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Authors: ANAMIKA KALITA, Akhtar Hussain Malik, and Neelotpal Sen Sarma

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Stimuli-Responsive Naphthalene Diimide as Invisible Ink: A Rewritable Fluorescent Platform for Anti-Counterfeiting

Anamika Kalita,*[a] Akhtar Hussain Malik,[b] and Neelotpal Sen Sarma[a]

Abstract: Herein, we report an approach to combat counterfeiting and storage of valuable information based on solid state fluorescence switching behavior of isoniazid functionalized naphthalene diimide (ISO_NDI) in response to the external stimuli *viz.* HCl vapor. The unique feature of ISO_NDI is further utilized to develop an invisible ink (ISO_NDI-PVA) with commercial polymer polyvinyl alcohol (PVA). The solid state fluorescence recovery was observed while loading with HCl vapors. This exclusive property of the material could be applied directly as a security ink for confidential data storage purpose. Based on above strategy, we successfully realized the rewritable application by using ISO_NDI-PVA ink and confirm its practical efficacy on various substrates by creating different patterns. The solid-state fluorescence switching behavior of ISO_NDI-PVA ink exhibited reversible on/off signal for multiple cycles under the influence of HCl/NH_3 vapors. Mechanistic investigation supports a clear participation of intermolecular charge transfer (ICT) phenomenon in solid state fluorescence switching property. The ease of fabricating the ink with invisible to visible characteristics in response to HCl vapors initiates new opportunities for exploring the application of ISO_NDI-PVA as invisible ink for targeted security applications.

Introduction

Counterfeiting/forging is a worldwide concern that originates negative impacts on the socio-economic as well as posing serious security threats to the whole nation. Counterfeiting of items especially banknotes, legal documents, certificates, electronics component, branded and pharmaceuticals products have become an important issue for industry as well as for governments.[1-3] Illegal counterfeiting activities particularly for currency notes has lead to the economic fallout.[4,5] Furthermore counterfeited pharmaceutical products put the patient's health in jeopardy as they may contain unidentified contents with incorrect specifications.[6] Therefore development of ground-breaking anti-counterfeiting technologies that circumvent the forgeries and make sure the security of products is highly desirable.[7] Development of materials having stimuli-responsive properties has attracted the scientific community around the globe due to their potential applications in security protection such as information storage, anti-counterfeiting,[8,9] and many more. Due to external stimuli, these smart materials (especially luminescent) can change their output response which can be explored to prevent the information being forged. From practical point of view, it is highly desirable that stimuli-responsive materials can be employed to fabricate ordered solid-state thin films, rather than powder or solutions that ultimately lead to the development of smart sensors.[10]

During past decades, a wide variety of anti-counterfeiting technologies, including plasmonic labels,[11,12] radio frequency identification (RFID),[13,14] holography,[15-17] bar/QR codes,[18-20] have been developed to combat the unauthorized counterfeiting. However, most of these anti-counterfeiting technologies suffer from disadvantages such as they can be easily replicate/cracked. Functional materials because of their unique optical properties offer improved security features due to the difficulty related to duplicate of their unique functions especially the colorimetric approach for authentication is of great interest as visible security features on banknotes, documents, etc. A library of materials, including lanthanides,[21-26] organic dyes,[27-29] conjugated polymer dots,[30] quantum dots,[31-35] carbon dots,[36-39] metal-organic frameworks (MOFs),[40-44] etc., have been explored with their respective technologies to serve the purpose. All the above-cited categories have some pros and cons[45] such as photo-stability, toxic nature, low emission property, emission at wide wavelength range, etc. which strictly obstruct their large scale industrial application.

On the other hand, luminescent systems, are considered as emerging tools for technological applications in various field as they broaden their application window switching between "non-fluorescent and fluorescent" upon excitation or in response to external stimuli like light, heat, pressure, solvent vapor etc.[46-51] These materials have innovative applications as security ink, confidential data storage/transfer.[52-54] Therefore, development of advanced alternative technique using simple, cost-effective approaches with good confidential information storage ability for security protection becomes a great challenge for research community. Therefore, design of smart active molecule appended with suitable functional groups, with specific features like security ink persists as a prime concern in this research area. Among various functional materials π-conjugated small molecular systems are emerging class of materials, that have used for various high-performance applications due to their unique features.[55] However, to the best of our knowledge, various systems available for anti-counterfeit application, a very few number of reports have been found on naphthalene diimide (NDI) based materials for invisible security ink based applications. Due to easy functionalization, fast stimuli-responsive property and cost-effectiveness made this small functional material an excellent candidate for this purpose. Therefore, in the present method a simple and advantageous approach have been introduced based on a π-conjugated system i.e. NDI to combat the counterfeit/forge phenomenon. Synthesized NDI derivative appended with isoniazid has been utilized for making ink with commercial low-cost polymer

[a] A. Kalita, N. S. Sarma
Physical Sciences Division
Institute of Advanced Study in Science and Technology, Paschim Boragaon, Guwahati-781035, Assam, India
E-mail: anamik.kalita01@gmail.com
[b] A. H. Malik
Department of Higher Education, Government Degree College, Sopore-193201, Jammu and Kashmir, India.

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poly(vinyl alcohol) (PVA) that displayed fluorescence switching behavior in response to HCl/NH_3 vapor under hand-held UV light. The content written on various substrates were hardly visible in the naked eye whereas clearly visible under UV light on exposure to external stimuli, which confirmed its possible application towards security purposes. To the best of our knowledge, this approach is an efficient example of a single π-conjugated system demonstrating such invisible to visible switching property. Finally to check its real-time application, a pen has also been successfully fabricated using the invisible ink developed here.

Results and Discussion

Synthesis of ISO_NDI (Figure 1a) involves a single step reaction using a previously reported procedure.[56] Product was characterized by standard techniques like ^{1}H-NMR, ^{13}C-NMR, HRMS etc. The detailed synthetic scheme and characterization spectra are presented in Scheme S1, Figure S1-S3 in the Supporting Information. Moreover, the high crystalline nature of the compound is characterized by powder XRD pattern (Figure S4 in the Supporting Information) as we are unable to grow good quality crystals for single crystal XRD analysis. Furthermore, the FT-IR (Figure S5 in the Supporting Information) analysis of ISO_NDI displayed major characteristic band at around 3492, 1692 for –NH, –C=O stretching and 1581, 1554 cm^{-1} for –NH bending vibrations. After a quick exposure(~40s) to HCl vapor, the –NH stretching band become broad and shifted to 3424 cm^{-1} along with the shift of –NH bending vibrations to 1587 and 1538 cm^{-1} indicate the protonation phenomenon.

To explore the optical property of ISO_NDI, its absorption and emission studies were conducted both in solution as well as in solid-state as shown in Figure 1b. The characteristic absorption peaks at 378nm, 359nm for 10^{-5} M solution in DMSO and 383nm, 362nm were obtained for solid film respectively. Similarly mirror image peaks were found for emission spectra also. It is clear from the emission spectra that in case of solution two characteristic peaks at λ_{max}=404nm, 435nm with low intensity were obtained for 10^{-5} M solution in DMSO. To investigate the solid-state fluorescence phenomenon of ISO_NDI, thin film of ISO_NDI was cast on a glass slide and dried to obtain a film which is non-fluorescent with negligible intensity to record. The observed solid-state emission spectra were recorded after exposure of the solid film for ~40s to HCl vapor, displayed characteristic peaks at 471, 483nm and 540nm.

Further expanding their applicability to solid-state optic related areas is fascinating and quite challenging. However, the prepared pristine ISO_NDI in the solid state generally suffer from self-quenching due to aggregated state or direct π−π interaction and hence results in insignificant fluorescence response. To avoid this phenomenon, dispersing ISO_NDI in the polymer matrix is considered as an efficient approach. Here, solid-state free standing films were prepared by dispersing ISO_NDI in PVA. PVA was preferred as polymer host matrix because of its unique features like high optical quality, desirable film forming properties, easy processing and application etc.[57] To confirm the practical feasibility of developed ink ISO_NDI-PVA, a simple detachable film was fabricated and examined, which could be a promising platform for many solid state device-based applications. Among various compositions (Figure S6 in the Supporting Information), the film was developed via mixing an optimized composition of ISO_NDI and PVA (7mg+5wt%) in DMSO solution (Figure 2a) under normal condition and drop

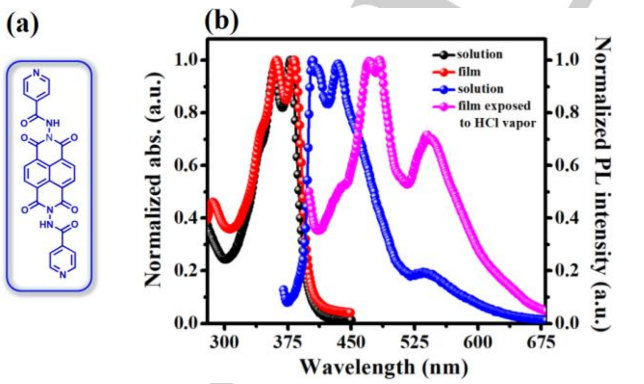

Figure 1. (a) Structure of synthesized molecule (ISO_NDI), (b) Absorption spectra of ISO_NDI in solution (10^{-5} M DMSO) (black line) and film (red line) and emission spectra of ISO_NDI in solution (10^{-5} M DMSO) (blue line) and film (pink line) after exposed to HCl vapour.

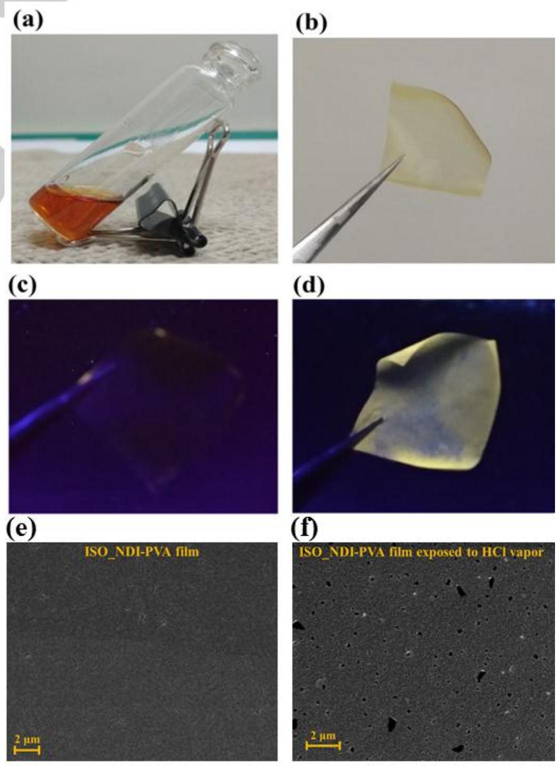

Figure 2. (a) Prepared ink solution of ISO_NDI-PVA (7mg+5 wt%), (b) Dried free film peeled off from glass slide under ambient light, (c) Film under UV 365nm, (d) Film after exposed to HCl vapor under UV 365nm, (e) FESEM image of pristine ISO_NDI-PVA film, (f) FESEM image of ISO_NDI-PVA film exposed to HCl vapor.

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cast over cleaned glass slide of desired size. After ensuing drying, the free film (Figure 2b) was peeled off from the glass slide which is non-fluorescent under UV light (Figure 2c). The free-standing film was showing fluorescence turn-on behavior under UV lamp upon brief exposure to HCl vapor for ~40s as shown in Figure 2d. The morphologies of ISO_NDI-PVA film and its acid exposed film were studied by FESEM analysis which clearly shows distinct change in both the films. The surface of pristine ISO_NDI-PVA film (Figure 2e) shows the presence of homogeneous interconnected network structure which leads to the formation of clear voids after exposed to HCl vapors (Figure 2f).

In order to explore the above property of the material and to test its practical application on various substrates (such as Glass, Whatman Filter paper, Silica Plate, Plastics (PET) etc.), we have manually written the alphabet "A" by utilizing a DMSO solution of ISO_NDI-PVA using a double head cotton earbud (Figure S7 in the Supporting Information). After drying the substrates, the alphabet "A" is not visible under ambient light (Figure 3a, 3d, 3g, 3j) and become non-fluorescent under UV 365nm (Figure 3b, 3e, 3h, 3k). Upon fuming with HCl vapor, this non-fluorescent "A" instantly transformed into yellowish fluorescent "A" under UV 365nm (Figure 3c, 3f, 3i, 3l).

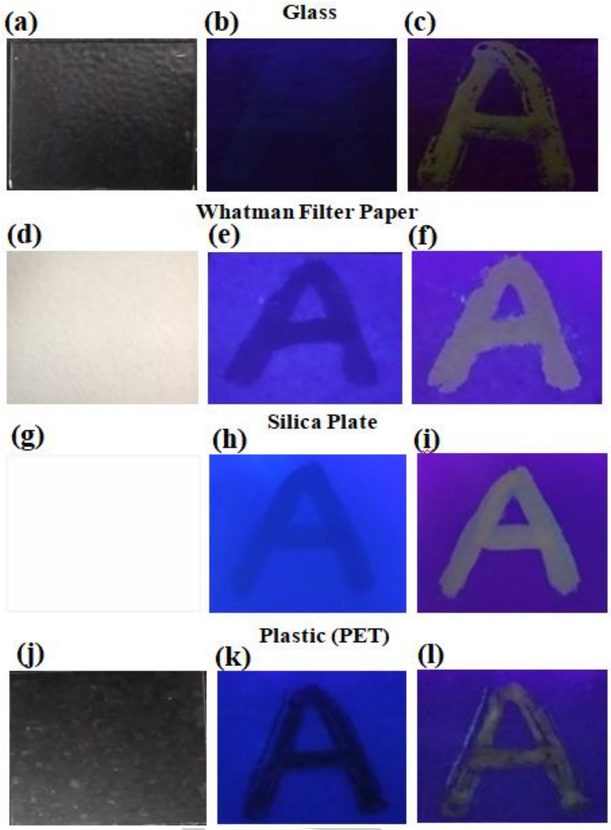

Figure 3. Alphabet "A" written using ISO_NDI-PVA ink solution on various substrate (such as Glass, Whatman Filter paper, Silica Plate, Plastics (PET) etc.) under ambient light (a), (d), (g), (j); non fluorescent alphabet "A" under UV 365nm (b), (e), (h), (k); yellowish fluorescent alphabet "A" upon exposure to HCl vapor observed under UV 365nm (c), (f), (i), (l).

The compatibility property of ISO_NDI-PVA as invisible ink on various paper materials such as Newspaper, Tissue paper, Whatman filter paper, Colored paper, Register copy paper collected from various sources of IASST which are mostly non fluorescent in nature was further explore by writing the short form of our institute name i.e. "Institute of Advanced Study in Science and Technology" (IASST). IASST is written on these paper materials by using the developed ink with the help of a microtip and then air-dried to check its feasibility. Under ambient light, the word "IASST" written on different paper materials is not visible, as shown in Figure 4a, 4d, 4g, 4j, 4m. Under UV 365nm the word "IASST" written on all the paper material is non-fluorescent (Figure 4b, 4e, 4h, 4k, 4n). The transformation of non-fluorescent to yellowish fluorescent "IASST" was observed on exposing the paper with HCl vapor for a very short time (~40s) under UV 365nm (Figure 4c, 4f, 4i, 4l, 4o). The paper materials were found to be in quite fine state without any damage by fuming HCl vapor.

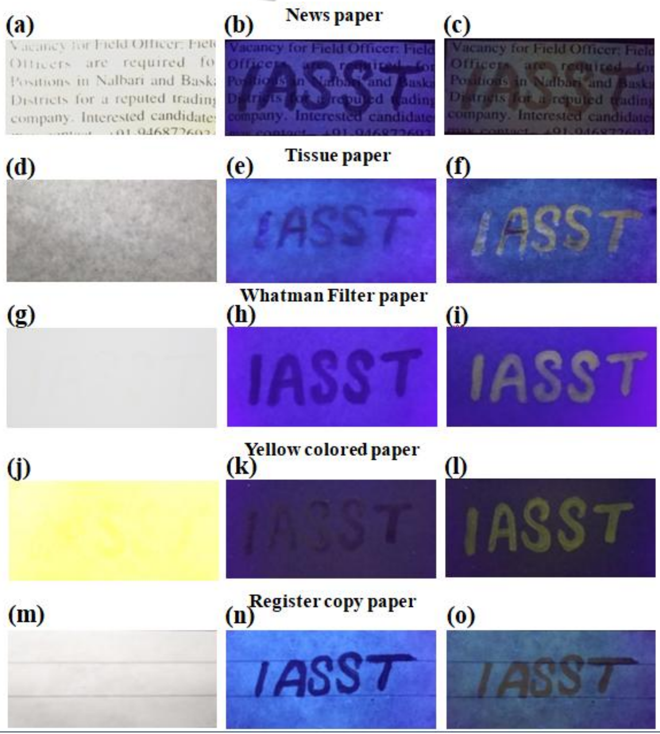

Figure 4. "IASST" written on Newspaper, Tissue paper, Whatman filter paper, Yellow-colored paper, Register copy paper observed under ambient light (a), (d), (g), (j), (m), Non fluorescent "IASST" observed under UV 365nm on different paper material (b), (e), (h), (k), (n); yellowish fluorescent "IASST" under UV 365nm on exposure to HCl vapor (c), (f), (i), (l), (o).

Similarly, a pen (Figure 5a) with ISO_NDI invisible ink was developed to make complicated patterns like butterfly on currency note to check its practicability. A butterfly was drawn on a ten-rupee currency note which is invisible under ambient light as shown in Figure 5b. When observed under UV light (365nm) the butterfly become non-fluorescent (Figure 5c). On exposure

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of the currency note with HCl vapor, the non-fluorescent butterfly immediately transformed into yellowish fluorescent one and is visible under UV 365nm as shown in Figure 5d. The zoomed view of the butterfly made on the currency note is shown in Figure 5e.

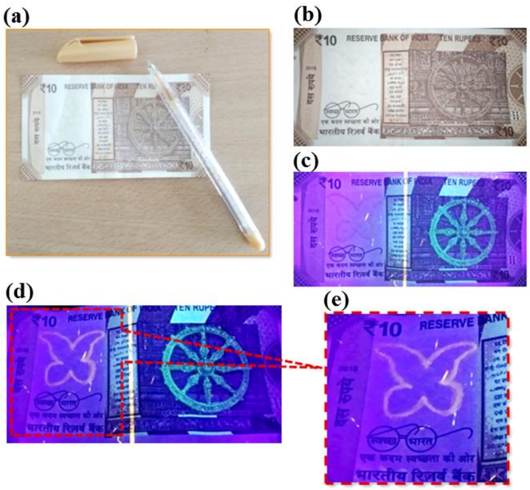


Figure 5. (a) Photograph of developed pen with ISO_NDI invisible ink. (b) A butterfly drawn on a ten-rupee currency note observed under ambientlight, (c) non fluorescent butterfly on ten-rupee currency note observed under UV light (365nm), (d) yellowish fluorescent butterfly on ten-rupee currency note observed under UV light (365nm) upon exposure to HCl vapor, (e) zoomed view of fluorescent butterfly.

Furthermore, this developed pen can be useful for writing a few long sentences on paper material (Figure S8 in the Supporting Information). Similar acid response was observed under UV light for this complicated sample patterns also.

To assess the performance of materials, reversibility and

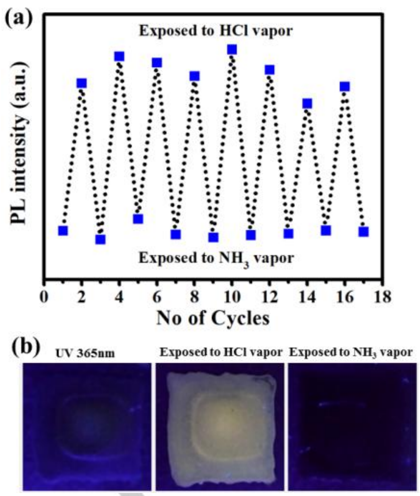
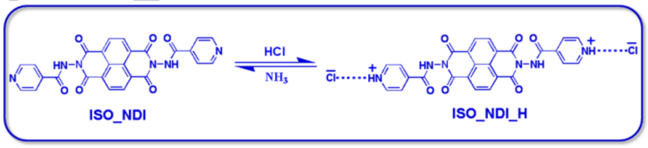


Figure 6. (a) Reversible on-off fluorescence switching property of ISO_NDI-PVA film upon exposure of HCl and NH_3 vapors, (b) Images of ISO_NDI-PVA film under UV 356nm, exposed to HCl vapor and NH_3 vapor.

repeatability are important parameters. The fluorescence switching phenomenon displayed by the ISO_NDI-PVA film upon exposure to saturated HCl (40s) and NH_3 (20s) vapor was found to be highly reversible and repeatable. The fluorescence spectra of ISO_NDI-PVA film were recorded with or without exposure to HCl vapor (Figure S9 in the Supporting Information). Furthermore, good reversibility of ISO_NDI-PVA film was observed upon alternate exposure of HCl/NH_3 vapors even after multiple cycles (Figure 6a), and the corresponding fluorescence color changes observed in film is shown in Figure 6b.

Similarly, the synthesized powder sample was also found to be non-fluorescent under UV light which transformed to yellowish fluorescence upon exposure of HCl vapors (Figure S10 in the Supporting Information).

As shown in Scheme 1, the proposed mechanism could be between ISO_NDI and vapor of HCl was most likely via the protonation at the nitrogen of pyridine ring of isoniazid unit that ultimately leads to the fluorescence switch on, while an instant fluorescence switch off behavior resulted from the exposure of NH_3 vapors is obtained via deprotonation mechanism.



Scheme 1. Proposed mechanism of on-off fluorescence switching in response to HCl and NH_3 vapors.

To further gain insight into the probable mechanism of solid state fluorescence switching behavior toward acid vapors, theoretical calculations were performed for both ISO_NDI and its corresponding protonated form ISO_NDI_H using time-dependent density functional theory (TD-DFT) with B3LYP/6-31G hybrid basic set incorporated in the Gaussian 09 program. As shown in Figure 7, the optimized geometry and HOMO/LUMO energy levels along with the electronic distribution over HOMO and LUMO for both ISO_NDI and ISO_NDI_H displayed exceedingly distinct structural conformations as well as electronic properties. The optimized geometry of ISO_NDI (Figure 7a) is found to undergo trans conformation with the pyridine rings of isoniazid pendent groups remain trans to each other to acquire a relaxed geometry, whereas the protonated form ISO_NDI_H undergo cis conformation. It is important to note that the electron density over HOMO of ISO_NDI as shown in Figure 7b, is mainly concentrated on one side of pyridine ring of isoniazid (donor moiety), whereas the electron density over LUMO is found only on the naphthalene core (accepter moiety). The complete charge separation between the donor and acceptor moieties confirms the presence of strong ICT process in ISO_NDI that could be the key reason for its non-fluorescent behavior.[58] In contrast to ISO_NDI, electron density over HOMO of the protonated form of ISO_NDI is distributed all over the molecule, while the electron density over LUMO is concentrated within both the pyridine ring of isoniazid moiety

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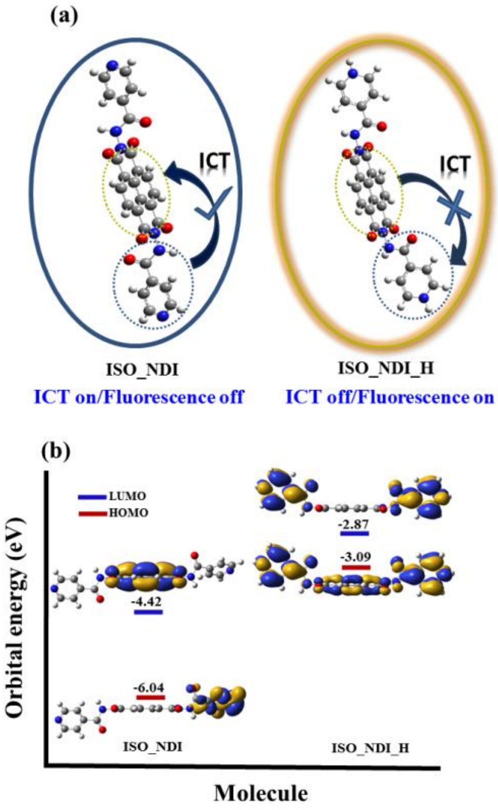

Figure 7. Optimized molecular geometries of ISO_NDI and ISO_NDI_H along with the electron distribution over HOMO and LUMO.

that give rise to the significant overlapping in the electron density over HOMO and LUMO. The comparative analysis of electronic distribution in ISO_NDI and its protonated form, we anticipated that the fluorescence turn-on response after protonation is mainly attributed due to the structural changes that restrict the ICT process[59] in ISO_NDI_H. Moreover, in agreement with the theoretical prediction, the significant oscillator strength (f=0.0471) found in ISO_NDI_H as compared to that of ISO_NDI (f=0.0000) also supports the fluorescence turn-on state after protonation.[60]

Conclusions

In brief, we have developed a simple, cost-effective platform which will help understand the erasable and rewritable feature based on solid state fluorescence switching properties of isoniazid functionalized naphthalene diimide probe (ISO_NDI) in response to external stimuli viz. acid/base vapors which will surely open up a potential avenue for security-based applications. The easy mixing of optimized concentration of ISO_NDI and commercial polymer PVA afforded an ink (ISO_NDI-PVA) with invisible property under ambient light. The ink is found to be highly substrate compatible ranging from glass, plastics, different paper materials etc. Upon instant contact with HCl vapor, this invisible property disappears and a yellowish fluorescence is recovered under a hand-held UV lamp (365nm). Moreover this solid-state fluorescence modulating behaviour of the ink is found to be reversible with multiple on/off cycles. This invisible to visible transformation of the developed platform is attributed due to protonation-deprotonation under the occurrence of conformational changes governed by ICT phenomenon. Hence this invisible to visible switching property of the ink made the approach an efficient one for advancement of the developed platform towards the areas like security, confidential data transfer/storage etc.

Experimental Section

Materials and Instrumentations

1,4,5,8-Naphthalenecarboxylic dianhydride (Sigma-Aldrich), Isoniazid (Alfa-Aeser), PVA (Mw=60000, Merck), DMF (Sigma-Aldrich), DMSO (Merck), HCl (35%; Merck), Ammonia (25%; Merck) were purchased and used as received. All other reagents were of analytical grade and used without further purification or treatment. Water used in this work was acquired from a Milli-Q system. Microscopic glass slides, Plastic (PET), double head earbud, flair glitter pen were purchased from local vendor. Silica Plate and Whatman filter paper were received from Merck. Variety of paper materials were collected from IASST-Guwahati. ^{1}H and ^{13}C spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer. FT-IR spectra were obtained from a Perkin Elmer, Spectrum two-102083 spectrophotometer. Mass spectrometric data were obtained by using THERMO 3000 Exactive Plus Orbitrap Mass Spectrometer. Fluorescence spectra were measured on a Jasco spectrofluorometer FP-8300. PXRD pattern was cottected on an XRD D8 Advance Bruker instrument. Scanning electron microscope (SEM) images were recorded on a Carl Zeiss Σigma VP instrument. Theoretical calculations were performed by using Gaussian 09 package with B3LYP hybrid functional and a 6-31G basis set. All the photographs were taken by using Nikon Coolpix digital camera.

Synthesis of ISO_NDI

The isoniazid functionalized naphthalene diimide (ISO_NDI) is synthesized using a single step reported procedure with modification (Scheme S1 in the Supporting Information). 1,4,5,8-Naphthalenetetracarboxylic dianhydride (500 mg, 1.86 mmol), isoniazid (509 mg, 3.72 mmol) was taken in a 50 ml round-bottom flask equipped with a magnetic stir bar. 8 ml of DMF was added to it as solvent. The reaction mixture was then heated at 100 °C for overnight with continuous stirring. After completion of reaction, the mixture was allowed to cool, dried under vacuum to obtain the product as bridge colour solid. ISO_NDI: Yield: (0.66g, 70%), ^{1}H-NMR (300 MHz, DMSO-d_6): δ 7.92 (d, 4H), 8.83 (s, 4H), 8.87 (d, 4H), 11.95 (s, 2H) ppm. ^{13}C-NMR (75 MHz, DMSO-d_6): δ 121.89, 126.76, 126.92, 131.99, 138.67, 151.07, 161.02, 164.41 ppm. HRMS: m/z calcd. for $C_{26}H_{14}N_6O_6$ (M+H)$^+$: 507.105, found: 507.103. FT-IR (cm^{-1}): 3492, 3194, 2954, 2834, 1954, 1728, 1692, 1580, 1554, 1444, 1412, 1360, 1296, 1198, 1131, 983, 912, 845, 756, 689, 579.

Preparation of ISO_NDI-PVA

To make an optimal solution of PVA, 1-10% of PVA was dissolved in DMSO with stirring to obtain a clear solution with different viscosity from low to high. We consider the 5% PVA solution to be optimized for making

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desired invisible ink with synthesized probe. The different amount of ISO_NDI (2mg, 5mg, 7mg, 10mg, and 12mg) was mixed separately to the above 5% PVA solution to obtain the desired invisible ink.

Procedure for fabricating pen

A flair glitter pen was purchased from a local vendor and removed the glitter ink from the refill and cleaned. Then the optimized concentration of 7mg+5wt% PVA ISO_NDI ink was inserted into the refill for application on different paper materials.

Writing procedure on different materials

For different substrates like glass, filter paper, plastic, silica plate, double-headed earbud was dipped into the prepared ink solution and write alphabet "A" on it, kept for air dry and used for its response towards acid-base vapors under UV chamber. Similarly for writing on various paper materials including currency notes, desired word or characters were made by using pen, air-dried and used as above.

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Keywords: invisible ink • naphthalene diimide • vapor exposure • fluorescence • anti-counterfeit

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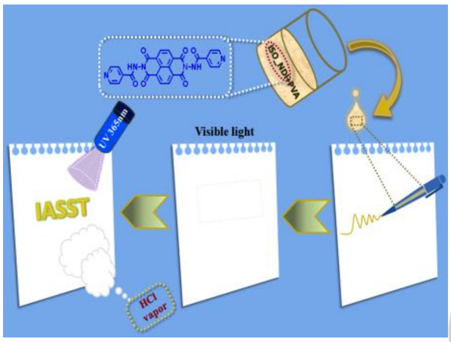
An efficient approach to combat counterfeiting along with detection and storage of manifold confidential information based on fluorescence switching behavior of stimuli responsive isoniazid functionalized naphthalene diimide (ISO_NDI) is demonstrated.



Anamika Kalita, Akhtar Hussain Malik, Neelotpal Sen Sarma*

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