

Combined Experimental and Theoretical Studies on the Rubbing-Induced Fluorescence Behavior of a Luminophore in the Solid State

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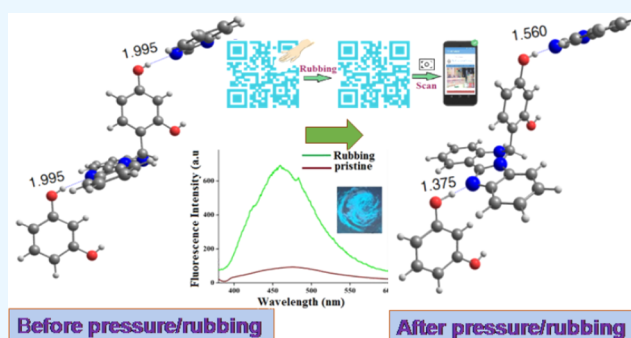


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Supporting Information

ABSTRACT: It is intricate to break and make chemical bonds in solid states compared to their solution states, so it is imperative to ascertain green proficient approaches by regulating the solid-state structures and their related material properties. Here, the rubbing-induced photoluminescence behavior of a luminophore (RIL) of the benzimidazole family in the solid state has been accomplished. Interestingly, upon gentle rubbing or mere scratching, solid-state fluorescence from the nonemissive pristine RIL was observed due to the aggregation-induced emission (AIE) phenomenon in the solid state, for which the phenolic moiety is present in the molecule and is accountable. The structure–property relationship of RIL and the mechanism responsible for this solid-state fluorescence characteristics have been explained with the help of experimental (using the single-crystal structure, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM) images, etc.) and theoretical (by DFT and TDDFT) studies. The crystal arrangements with different stacking interactions and the SEM images after being rubbed revealed that the mechanical force- or pressure-induced slight deformation in the crystal arrangement notably facilitated the strong emission in the solid state. This rubbing-induced solid-state fluorescence in a new luminophore (RIL) through stacking of layers restricting the molecular motion has been developed here for the first time, and it can be explicitly employed in steganography techniques for data security. This present study will open up a new insight into the use of this RIL as a solid-state smart material for data security in coding devices in the future, and this developed approach may be helpful to ameliorate the design of new-generation smart materials by modifying the structure to attain other characteristics.



INTRODUCTION

Data security is of supreme importance in the world of spying at this moment, and it will become much more significant as the future is bright for globalization and global collaboration.¹ We have seen numerous interesting techniques over the ages to hide the inherent messages from enemies, such as invisible inks which become visible upon heating, light exposure, and application of chemical solutions, and so forth.² Plant extracts were used by the Roman author Pliny the Elder and others to make it invisible.³ However, nowadays, these are mostly used for fun among children, as these tricks have become so popular among folks and can easily be decoded. Nevertheless, the knowledge of these past practices makes us smarter and lays the foundation stone for modern-day data security measures.⁴ The day-to-day use of QR codes or barcodes for transactions and shopping is the result of the steganography technique of hiding secrets under the cover of a meaningless file or message.⁵ This, when coupled with encryption, that is, conversion into a cipher, makes data security robust which can only be accessed by the receiver if he knows the decipher route.⁶ The scientists working in the field of chemistry are also

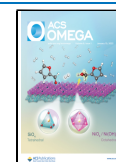
working with tremendous interest to make data secure by designing and preparing some chemical compounds which will respond to some specific mechanical and chemical stimuli.⁷ The most exciting and accurate among all other available techniques is the use of solid-state fluorescent sensors, which can be used to conceal hidden messages. This can be achieved by mechanochromic, photochromic, and thermochromic fluorescent compounds.^{8–10} Upon external stimuli (pressure, temperature, and heat), these compounds respond swiftly by turn off/on fluorescence. The mechanism of action mostly depends on the coherent aggregation of molecules or losing coherency.

For the development of new-generation smart materials, changes in solid-state molecular properties caused by external

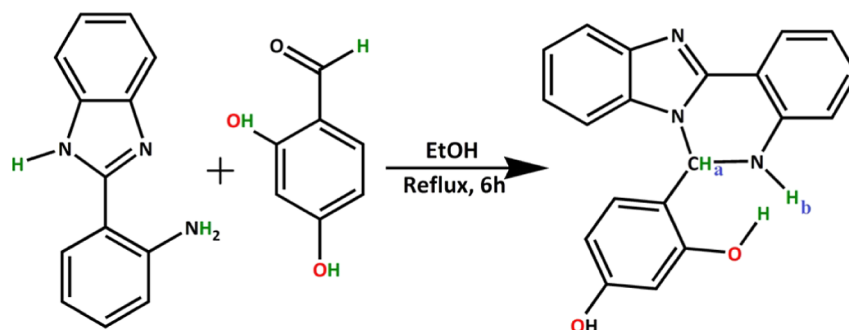
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Scheme 1. Synthetic Route of RIL



stimuli are crucially significant.^{11–16} To fulfill this requirement, a number of external stimuli-responsive materials have been reported using heat, magnetic field, light, pressure, and mechanical forces,^{17–26} although most of these processes are too sluggish and imperfect in fostering their applications as materials. To date, a probe with solid-state fluorescence due to intermolecular proton transfer after rubbing with rubber has been reported.²⁷ Interestingly, our probe RIL has no need for any external materials like rubber to show rubbing-induced photoluminescence in the solid state. This observation can be achieved by a simple touch. The superior photoluminescence enhancement behavior in this system can be efficiently utilized to picturize visually and quantify the overall stimuli-responsive process.

To establish the aggregation-induced emission (AIE) phenomenon in the solid state due to the presence of a phenolic moiety in RIL having a strained ring system, a previously reported organic moiety PS2²⁸ has been taken for comparison. The phenolic moiety present in the molecule perpendicular to the rest of the molecule in RIL is indispensable and responsible for the AIE phenomenon. Additionally, this group has an amazing role in observing the nonemissive property in the solid state because of the absence of remarkable π – π stacking among the molecules. Moreover, weak intermolecular interactions, including the C–H \cdots N interaction and other interactions with solvent molecules, play a crucial role in the stability of the compound in the solid state. Thus, the stability and flexibility may be perturbed by external stimuli, and subsequently the slight deformation in the crystal arrangements leads to solid-state fluorescence.

In this work, we have observed the enhancement of solid-state fluorescence of the benzimidazole-based Schiff base (RIL) by gently rubbing or merely scratching on the solid surface.^{27,29} Upon gentle rubbing, the compound attains a particular arrangement of the layered structure, which facilitates the radiative decay of energy and is responsible for the observed turn-on fluorescence (bluish-green color) under 365 nm UV light. While heating the substance, fluorescence turn-off occurs, and the fluorescence again turns on after cooling to room temperature. Thus, the compound (RIL) has three degrees of fluorescence responses to external stimuli, and RIL can be a good candidate for storing encrypted codes. This overall phenomenon has been reported for the first time in literature and can become a good option in the future for data security.

EXPERIMENTAL SECTION

Sample Preparation for UV–Vis and Fluorescence Spectroscopic Studies. To know the characteristic spectra of

RIL, different solvents such as MeOH, DMF, DCM, and THF were used for the UV–Vis and fluorescence studies. A stock solution of RIL was prepared in tetrahydrofuran (THF) solution and used for UV–Vis and fluorescence measurements to observe the aggregation-induced emission (AIE) properties of RIL. The room temperature during the measurements of all the spectroscopic data was 27 °C. UV–Vis absorption spectra and fluorescence emission spectra of the samples were taken using a Shimadzu-2450 UV–Vis spectrophotometer and a Hitachi-7000 spectrofluorimeter, respectively, in a 10 mm path length cuvette. To study the rubbing-induced fluorescence signature properties of RIL in the solid state, a mortar and pestle has been used for visual fluorescence color change under a 365 nm UV lamp during the rubbing process. To showcase an application of information encryption, black paper and a ball pen with no ink were used to make a film of a nonfluorescent material.

Computational Details. A density functional theory (DFT) study is carried out to understand the electronic structure of the RIL. The geometry optimization of the investigated compound (RIL) is carried out using the density functional theory method at the CAM-B3LYP level with the split-valence 6-31 + G(d,p) basis set applied using the Gaussian 09 program package.³⁰ The starting coordinates for the DFT calculations were obtained from the single crystal structure of RIL. The TDDFT calculations have been performed for 60 states.

RESULTS AND DISCUSSION

Synthesis and Characterization: A benzimidazole-based RIL was synthesized following a literature procedure with a slight modification^{28,31–33} (details in the [Supporting Information](#)). The probe was characterized by NMR ([Figures S1 and S2](#)), ESI-MS ([Figure S3](#)), IR ([Figure S4](#)), and finally single-crystal X-ray diffraction ([Figure S5](#)) for detailed structural analyses. The peak at 7.23 ppm for the N–H_b proton and 6.37 ppm for the proton H_a validated the cyclization process instead of the Schiff base formation under the same reaction conditions ([Scheme 1](#)). On the other hand, no singlet peak at 8.5–9 ppm for the –N=C–H azomethine functional group was observed. The single-crystal X-ray diffraction also confirmed that no Schiff base formation is happening; rather, it is a nonplanar ring compound due to the existence of an sp³ carbon. Additionally, for comparison, PS2 was synthesized as a reference compound ([Figure S5](#)).²⁸

AIE Properties of RIL. The title compound, RIL, exhibits high stability under ambient conditions. In diluted solutions in THF, RIL showed blue emission, but upon incremental volume percentages of water as a poor solvent in THF

solutions, the red-shifted emission was noticed. From structural features and this spectral behavior, it is anticipated that RIL could be able to show AIE properties due to the probability of stacking interactions. Here, the aggregation-induced emission initiated by the H-bonding hinders the intramolecular rotation. After 70% water in THF, quenching of fluorescence takes place (Figure 1), which is also consistent

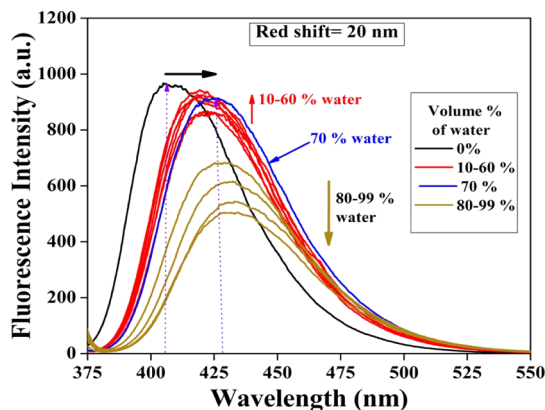


Figure 1. Aggregation-induced properties of RIL in the THF/H₂O medium, 10–60% water (red region: incremental addition of water at 10, 20, 30, 40, 50, and 60%), and 80–99% water (yellow region: 80, 85, 90, and 99%).

with the absorption profiles of RIL in the THF/H₂O medium (Figure S6). From these spectral phenomena, it is articulated that here, the red shifting³⁴ (20 nm Stokes shift) is in agreement with the J-type aggregation toward AIE property^{35,36} and the optimum level of aggregation with a higher emission intensity in solution betides at 70% water fraction.

Solid-State Fluorescence of RIL. The pristine powder of RIL obtained from MeOH/DMF mixtures by slow evaporation was nonemissive. In general, AIE active compounds often show strong fluorescence in the aggregated state or solid state. However, an intriguing, unusual phenomenon appeared in the present case. Astoundingly, when the pristine powder of RIL was gently scratched using a spatula or gently rubbed by a finger, bright cyan-blue fluorescence was immediately observed under a 365 nm UV light (Figure 2 and video1).

Powder X-ray Diffraction. Interestingly, when these nonemissive RIL crystals obtained from the DMF medium

were gently rubbed/scratched by any means (fingers/glass rod) at 27 °C (room temperature), the title compound became luminescent (Figure S9 and video 1). Such a remarkable phenomenon obligated us to make a detailed analysis of its pristine powder and its powder after rubbing through the powder X-ray diffraction (PXRD) technique (Figure 3).

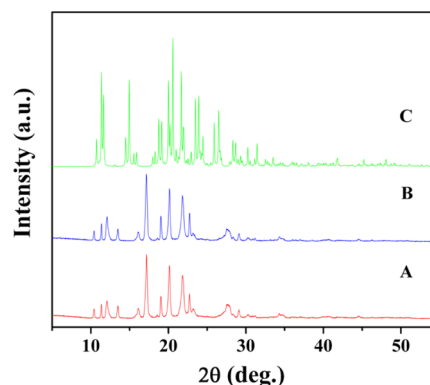


Figure 3. PXRD patterns of RIL (A) before and (B) after rubbing and (C) simulated from the crystal structure.

From the figure, it can be easily observed that after rubbing, the peaks become sharper and more intense without any shift and tend to attain a pattern comparable to that of crystal structure.²⁹ Thus, the results signify that mechanical forces facilitate the crystallization of the RIL powder. The visual morphological changes due to the solid-state fluorescence behavior were recorded by acquiring photographs of the microcrystals of RIL produced through gentle rubbing of its powder/crystals obtained from the DMF medium at 27 °C (room temperature) (Figure S9). The RIL with the DMF structure is similar to the DMSO solvate reported earlier³⁷ but shows different behavior, especially in the solid state. This observation led us to study and explore the behavior of RIL as a solid-state luminophore.

Stacking Arrangement in RIL with Distance. To authenticate the crystal packing of RIL in favor of the AIE characteristic phenomenon, the detailed structural analysis of RIL was studied by single crystal X-ray diffraction, and the structural features of RIL were compared with those of its homologue, PS2 (previously reported by our group).²⁸ The

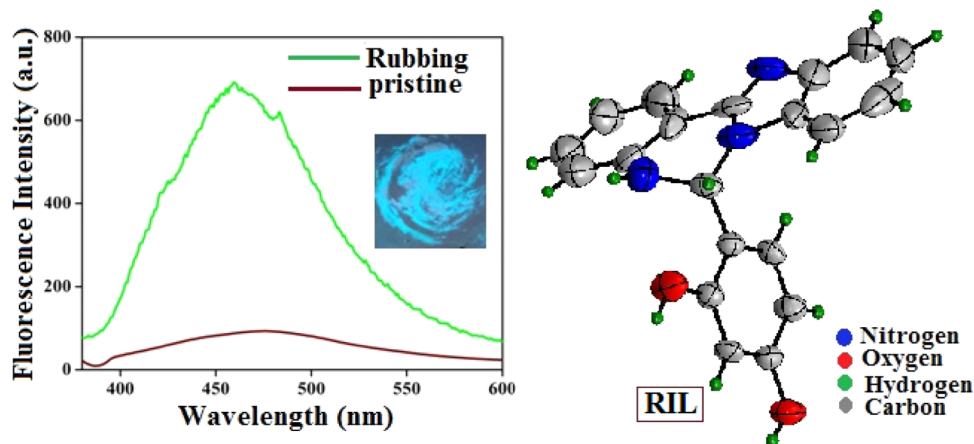


Figure 2. Solid-state fluorescence of RIL after rubbing (left side), and the structure of RIL (right side).

single-crystal X-ray diffraction studies of RIL and PS2 clearly demonstrate the different molecular arrangements in their pristine forms. In the crystals of RIL, molecules form effective H-type arrangements. The phenyl group perpendicular to the rest of the molecule results in increased steric hindrance between two adjacent molecules (10.016 Å), which is greatly responsible for the nonemissive nature of RIL in the solid state (Figures 4, S10, S11). However, the distance between the central benzene planes of molecules and the adjacent molecule is 4.364 Å, which is greater than the H-bonding range (Figure 4).

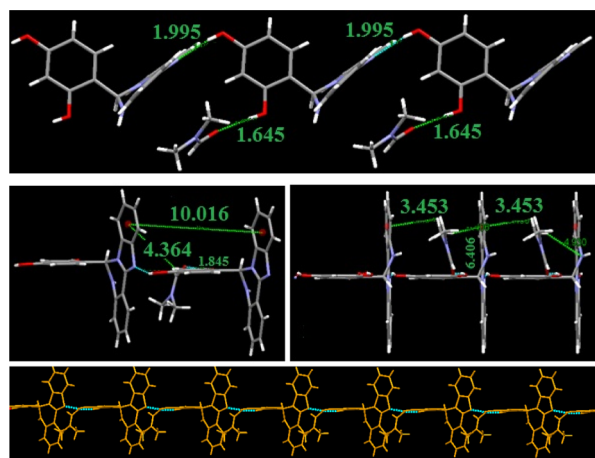


Figure 4. Different types of stacking arrangements of RIL, including distances.

Nevertheless, it could hamper strong intermolecular π - π interactions, leading to the quenching of fluorescence in the solid state.³⁸ However, the presence of one -OH group (para) in the central phenyl plays a decisive role in the building of the chain structure in the solid state. However, the remaining ortho -OH group interacts with solvent molecules (DMF). Contrarily, in the crystals of PS2, molecules stack up in an ordered arrangement with a zig-zag-like shape (Figure S12). The interplanar spacing among the molecules is enough for π - π interactions to observe the fluorescence in the solid and aggregate states.

Scanning Electron Microscopy and Optical Fluorescence Microscopy Images of RIL. Accordingly, to understand the morphological change of RIL, we have captured the scanning electron microscopy (SEM) images and investigated carefully the changes before and after gentle rubbing or mere scratching. The figures (Figure S7) easily indicate that the morphological features of RIL before and after external stimuli (rubbing/scratching) are quite different to ascertain the solid-state emission due to AIE (viz. Figure S7A–7C). Furthermore, in MeOH solvent, RIL showed different solid-state fluorescence colors, that is, large-sized crystalline particles of RIL showed a bluish color, whereas small-sized particles showed a cyan-blue color. This observation also supports the idea that the formation of microcrystals is responsible for cyan-blue emission in the solid state (Figure S8, right side).

Theoretical Study. To find the probable reason behind the above incident, density functional theory (DFT) and time-dependent density functional theory (TDDFT)³⁰ calculations based on the crystal structure of RIL were also explored (Figure 5). The results show that the intensity of the $S_1 \rightarrow S_0$ transition of the crystal is extremely small ($f = 0.001$). Thus, the initial crystal state of compound RIL is nonemissive. To make the situation more realistic, we have chosen a trimer of the molecule in a special way, as shown in Figure 5, and the full structure of the said molecule was selected as the middle layer along with two truncated molecules, one in the upper layer and another in the lower layer. Now, to search the excited state, we have kept the upper and lower layers fixed, while the middle layer containing the full structure was allowed to move without any constraints. Although the emission spectra of the optimized trimer show the $S_1 \rightarrow S_0$ emission ca.562 nm with low intensity ($f = 0.0004$), a strong emission peak ($f = 0.1751$) from $S_3 \rightarrow S_0$ has been observed at 410 nm (Figure 6A), which is in good agreement with the experimental results at 458 nm. FMOs of the trimer are shown in Figure 6B. The results (Table S2) show that this strong peak may be assigned to the transition from HOMO-1 to LUMO (99%). Further analysis of the FMOs shows that HOMO-1 is located on the π -orbital of the phenolic ring of layer three, while the LUMO is located at π^* orbital of the benzimidazole ring of layer 2 (Figure 6B). Thus, it may be concluded that due to the rubbing of the RIL molecule, a particular orientation is reached where the

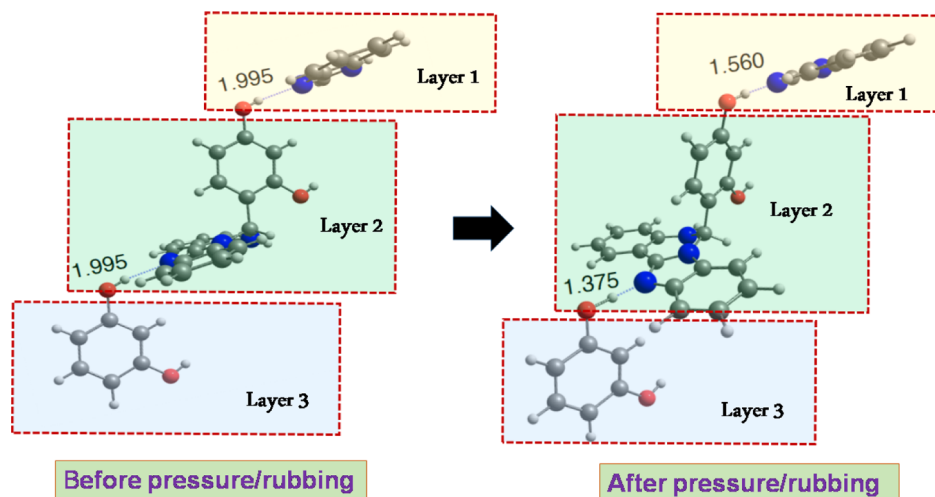


Figure 5. Optimized structure of the first excited state S_1 of the trimer of the compound RIL calculated at the CAM-B3LYP/6-31 + G(d,p) level.

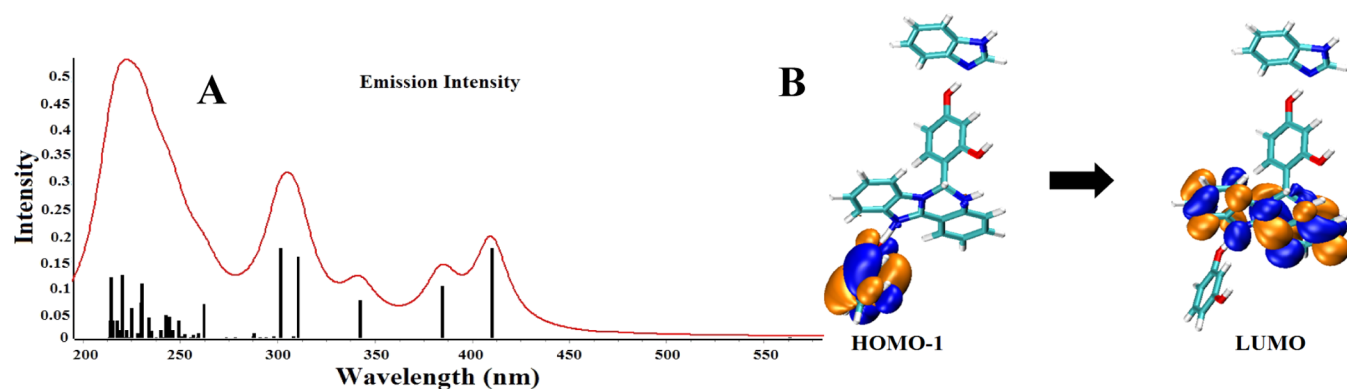


Figure 6. (A) Emission spectra of RIL in a trimeric form calculated at the CAM-B3LYP/6-31 + G(d,p) level and (B) Corresponding FMOs orbital for transition.

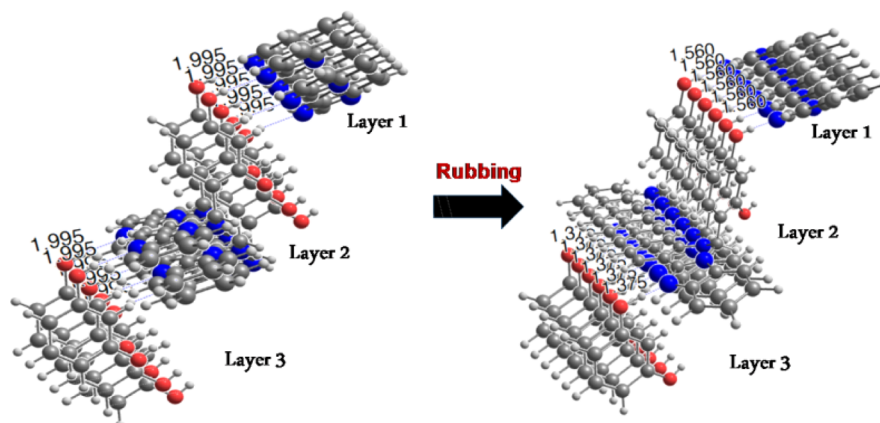


Figure 7. Mechanism to observe rubbing-induced photoluminescence of RIL.

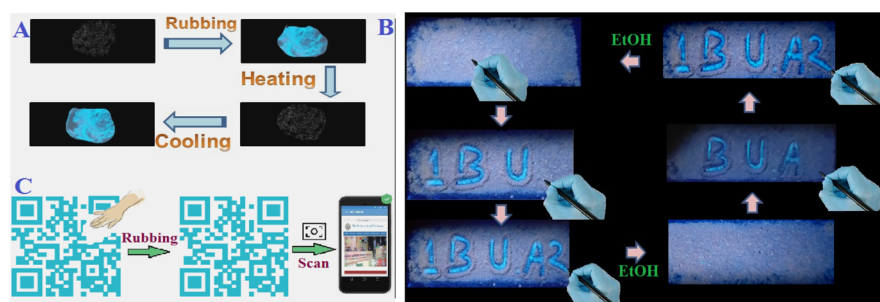


Figure 8. Photographs of RIL (A) before and after rubbing and the heating and cooling effect on the solid (under a 365 nm UV light); (B) during writing on the solid surface block of RIL using a ball pen having no ink; and (C) photographs of a QR code printed using RIL to showcase an application of information encryption.

transition from one layer to another layer becomes more feasible.

Mechanism of Solid-State Fluorescence in RIL. A short video in support of our claim is also supplemented, in which it can be seen that just rubbing with the thumb makes the compound fluorescent. We have also measured the melting point of both the pristine form (m.p. 186 ± 2)°C and the scratched/rubbed form (m.p. 197 ± 2)°C of RIL, which demonstrated the special favorable arrangement of RIL after rubbing (Figure S13), which has also increased melting point. It is also noteworthy to mention that the solid-state fluorescence was observed by gentle rubbing with a spatula on the solid surface of RIL under 365 nm (Figure S14).

From the experimental and theoretical studies, it is reflected that ring-opening of RIL is not taking place by external forces

for promoting the excited state intramolecular proton transfer (ESIPT) to increase the conjugation, but by rubbing/mere scratching, a particular fluorescence facilitating layered structure of the pristine RIL was attained (Figures 5 and 7). Consequently, the fluorescence intensity increases in the solid state of RIL by applying pressure, scratching, grinding, or gentle rubbing without assistance from any metal ions. On the other hand, the analogous compound, PS2, does not behave like RIL. However, there is no chance for generation of fluorescence by rubbing/scratching of the pristine PS2, which showed solid-state fluorescence without any mere scratching/gentle rubbing (Figure S9) as the molecular arrangement of PS2 pristine crystals is already favorable for fluorescence (viz Figure S12).

Thermochromism. Here, the compound (RIL) in an ordered state after rubbing was made disordered by applying heat (giving energy to the system). It was found that the rubbed solid became nonfluorescent after heating at 100 °C, and surprisingly, it regained its lost fluorescence after cooling to room temperature (Figure 8A). This inferred that it reaches a particular arrangement in the packing of RIL in rubbed/scratched solid state favorable for ACQ by applying heat making nonfluorescent RIL. This heat-induced transformation of fluorescence was restored after cooling to room temperature (27 °C) due to AIE. This phenomenon is due to the attainment of the original structure from the fluorescence facilitating a layered structure.

Application of RIL. To examine the utility of this compound, the slurry of RIL in ethanol was poured on black paper, followed by evaporation to make a film of a nonfluorescent material, and then, on this film, we could successfully write letters/words by pressing using a ball pen having no ink (Figure 8B). Interestingly, these written letters/words disappeared when we dispensed the solvent (ethanol) on the film, and again, we can write by pressing. This reversibility of ON-OFF-ON fluorescence characteristics of RIL could be useful as a nonfluorescent material to decode the hidden information in solid-state devices, as shown in Figure 8C.

CONCLUSIONS

Conclusively, through this account, we have studied and demonstrated a simple benzimidazole-based Schiff base having solid-state emissive properties upon external stimuli like mechanical force/pressure. The rubbing-induced aggregation phenomenon is proven by SEM, optical microscopy, XRD, and PXRD studies. The solid-state fluorescence turn-on switching by rubbing the pristine powder as well as off-on fluorescence switching upon heating and cooling to room temperature (27 °C) has been reported. This RIL can be utilized in the future in solid-state coding devices, smart sensors, rewritable media, and so forth. Thus, promising RIL has significant contribution to develop as a new-generation smart material.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c04803>.

Experimental studies, safety procedures, and NMR and mass spectra, together with detailed experiments (PDF)

Crystallographic data for RIL compounds deposited in the Cambridge Crystallographic Data Centre under CCDC no. 2128391 (CIF)

Solid-state fluorescence of RIL after rubbing (MP4)

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Notes

The authors declare no competing financial interest.

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