the alkaline medium, the fluorescence vanishes (Figure 1b), suggesting its probable use in rewritable fluorescent color code for authentication purposes in future.

## EXPERIMENTAL SECTION

**Materials.** L-Phenylalanine (L-Phe), 11-aminoundecanoic acid (Und), 6-aminocaproic acid (Acp), and 1,4,5,8-naphthalenetetracarboxylic dianhydride were purchased from Aldrich. 1-Hydroxybenzotriazole (HOBt) and  $N,N'$ -dicyclohexylcarbodiimide were purchased from SRL, India.

**Instrumentation.** *NMR.* All NMR studies were carried out on a Bruker DPX 500 MHz spectrometer at 300 K. Concentrations were in the range of 5–10 mmol in  $(CD_3)_2SO$ .

*Matrix-Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF MS).* MALDI-TOF MS analysis was performed by using Applied Biosystems MALDI-TOF/TOF Analyzer in dithranol as a matrix.

*Fourier-Transform Infrared Spectroscopy (FT-IR).* All FT-IR spectra were recorded in a  $CaF_2$  cell and a Nicolet 380 FT-IR spectrophotometer (Thermo Scientific).

*X-ray Diffraction (XRD).* X-ray diffraction study of the dried sample was carried out by placing the sample on a glass plate. Experiments were carried out by using an X-ray diffractometer (Bruker AXS, Model No. D8 Advance). The instrument was operated at 40 kV voltage and 40 mA current using Ni-filtered  $Cu K\alpha$  radiation, and the instrument was calibrated with a standard  $Al_2O_3$  (corundum) sample before use. For scan 5–28°, the Lynx Eye superspeed detector was used with scan speed 0.3 s and step size 0.02°.

*UV–Vis Spectroscopy.* UV–vis absorption spectra were recorded on a Hewlett-Packard (model 8453) UV–vis spectrophotometer (Varian carry 50.bio).

*Photoluminescence Spectroscopy.* Fluorescence studies of the samples were carried out in a Perkin Elmer LS55 Fluorescence Spectrometer instrument using the front face geometry. The samples were excited at 340 nm wavelength, and emission scans were recorded from 350 to 750 nm.

*Transmission Electron Microscopy (TEM).* TEM images were recorded on a JEM 2010 electron microscope at an accelerating voltage of 200 kV. A drop of dilute solution of the aggregated compound was placed on carbon-coated copper grids (300 mesh) and dried by slow evaporation. Each grid was then allowed to dry in a vacuum for two days and then the images were taken.

*Time-Correlated Single Proton Counting (TCSPC).* TCSPC measurements were performed by Horiba JobinYvon IBH instrument having MCP PMT Hamamatsu R3809 detector.

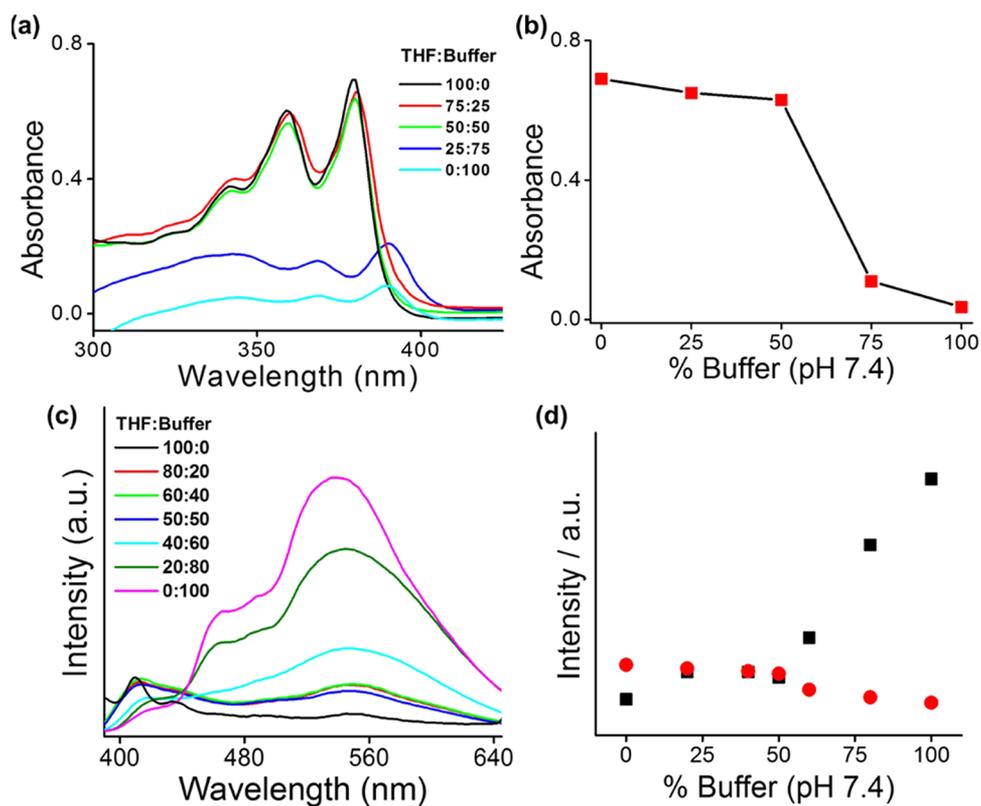
*Quantum Yield Measurement.* For the compound **P2**, the quantum yield ( $\Phi$ ) was calculated using quinine sulfate as a standard reference dye using a standard procedure.<sup>62</sup>

*Synthetic Procedures.* The detailed synthetic procedure of compound **P1** (MeOOC-Phe-Acp-Und-NDI-Und-Acp-Phe-COOMe) has been given in the electronic supporting information of ref 48.

*HOOC-Phe-Acp-Und-NDI-Und-Acp-Phe-COOH (P2).* To 250 mg (0.25 mmol) OMe-Phe-Acp-Und-NDI-Und-Acp-Phe-OMe, 15 mL MeOH and 5 mL 1 N NaOH were added, and the progress of saponification was monitored by thin-layer chromatography. The reaction mixture was stirred. After 10 h, methanol was removed under vacuum; the residue was taken in 25 mL of water and washed with diethylether ( $2 \times 50$  mL). Then, the pH of the aqueous layer was adjusted to 2 using 1 N HCl. A precipitate appeared, and it was collected. The precipitate was washed with 50 mL methanol and dried under vacuum. A light-brown solid material was obtained.

Yield: 90 mg (0.09 mmol, 36.0%).

$^1H$  NMR (500 MHz,  $(CD_3)_2SO$ , 25 °C):  $\delta$  12.6 (COOH, 2H, br), 8.64 (aromatic Hs of NDI, 4H, s), 8.07–8.05 (NH, 2H, d,  $J = 8.0$ ), 7.65 (NH, 2H, br), 7.25–7.14 (aromatic Hs of Phe, 10H, m), 4.41–4.36 ( $C^{\alpha}H$ , 2H, m), 4.02 ( $^{\alpha}CH_2$ , 4H, s), 3.03–2.77 ( $^{\alpha}CH_2$ ,  $C^{\beta}H$ , 8H, m), 2.00–1.99 ( $^{\alpha}CH_2$ , 8H, m), 1.63 ( $^{\beta}CH_2$ , 4H, s), 1.43–1.08 (20 $CH_2$ , 40H, m).  $^{13}C$  NMR (125 MHz,  $(CD_3)_2SO$ , 25 °C):  $\delta$  173.79, 172.66, 172.45,



**Figure 2.** (a) UV–vis spectra of the peptide, **P2**, from the monomeric state in THF to the aggregated state (buffer solution, pH 7.4) at 0.05 mM concentration. (b) Absorbance versus % buffer (pH 7.4) plot shows the sharp decrease in absorbance with the increased buffer in percentage (monitored at 379 nm). (c) Emission spectra of compound **P2** (2 mM) from the monomeric state (THF) to the aggregated state (aqueous medium) and also in mixed solvent system of various compositions of THF and buffer solution at pH 7.4. (d) Intensity versus % buffer (pH 7.4) shows that a change in the fluorescence occurs after 50% water in mixed solvent. The red dots and black dots indicate the fluorescence measured at 410 and 540 nm, respectively.

163.23, 138.36, 131.04, 129.65, 128.69, 126.92, 53.85, 38.88, 37.39, 36.05, 35.63, 29.48, 29.33, 26.52, 25.93, 25.51. MALDI-TOF MS: calculated 1154.630, found 1178.030  $[M + Na]^+$ .

## RESULTS AND DISCUSSION

**Aggregation of the Peptide Molecule.** In supra-molecular  $\pi$ -conjugated system, control over the molecular orientation is important to form significant functions. For this purpose, a peptide-appended NDI-based molecule, **P2**, has been designed and synthesized (Figure 1a). The molecule, **P2**, has a centrally located NDI core and intervening amide ( $-\text{CONH}$ ) groups for hydrogen bonding interactions as well as carboxylic acid ( $-\text{COOH}$ ) group at both ends to meet the bolaamphiphilic character. The carboxylic acid ( $-\text{COOH}$ ) groups at both termini of the molecule can interact with water molecules, which can promote the solubility of the molecule in aqueous medium.

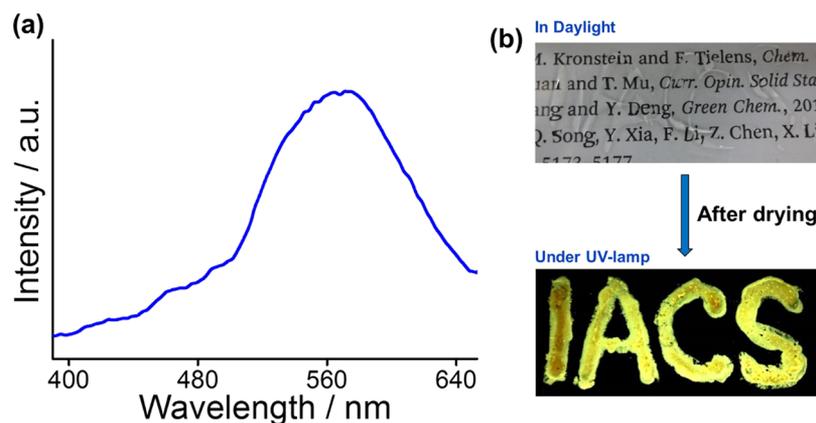
The NDI-based molecule, **P2**, was completely soluble in phosphate buffer solution with a pH range of 7.25–9.0. On heating the compound, **P2**, in buffer solution above 80°C for 10–15 min, it was readily dissolved. Upon cooling to room temperature slowly, a highly viscous transparent solution appeared with a brown color. Similarly, the compound was highly soluble in 10 mM NaOH solution. However, the solution gives a light pink precipitation when acidified by dropwise addition of 10 mM HCl. This study indicates that the compound, **P2**, is completely soluble in aqueous medium within a certain pH range (7.5–9.0) to form a soluble

aggregate. This type of aggregate is well-characterized by using various spectroscopic techniques in the subsequent sections of this manuscript.

**Spectroscopic Studies.** UV–vis spectroscopic studies were carried out to probe the aggregation behavior of the compound, **P2**, from monomeric state to the aggregated state keeping the concentrations fixed at 0.05 mM. The compound, **P2**, forms a viscous solution in aqueous medium, and it forms a clear solution in organic solvent (tetrahydrofuran (THF)). This prompted us to examine a solvent-dependent change of the absorption spectra in only THF, only buffer (pH 7.4), and also in the mixed solvent system (containing THF and buffer solution) in various ratios. In THF, absorption peaks appeared at 359 and 379 nm with a shoulder at 340 nm corresponding to the characteristic NDI moiety in the monomeric state.<sup>44</sup> In the solvent mixture of composition THF/buffer (75:25), there is no significant change in the absorption peak. At the composition THF/buffer (50:50), there is only a slight change in the absorption peak. However, when the solvent composition is changed to 25:75, there is a significant change in the absorption spectra with respect to the other compositions of the solvent system. There is a considerable decrease in the intensity accompanied by a red shift of the major absorption peak in fully aqueous medium compared to that of in pure organic medium (THF). The absorption peak in THF (379 nm) is 10 nm red shifted to 389 nm in buffer solution (Figure 2a). Intensities of all absorption peaks are significantly decreased (hypochromic shift), and a red shift

**Table 1. Fluorescence Lifetime in Excited State (with Time Components  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ ) and Quantum Yield ( $\Phi$ ) Obtained from TCSPC Measurements of Peptide P2 (in THF and Buffer Solution)**

sample	quantum yield $\Phi$ (%)	$\tau_1$ (%) ns	$\tau_2$ (%) ns	$\tau_3$ (%) ns	average lifetime $\tau_{\text{avg}}$ (%) ns
peptide P2 (in THF)		0.008 (0.5)	0.030 (99.2)	0.010 (0.3)	0.0477
peptide P2 (in buffer)	4.98	0.321 (58.5)	0.598 (34.7)	0.397 (6.8)	1.3158

**Figure 3.** (a) Emission spectrum of compound P2 at solid state obtained from phosphate buffer (pH 7.4) solutions after freeze-drying and evaporation. (b) Upper panel shows the writing marks written on a glass slide with the buffer solution of P2 in daylight, and lower panel shows the readable word (IACS) after drying (in solid state) the writing marks under UV lamp (365 nm).

(bathochromic shift) of the lowest energy absorption band (379 nm) is observed for the aggregates (Figure 2a) in aqueous medium. The absorption intensity of the major peak of the compound, P2, in phosphate buffer solution (pH 7.4) is decreased by 89% with a 10 nm red shift compared to that of in pure THF solvent. The decrease in intensity with a red shift of the absorption band indicates the involvement of a slipped J-type aggregation.<sup>44</sup> Moreover, plotting of absorption in a fixed wavelength (379 nm) against % of buffer added reveals that after reaching the composition 1:1 (THF/water) mixture, the aggregate starts to form considerably, as is evident from Figure 2b. There is also an increment in the intensity of the absorption peak for the self-association of this molecule with an increase in concentration of compound P2 in phosphate buffer solution of pH 7.4 (Figure S4a).

Generally, the fluorescence of a fluorophore is quenched upon aggregation in water, as water is known to be a good quencher.<sup>35</sup> However, in this study, compound P2 shows an unexpected enhancement in fluorescence upon aggregation in aqueous medium. In THF, NDI-based peptide P2 exhibits a very feeble fluorescence with a broad nonsignificant peak centered at around 379 nm. A change in the solvent system from THF to aqueous medium not only triggers the self-association from monomeric state to aggregated state of compound P2, but also exhibits a strong and intense yellow fluorescence with a peak at 389 nm. It should be noted that the concentration of compound P2 is identical in THF as well as in buffer solution. As the percentage of aqueous solution increases by keeping the concentration of P2 fixed at 2 mM, the monomeric peak is diminished and a new broad peak with an enhanced intensity appears at around 540 nm. It is observed from Figure 2c that after 1:1 composition of THF and buffer solution, the fluorescence increases drastically and at 100% phosphate buffer the emission appears around 540 nm. Plotting of the intensity of emission with respect to the percentage of aqueous solution, it was observed that the peak at 410 nm was diminished and the peak around 540 nm was increased

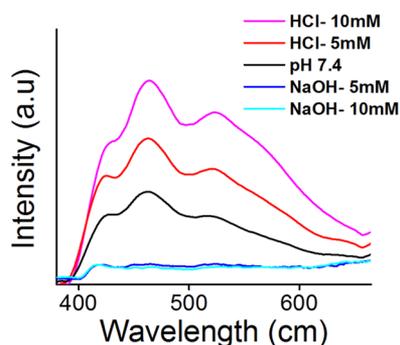
consistently with the addition of buffer solution (Figure 2d). At 1:1 ratio of THF and the buffer solution, an intersection was observed between the intensity of these two peaks (410 and 540 nm, respectively). This study also proves that the AIEE phenomenon is involved in this case. The concentration-dependent fluorescence experiments were performed for compound P2 in phosphate buffer solution at pH 7.4 (Figure S4b), and a steady increase in emission peak was observed (at 540 nm) with an increase in concentration of compound P2.

The fluorescence quantum yield of compound P2 was measured using a standard dye (quinine sulfate) as a reference dye. By comparing the integrated area of the corrected emission spectrum with the reference of quinine sulfate,<sup>62</sup> the quantum yield of compound P2 was found to be 4.98% (Table 1) upon being excited at 340 nm.

Usually, rylene-based derivatives exhibit low fluorescence intensity in solid state. Although there are many reports of other rylene moieties showing solid-state fluorescence, NDI-based compounds that exhibit solid-state fluorescence are rarely found.<sup>40–43</sup> Interestingly, after evaporating the solvent completely, compound P2 exhibits an intense yellow fluorescence in the solid state (Figure 3). The photoluminescence study was performed in the solid state (by taking a freeze-dried sample) obtained from phosphate buffer solution using the front face technique. The fluorescence spectrum of compound P2 in solid state shows a similar behavior as shown in solution state (Figure 3a). However, the emission peak shifts to 572 nm in solid state compared to that in phosphate buffer solution of pH 7.4. An illustration for the solid-state fluorescence of molecule P2 has been presented in Figure 3b. Figure 3b shows that a word has been written on a glass slide that is invisible to the naked eye. However, when the system is allowed to undergo drying process, the aggregated solidified writing marks glow upon UV irradiation and become visible clearly.

**H<sup>+</sup> Ion Concentration-Dependent Spectroscopic Studies.** The optical response of the NDI-appended peptide, P2,

was examined both in acidic and in basic media to investigate whether the response is the same or different in these two media. Interestingly, in acidic medium containing 10 mM HCl solution, compound **P2** (2 mM) shows a strong yellow fluorescence (at 550 nm), whereas this fluorescence property almost disappears in basic medium. It is evident from Figure 4



**Figure 4.** Emission spectra of compound **P2** in phosphate buffer solution (pH 7.4) and under their acidic and basic conditions by adding HCl and NaOH, respectively.

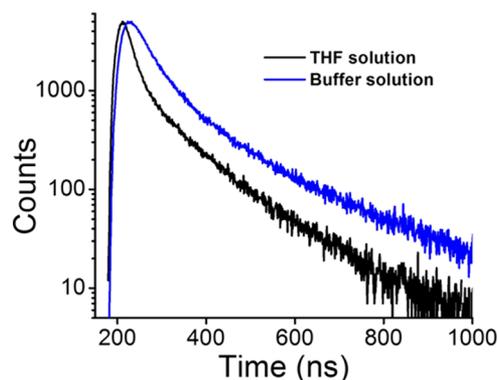
that in acidic medium, the aggregated peptide, **P2**, shows a strong yellow fluorescence. However, in basic medium (10 mM NaOH), no significant fluorescence peak is observed. This system can be switched on or off in a totally reversible manner by making the environment acidic and alkaline, respectively (Figure S5). A pH-dependent fluorescence study has been accomplished within the pH range 7.4–9.0 in phosphate buffer solution, and Figure S6 shows a gradual decrease in fluorescence intensity without any significant change in peak shift with a gradual increase in pH of the solution keeping the concentration of the peptide, **P2**, identical (2 mM) in all cases. The compound is soluble in phosphate buffer, and hence the pH range from 7.4 to 9.0 has been chosen for the experimental purpose. A UV–vis spectroscopic study (Figure S7) was performed by varying the  $H^+$  ion concentration (by adding HCl or NaOH) on the phosphate buffer solution of compound **P2** (0.05 mM concentration). There is a slight change or decrease in the absorbance peak upon a decrease in pH (due to the addition of acid solution) of the medium, and this can be attributed to the fact that the extent of J aggregation may be stronger in the acidic medium compared to that under the other conditions (basic or neutral pH).<sup>63</sup>

The molecule exhibits a bright yellow emission in aqueous medium as well as in solid state upon the irradiation of UV lamp at 365 nm. The preservation of luminescence in the aggregated state of the molecule may be utilized for writing words that are invisible to the naked eye but glow upon UV irradiation. Thus, this soft material can act as an invisible fluorescence ink. In addition, the system can be switched on or off in a totally reversible manner by making the environment acidic and alkaline, respectively. Such  $H^+$  ion-dependent fluorescence switching makes it possible to use the system for an overall write–erase–rewrite process of information.

A systematic investigation was also carried out to understand the absorption properties of peptide **P2** in three different media (pH 7.4, acidic, and basic) keeping the concentration same (0.05 mM). Figure S7 shows that in basic medium, the intensity of the major peak is more intense than that in acidic medium and in pH 7.4. However, no significant peak shift was observed. In pH 7.4 and acidic medium, the peak position and the

intensities are almost same. This indicates that the aggregation pattern (J aggregation) is almost similar in three different media (pH 7.4, acidic, and basic).

**TCSPC Study.** Time-correlated single-photon-counting (TCSPC) experiments were performed (Figure 5) for lifetime



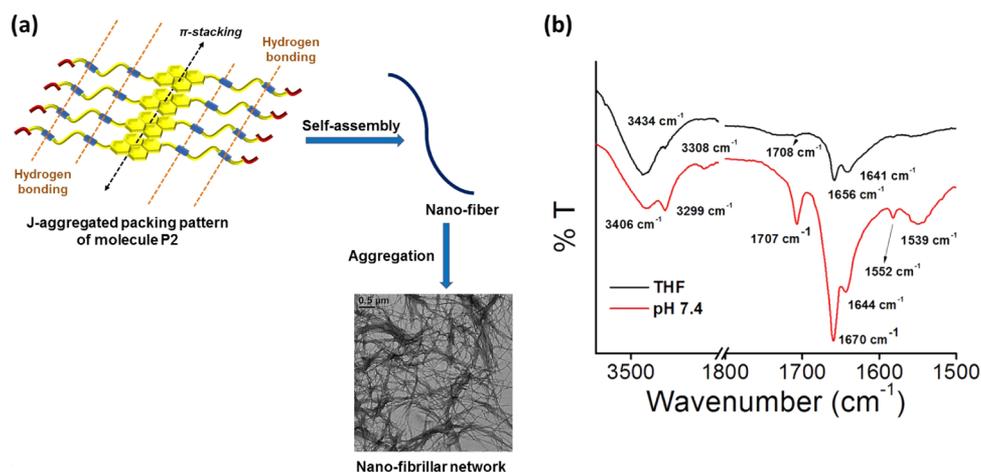
**Figure 5.** TCSPC decay profiles of peptide **P2** in THF (monitored = 410 nm) and aqueous solution (pH 7.4) (monitored = 540 nm) at 0.2 mM concentration.

measurement of this soft material. For peptide **P2** in THF, molecules were excited at 340 nm and emission was observed at 410 nm. A triexponential short-lived decay was noticed with an average lifetime of 477 ps, arising for the monomeric species. Similar experiments were performed in buffer solution at pH 7.4 with excitation at 340 nm, and the emission was monitored at 540 nm. Triexponential decay was observed with a significantly longer average lifetime of 1.316 ns. In aqueous medium (pH 7.4), NDI-based peptide molecules formed an aggregated species and it exhibited aggregation-induced fluorescence. This may be the reason for the relatively longer lifetime of **P2** in aqueous medium than that in nonaqueous environment.<sup>47</sup> The detailed TCSPC data has been tabularized in Table 1.

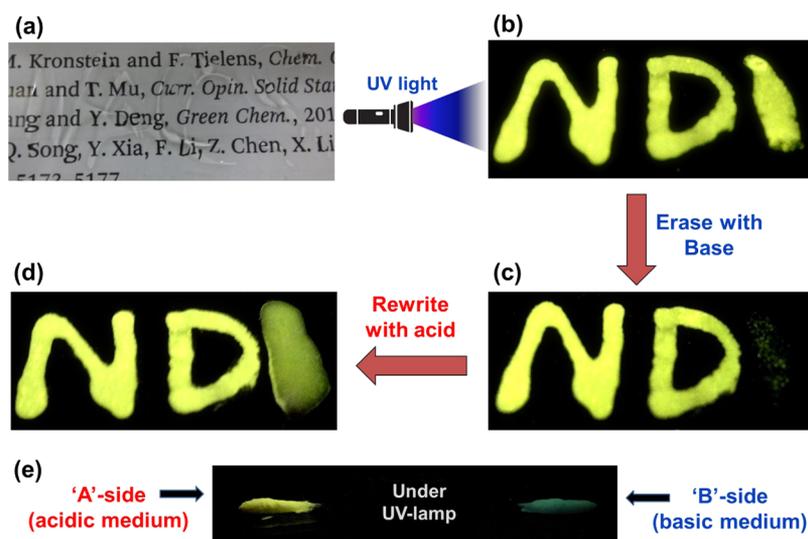
**Morphological and Structural Studies.** High-resolution transmission electron microscopic study (HR-TEM) was performed to examine the morphological feature of the soluble aggregate of the NDI containing peptide **P2** in aqueous medium (Figure 6a). It shows the presence of an intertwined nanofibrillar network structure for the supramolecular aggregate in buffer solution (pH 7.4). These fibers are several micrometers in length, and their widths are in the range of 50–70 nm. There are some thin fibrils, which are combined to form relatively thick fibrils in their assembled states.

FT-IR study was performed to examine the role of hydrogen bonding in aggregate formation (Figure 6b) in buffer solution. A peak appeared at  $3427\text{ cm}^{-1}$  corresponding to monomeric nonhydrogen-bonded N–H stretching of **P2** in THF. However, the sample (freeze-dried) obtained from phosphate buffer solution showed a peak at  $3304\text{ cm}^{-1}$  corresponding to hydrogen-bonded N–H stretching. In the monomeric form, the amide C=O stretching frequency was observed at  $1641\text{ cm}^{-1}$ , whereas in the aggregated state in buffer at pH 7.4, this C=O stretching frequency was observed at  $1644\text{ cm}^{-1}$ , indicating the presence of a H-bonded sheet-like structure.

The UV–vis study, as discussed in the previous section of this manuscript, clearly indicates the involvement of  $\pi$ – $\pi$  interactions among NDI-based peptide molecules to form a J-aggregated species. Furthermore, the wide-angle XRD study



**Figure 6.** (a) Typical illustration of self-assembly of peptide **P2** in J-aggregate fashion toward the formation of a nanofibrillar network structure, as evident from the HR-TEM image obtained from the solution of **P2** at pH 7.4. (b) FT-IR study of compound **P2** in THF and phosphate buffer solution (pH 7.4). Temperature and concentration maintained at 25 °C and 2 mM, respectively.



**Figure 7.** (a)–(d) are the photographs of the writing marks on a glass slide in daylight (upper panel) and in UV light (lower panel) with the aqueous solution of **P2**. (e) A-side and B-side of a cotton stick soaked in the acid-mixed and base-mixed buffer solution of **P2** show bright and weak emission, respectively (under UV lamp at 365 nm).

(Figure S8) convincingly demonstrates the presence of  $\pi$ - $\pi$  stacking between the NDI core in the aggregation formation. This is because the peak that appeared at  $2\theta = 27.46^\circ$  corresponds to the  $d$ -spacing value of 3.22 Å. Moreover, the FT-IR study suggests the involvement of hydrogen bonding to form the aggregated species. On the basis of these three above-mentioned studies and the involvement of various noncovalent interactions, a schematic model has been developed and is shown in Figure 6a.

**Fluorescence Color Code.** External stimuli, including pressure, heat, light, interaction with guest molecules, and pH, can cause a change in the emission properties of fluorescent organic solids.<sup>64–66</sup> In recent years, fluorescent dyes have been incorporated into valuable documents and used as anticounterfeiting labels widely. In this study, NDI-appended peptide not only exhibits aggregation-induced enhanced emission, but also shows fluorescent on/off depending on the medium that is chosen (pH 7.4/acidic/basic). Interestingly, it also shows intense solid-state fluorescence, and this is useful for several applications, including optoelectronic devices, organic field-

effect transistors, field-effect transistors, and so on. Owing to the remarkable  $H^+$  ion concentration-dependent luminescence property, the capability of peptide **P2** for potential use as an invisible fluorescent ink was tested. For this purpose, the word “NDI” was written on a glass slide with the aqueous solution of **P2**, and the photographs are presented in Figure 7 under the exposure of normal light and UV light (365 nm). Figure 7a,b clearly illustrates that the writing marks are clearly visible (with an intense yellow color) under the UV lamp excited at 365 nm, whereas this image is not visible under normal daylight. Interestingly, this aggregated species exhibits significant fluorescence both at pH 7.4 and under acidic condition, implying its probable use as a fluorescence ink over a wide range of  $H^+$  concentrations. A practical application based on the acid-induced luminescence of **P2** is used for the write–erase–rewrite process. Figure 7c clearly shows that the fluorescence disappears in the presence of alkali (10 mM NaOH solution), and this property has been nicely utilized for erasing the writings. Moreover, this fluorescence property is regained in the presence of an acid (10 mM HCl solution), as is evident from

Figure 7d. Thus, this fluorescent NDI-containing peptide-based soft material has been used for writing–erasing–rewriting purposes depending on chemical stimuli. It is evident from Figure 7e that the side marked as “A”-side of a cotton stick glows with a bright yellow color after dipping and soaking it in an acid-mixed aqueous solution of **P2**, under the exposure of the UV lamp (365 nm). However, the side marked as “B”-side of the same cotton stick, which is dipped in an alkaline solution of **P2**, does not show any significant emission. Although there are examples of several molecular scaffolds that exhibit write–erase–rewrite application,<sup>57–61</sup> NDI-appended peptide-based soft material showing this type of interesting property has not yet been reported before to the best of our knowledge. On the basis of the remarkable fluorescence properties, compound **P2** may provide an opportunity for various purposes, such as information encryption and storage. This type of write–erase–rewrite phenomenon is potentially useful as an authentication tool for security purposes. There are several examples of self-assembled, water process-able organic materials showing the write–erase–rewrite application.<sup>59,60,67</sup> However, this self-assembled NDI-appended peptide-based soft material is different from other above-stated examples. This is because none of these above-mentioned reported organic materials exhibit pH-dependent fluorescent on/off property, which ultimately leads to a write–erase–rewrite application. In this way, our NDI-appended peptide-based soft material in water (without any cosolvent) stands for a unique and fascinating example of self-assembled water process-able organic soft organic material showing a potential write–erase–rewrite property.

## CONCLUSIONS

In conclusion, a water-soluble fluorescent peptide-based NDI derivative has been discovered that has shown bright yellow emission in the aggregated state in water medium as well as in solid state. UV–vis and fluorescence spectroscopic data clearly suggest the presence of a J-type aggregate in the self-assembled state in buffer solution. This new aggregated species based on NDI-appended peptide also acts as any invisible ink under normal light illumination, but it does strongly fluoresce (yellow) under UV light, and this fluorescent soft material is reusable for several times without any significant loss of fluorescence. Moreover, this NDI-containing peptide-based soft fluorescence material is endowed with wonderful erasing and rewriting property, indicating its probable application for security purposes against forgery as a rewritable fluorescence color code.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01813.

NMR, MALDI-TOF, spectroscopic studies, XRD studies (PDF)

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## Notes

The authors declare no competing financial interest.

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