**Tunable solid-state emitters based on benzimidazole derivatives: aggregation induced red emission and mechanochromism of D-*π*-A fluorophore**

Ema Horak\*, Marko Robić, Aleksandra Šimanović, Vilko Mandić, Robert Vianello, Marijana Hranjec, Ivana Murković Steinberg

**Corresponding author**: Dr Ema Horak, *Computational Organic Chemistry and Biochemistry Group, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, Bijenička cesta 54, 10000 Zagreb, Croatia, e-mail: Ema.Horak@irb.hr*

**ABSTRACT**

Photoluminescent solid-state materials are widely applied in modern technology, whereby molecular materials with luminescent “switching” properties when exposed to external stimuli are of the special interest. However, development of solid-state materials that exhibit broad spectrum of tuneable luminescence, especially red, still remains a major challenge. Aggregation induced emission phenomenon (AIE) was successfully demonstrated as a strategy for the design and development of novel solid-state emitters, particularly when combined with excited-state proton transfer reactions (ESIPT). Yet, extensive and complicated synthesis of AIE molecular systems, which are mostly large rotor molecules with luminescence in blue and green spectral region, is a major drawback.

In this work we present a systematic study of the spectral properties of five AIE- and ESIPT-based solid-state emitters built on simple and easily synthesised benzimidazole (BI) derivatives, a class of compounds that have not yet been reported as solid–state emitters. BI-based Schiff bases **1**-**5** are characterised by absorption and fluorescence spectroscopies in solution and solid state. **1**-**5** are D-*π*-A structures with bulky aromatic groups that can undergo twisted molecular conformation, while presence of the –OH group causes excited state intramolecular proton transfer (ESIPT). Different substituents on *π*-conjugated backbone generate tuneable solid-state emission from blue to red. All examined compounds can form aggregates in “poor” solvent, such as water, while at the same time novel emission band appears at higher wavelengths. Although weakly emissive in solution, aggregation induced emission phenomena (AIE) are to varying degrees responsible for a pronounced solid-state emission of **1**-**5**. Since AIE can be easily disrupted, spectral properties of solid-state fluorophores are sensitised to external stimuli, such as external mechanical stimuli or vapours of organic solvents. Reversible mechanochromic luminescence is observed for fluorophores **2**-**5** with wavelength shifts of 16 nm, 19 nm, 26 nm and 48 nm. Red fluorescence is observed for **5** and its application is demonstrated by developing simple reversible mechanochromic material.

**Keywords**: benzimidazole; Schiff base; solid state emission; aggregation induced emission; mechanochromism

**1. Introduction**

Solid-state emitters and molecular smart materials are an attractive research topic that simultaneously supports modern technology and advances in optoelectronic devices (e.g. OLEDs) [1], memory systems or security printing [2], fluorescent imaging or fluorescent sensors [3]. The exploitation of organic materials with fluorescence emission in solid state is highly desirable in material sciences, especially those with efficient red emission [4-7]. Red-emitting materials are of particular importance in bioimaging, where they can enable deep tissue penetration with minimum photo damage to living organisms. However, designing the solid-state emitters is a challenging task due to unclear molecular interactions and mechanism of molecular relaxation from the excited state in solid fluorophores. Designing the red solid-state fluorophores is especially challenging, because of the common aggregation caused quenching (ACQ) of D-*π*-A fluorophores (red fluorophores).

Recently, researches presented different molecular structures and families of solid-state emitters [4, 5, 8-14]. Special focus is placed on fluorophores that exhibit a proton transfer in the excited state (ESIPT), due to remarkable properties such as large Stokes shift, dual emission and spectral sensitivity to the surrounding medium. Solid state ESIPT emitters are summarised and discussed in a review paper by Padalkar and Sehi [15], where the importance of solid-state red emitters is once again underlined. Authors also discuss various strategies in developing novel ESIPT chromophores with solid-state emission, focusing on the fact that highly emissive solid-state ESIPT chromophores, which are none or weakly emissive in solution, are more appropriate for optoelectronic applications.

Aside red fluorophores, even developing wide-spectrum tuneable solid-state emitters remains a challenge. Subtle structure modifications, such as changing a heteroatom and substituent positions of arylmaleimides, is demonstrated as an effective method for large changes in the fluorescent colour [16]. Hetero[n] rotaxanes are developed as solid-state fluorescent materials used for the supramolecular encryption [2]. Benzthiazole and benzoxazole derivatives are recognized as potential cores in design of novel solid-state emitters, yet benzimidazole solid-state emitters are not common [17-20].

Recent reports demonstrated a convenient way for developing solid-state emitters by exploiting the photophysical phenomenon aggregation caused emission (AIE) or aggregation caused enhanced emission (AIEE) [10, 21-24]. Fluorophores with AIE properties are investigated for diverse functional applications, focusing on their unique properties such as mechanochromism or other external stimuli responses [2-4, 13, 25, 26]. Mechanochromic fluorescent materials change their emission colours when external stimuli, such as grinding, crushing or pressing, are applied. It can be generally achieved by chemical or physical structural changes to the materials. However, molecular design of such materials is difficult. The main problem in developing mechanochromic materials is aggregation caused quenching (ACQ) [27], which is why recently developed mechanochromic materials are mostly ICT dyes with AIE-active properties [19]. Several molecular systems are presented as mechanoflurorochromic materials, such as aminosryrylquinoxalines [28] or AIE-dependent scorpion-like carbazole [29], triphenylamine [30] or acrylonitrile derivatives [31]. However, extensive and complicated synthesis of AIE molecular systems, which are mostly large rotor molecules with luminescence in blue and green spectral region, is a major drawback. Some authors explicitly claim that novel AIE molecular systems with facile synthetic procedures are desirable, avoiding large organic systems and focusing on small organic molecules [32].

In this work we present solid-state emission and stimuli-responsive properties of some benzimidazole-based Schiff bases previously synthesised in our research group [33]. Investigated compounds are able to form emissive nanoaggregates in water and undergo excited state intramolecular proton transfer reactions. ESIPT chromophores are weakly emissive in solution, but exhibit strong solid-state emission that can be easily modified by altering the substituent on the benzimidazole core or external stimuli. This work will help and guide in a further design of multi-stimuli responsive materials, especially aspiring towards facile and economic synthesis and exploitation of small organic molecular systems.

**2. Experimental section**

***2.1 General methods***

All chemicals and solvents for synthesis and characterisation were purchased from commercial suppliers Acros, Aldrich or Fluka. Organic solvents were obtained from Kemika d.d., Zagreb. Milli-Q water was used for the preparation of aqueous solutions. Absorbance spectra were recorded on a Cary 100 Scan Varian spectrophotometer. Absorbance measurements were carried out using quartz cells of 1 cm path length and absorbance values were recorded at 1 nm. Wavelength scan was performed between 200 nm and 800 nm. Baseline was recorded prior to each set of experiments. Fluorescence measurements were carried out on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature using 1 cm path quartz cells. Excitation wavelengths were determined from absorbance maxima. Emission spectra were recorded from 300 nm to 800 nm. Solid-state emission was recorded on the Agilent Cary Eclipse spectrofluorimeter, using the solid sample holder accessory (Agilent). Solid sample holder enables fluorescence measurements on solid samples. It consists of a vertical sample mounting ‘slide’ supported by optical rails attached to the accessory baseplate. The angle of incidence of the excitation (the angle between the exciting light and a line perpendicular to the surface of the sample mounting slide) was 35°.

The 1H spectra were recorded on a Varian Gemini 300 at 300 MHz. All NMR spectra were measured in DMSO-*d*6 solutions, while chemical shifts are reported in ppm (*δ*) relative to TMS as internal standard.

***2.2 Aggregation induced emission investigation***

Due to low solubility in water, **1-5** were initially dissolved in ethanol or DMSO and stock solutions were prepared, *c* (stock) = 1×10-3 mol dm-3. Working solutions were prepared by dilution of concentrated stock solutions. The ethanol/water or DMSO/water mixtures with different water fractions were prepared by slowly adding the target molecule in solvent mixture at room temperature. The concentration was maintained at 10 µM. The emission and absorption measurements were performed immediately.

Dynamic light scattering (DLS) experiments were carried out in aqueous (*f*w = 99% water/ethanol) and in ethanol solution, *c* = 10 μM on Malvern Zetasizer Nano instrument.

***2.3 Mechanofluorochromism study***

The ground powder was obtained by grinding the pristine sample with a pestle in the mortar. The fumed sample was prepared by fuming the ground powder with ethanol vapour for 5 min.

The crystal phases in samples were analysed by powder X-ray diffraction (PXRD) using Shimadzu XRD6000 with CuK*α* radiation. Data were collected 2-70 °2*θ* in a step scan mode with step of 0.02° and counting time of 0.6 s.

**3. Results and discussion**

***3.1 Design and spectral properties of solid-state emitters***

Benzimidazole-based Schiff bases **1**-**5** (Figure 1a) are molecular systems that possess ICT character due to the introduction of an electron donating *N*,*N*-diethyl amino group and strong electron withdrawing -CN and –NO2 groups on the benzimidazole acceptor moiety. The structural core of **4** and **5** also contains a salicylidene moiety that potentially introduces photoinduced proton transfer reactivity (ESIPT). Benzimidazole moiety is an attractive building block of electron donor-*π*-electron acceptor (D-*π*-A) molecular systems due to the multifunctionality of its heteroaromatic conjugated planar structure [34]. As we previously demonstrated, benzimidazole-based D-*π*-A molecular systems based on charge-transfer interactions are excellent candidates for designing optical chemosensors in solution and polymer matrices. Their properties as chromophores (fluorophores) enabled development of novel sensing systems, such as ion-selective optodes, as well as chemosensors for metal ions [35, 36].



**Figure 1.** A) Benzimidazole-based Schiff bases **1**-**5**; B) Solid-state emission spectra and photographs taken under UV lamp (*λ*exc = 365 nm) of **1**-**5**.

Absorbance and fluorescence emission spectra of **1**-**5** in ethanol are presented in Fig S1.

Charge transfer in chromophores **1**-**5** induces strong absorption in the violet-blue region of the visible spectrum with pronounced molar extinction coefficients. Absorbance maxima in ethanol are detected at *λ*abs = 397 nm, *λ*abs = 408 nm, *λ*abs = 419 nm, *λ*abs = 427 nm and *λ*abs = 440 nm, respectively, which is observed as yellow solution. They are weakly emissive in ethanol in the green spectral region (*λ*emiss = 460-501 nm). The spectral properties of **1**-**5** in solution were also characterised by the UV-visible absorption and fluorescence spectrophotometries in different aprotic and protic solvents. A pronounced difference in spectral properties of fluorophores in organic solvents and water was observed both in absorption and emission spectra, which suggested that **1**-**5** likely form nanostructures in water. Novel emission maxima at longer wavelengths in water (*λ*emiss = 405-625 nm) also led us to assume that such fluorescence properties come from the formation of aggregates and possibly aggregation induced emission. Basic photophysical properties of **1**-**5** in ethanol, H2O and solid state are summarised in Table 1.

**Table 1.** Photophysical properties of **1**-**5** in ethanol, H2O and solid state.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Comp.** | ***λ*abs /nm** | | ***λ*emiss/nm** | | ***ε*/**  **mol-1 dm3 cm-1** | | **Stokes shift / nm** | | ***λ*emiss/nm** |
| H2O | EtOH | H2O | EtOH | H2O | EtOH | H2O | EtOH | **solid state** |
| **1** | 429 | 397 | 512 | 460 | 20 730 | 34 970 | 83 | 63 | 525 |
| **2** | 356 | 408 | 490 | 473 | 19 840 | 32 390 | 49 | 65 | 571 |
| **3** | 355 | 419 | 630 | 501 | 4 400 | 40 010 | 286 | 82 | 580 |
| **4** | 364 | 427 | 570 | 468  488 | 22510 | 42690 | 206 | 41 | 536 |
| **5** | 390 | 440 | 612 | 483 | 20 680 | 61800 | 220 | 43 | 620 |

Although **1**-**5** are weakly emissive in solution, they showed strong fluorescence under 365 nm illumination in powder form (Figure 1b). Thus, solid state emission in compounds **2**-**5** is a surprising factor. Emission can be explained by the formation of emissive aggregates, which, in a combination with specific properties arising from the electron-withdrawing substituents in **2** and **3** and ESIPT ability of **4** and **5**, resulted in emission covering broad wavelength spectrum, with emission maxima *λ*emiss = 525 – 620 nm (Figure 1b.).

Solid-state emission can be easily tuned by introducing different electron-withdrawing substituent on the benzimidazole core (Figure 1b). When weak electron-withdrawing methyl group is present (**1**), emission at lowest wavelengths is observed (*λ*emiss = 525 nm). By introducing stronger electron-withdrawing -CN and –NO2 groups, solid state emission can be tuned towards higher wavelengths. Notably attractive observation is the red emission in ESIPT-inspired solid-state fluorophore **5** (*λ*emiss = 625 nm). Once again, tuning the fluorescence is directly dependent on the nature and position of substituted groups. Thus, weakly emissive **1** was excluded from further experiments.

Solid state emission is achieved by suppressing other radiationless deactivation pathways which occur in the excited state. Strategies for the design of novel solid state emitters are e.g. restriction of twisted intramolecular charge transfer (TICT), restriction of *cis-trans* isomerisation, aggregation induced emission, aggregation induced enhanced emission, or often combination of several such phenomena. ESIPT emitters are preferably part of such designs because of their unique desirable photophysical properties. Basic flexible imine group and acidic phenolic hydrogen are suitable for ESIPT in dyes **4** and **5**. *Cis-trans* isomerisation of the keto form can effectively deactivate the excited state which causes quenching of fluorescence in solution. However, in the aggregated state *cis-trans* isomerisation is effectively blocked through tight molecular packing. Conformational changes significantly suppress nonradiative deactivation pathways and favour the radiative decay.

***3.2 Aggregation induced emission (AIE) investigation***

The intramolecular charge transfer (ICT) compounds, such as dyes **1**-**5**, are strong candidates for the design and development of novel aggregation-induced emission molecular systems (AIEGens). Self-assembled nanoaggregates of structurally similar benzimidazole derivative were previously presented as sensing system for pH, based on aggregation-deaggregation mechanism and aggregation induced emission [37]. After careful consideration, it is clear that **1**-**5** are another class of benzimidazole-based derivatives found to form nanoaggregates in water.

Aggregation induced emission phenomenon of **2**-**5** was investigated by UV-visible absorbance and fluorescence spectroscopies, and light scattering on the nanostructures was also examined by dynamic light scattering (DLS) measurements in aqueous (*f*w = 99% water/ethanol) and ethanol solutions. Absorption and emission properties of **2-5** have been studied in binary solvent-nonsolvent mixtures (ethanol-H2O and DMSO-H2O) by changing the volume percentage of water (*f*w), as shown for **5** in Figure 2a and for **2**-**4** in Fig S2-S4.



**Figure 2**. A) Emission spectra of **5** in DMSO at different volume fraction of water; B) effect of water fraction on the emission intensity, (*c* = 10 µM, *λ*exc = 365 nm) and C) dynamic light scattering results of **5** in aqueous solution (*f*w = 99%).

Compounds were soluble in common organic solvents but insoluble in water (*aqueous solution*, H2O, refers to solutions prepared by diluting stock ethanol solution in a large quantity of water, volume fraction *f*w = 99 %). Spectral properties of examined systems are significantly different in so called “good” solvents (organic solvents) and “bad” solvent-water, especially in fluorescence spectra where novel emission band appeared at higher wavelengths. On the addition of water to a solution of **1**-**5** in DMSO, the absorbance spectra remain virtually unchanged until the water fraction *f*w reached the threshold value (70-80 %) (Fig S5). Above this threshold value the absorption spectra show a blue shift with a maximum at *λ* = 355-390 nm and a *level-off* red tail indicating presence of light scattering effects on nanoparticles [38], while new fluorescence emission band appears at *λ*emiss = 450-640 nm (Fig. 2a). At the same time, aqueous mixtures appear completely homogenous and without precipitates. Although all examined compounds formed aggregates in water with new emission maxima, the most pronounced aggregation induced emission was observed for **5**. The intensity of nanoaggregate emission in aqueous solution, (*fw* = 99 %) is around 7-fold the emission in organic solvents at given wavelength (*λ*emiss = 620 nm) for **5** (Fig. 2b).

The presence of nanoaggregates in aqueous solution was also confirmed by a simple test for the Tyndall effect in aqueous solutions (Fig S6). Nanoaggregates of **2-5** in water cause light scattering, seen as a *red-line* through the solution when a red laser beam is directed through solutions. Light scattering in ethanol solution is not observed. Very weak light scattering was observed for **1**.

The dynamic light scattering (DLS) measurements confirmed absence of any particles in pure ethanol, but revealed the presence of aggregates in aqueous solutions with sizes 15 nm, 33 nm, 79/450 nm, 206 nm and 40 nm for fluorophores **1**-**5**, respectively (Fig 2c, Fig S2-S4).

Suppression of intramolecular motion, *cis-trans* isomerisation and increased rigidity in aggregated state resulted in suppression of non-radiative relaxation, which can also be demonstrated by changing the viscosity of the medium surrounding the molecules. The effects of solvent viscosity on spectral properties of **2**-**5** were studied in mixtures of solvents of varying viscosity (glycerol-methanol mixtures of different volume ratios) (Fig. S7). As the volume fraction of glycerol increased, fluorescence intensity became stronger, which in the case of **2-5** can be attributed to the restriction of the intramolecular rotation of the dimethylamino or diethylamino groups conjugated to the aromatic ring, as well as the restriction of the *cis-trans* isomerisation leading to a more rigid molecular arrangement. The restricted rotation enhances electron donating ability towards the acceptor moiety, possibly stabilising the TICT state in viscous medium and enabling ESIPT. Absorption spectra showed no evidence of aggregation (absence of *level-off* red tail).

To conclude this section, we can confirm that **2**-**5** form self-assembled nanostructures in water. Nanoaggregates emit fluorescence at higher wavelengths, which is prominent for **5** and can be attributed to aggregation induced emission phenomena caused by molecular packing and restriction of molecular motions in aggregated state. Formation, size and morphology of aggregates in water and its influence on the emission intensity were not in the focus of this work, but we can observe strong difference between **1**, which forms small number of very small aggregates, and other compounds with pronounced aggregation, such as **5**.

***3.3 Stimuli-responsive solid-state emission***

Solid-state fluorescence and aggregation properties of **2**-**5** encouraged us to study the stimuli responsive properties of investigated compounds. Optical properties that can be altered by external stimuli in controlled environment, such as mechanofluorochromism and effect of microenvironment (atmosphere saturated with vapours of different organic solvents) can be observed to varying degrees for compounds **2**-**5**.

**2**-**5** showed different fluorescence behaviours upon the treatment of grinding and fuming. As shown in Figure 3a, the pristine (as prepared) sample of **5** emits red fluorescence with emission maxima *λ*max = 620 nm. Upon grinding using a mortar and pestle, the pristine sample showed very small batochromic shift to longer wavelengths (5 nm). However, after fuming the sample with acetone or ethanol vapours for 10 min, emission converted to yellow-orange fluorescence and emission maxima switched to *λ*max = 572 nm. When the powder **5** was reground, the fluorescence emission restored its original state an emitted red colour with emission at *λ*max ≈ 625 nm. If the powder **5** was fumed again, its emission shifted to *λ*max ≈ 572 nm. Wavelength switches are reversible, after the first fuming, as shown in Fig 3b. Simultaneously, fluorescence intensity drops with every cycle. This mechanochromic conversion could be repeated without any chemical change, as shown by NMR spectroscopy (Figure 4b). It appears that molecules of **5** in its pristine form (as prepared) are arranged in more planar structures, which is disrupted by fuming the sample and causing the new molecular arrangement and blue shifted fluorescence. By grinding the sample, red shifted fluorescence is observed due to possibly better molecular interactions.



**Figure 3.** (A)Solid-state emission of ground/fumed **5**; (B) Photographs of **5** ground / fumed in several cycles, observed in daylight and under UV lamp (*λ*exc = 365 nm).

Fluorescent properties of molecules in solid state depend on the molecular arrangement, conformational flexibility and intermolecular interactions in the material. Thus, HOMO-LUMO energy levels, and consequently fluorescent properties of materials, are significantly affected by any modification in the molecular packaging. Since the aggregation directly affects the molecular arrangement, novel solid-state fluorophores are often based on the AIE phenomena. Also, aggregation can be easily disrupted, wherefore solid-state fluorescence originated from AIE molecular systems can be easily modified. Thus, AIE materials are recently becoming the main interest in developing stimuli responsive materials, especially those with red fluorescence. It is also highly desirable to exploit AIE systems (especially small organic molecule that are not often presented as AIE systems) with facile and economic synthesis as novel stimuli-responsive materials. Schiff bases **1**-**5** are easily and economically synthesized. Although they are simple molecules and similar systems are well known ligands in coordination chemistry, their AIE properties have not been reported in the literature.

To evaluate differences between pristine, ground and fumed states, characteristics of **5** were investigated by powder X-ray diffraction (XRD) (Figure 4a). Raw as-derived sample **5** displays a pattern typical of well crystalline compound. Structurally, the compound was not described, thus no ICDD assignation was possible. On behalf of only one very strong peak at about 13.3 °2θ it is suggested the pattern may be the consequence of the preferential orientation of the crystallites. Additionally, based on a sole low-angle peak at about 4.5 °2θ the presence of the ordering at meso-level is suggested (size of the domains is about 2 nm). Therefore, raw sample is a well crystalline mesostructured sample with notably preferred orientation of the crystallites. The crystallites size was calculated using Scherrer's equation and found to be about 72 nm (Figure 4a Inset). The grinded sample is basically amorphised. These patterns follow the same qualitative and quantitative relations, just heavily reduced in the intensity. From the semiquantitative peak ratio we observe the intensity is quartered (Figure 4a Inset). From the microstructural point of view, the crystallite size decreased to nanosizes (about 44 nm), which is actually the main difference and occurs as the expected consequence of the amorphisation process. Therefore, grinded sample is partially amorphised raw sample.

The fumed sample displays recrystallisation based intensity increase (Figure 4a Inset); this pattern is the same as the previous two, yet the peak intensity ratio differs. Namely, the peak latter does not support preferred orientation in the same extent as in the raw sample. Peaks below 15°2θ preserve peak intensity ratio but those above 30 °2θ grow in intensity and get narrower, pointing out to a higher crystallite size (about 83 nm). Therefore, humidified (fumed) sample is structurally the same as the previous two, but definitively with some microstructural differences. Specifically, greater crystallites and somewhat lower preferential orientation are observed. Such behaviour clearly indicates differences in structural properties, and it is observed as a consequence of different rates of crystallization occurring in the course of syntheses and during humidifying. Namely, different growth rate will surely influence the distribution of the crystallographic fringes having different surface energies.

To conclude, powder X-ray diffraction (XRD) showed that mechanochromic properties of investigated compounds can be assigned to morphological transition between crystalline and amorphous state, as shown in Figure 4a for **5**.

Mechanofluorochromic properties of **2**-**4** are less expressed as shown in Figures S8-S10. Reversible fluorescent wavelength switch of 16 nm, 19 nm or 26 nm was observed. In contrast to **5**, **2**-**4** exhibit a batochromic switch of emission maxima upon grinding of pristine sample, without the need for initial fuming, indicating that they are in crystalline form as prepared (Figure S11).





**Figure 4.** A) The diffraction patterns of the as-derived, grinded and humidified samples. Inset 1. Scherrer’s crystallite sizes, Inset 2. Semiquantitative relative peak ratio; B) NMR spectra of **5** as-derived and after grinding.

Stimuli-responsive characteristics were further investigated by exposing the samples to atmosphere of organic solvents vapours. Effect of vapours on the solid-state fluorescence of **2**-**5** was investigated in sealed Petri dish. When left overnight in the atmosphere of different organic solvents, **2**-**5** exhibit solid-state emission at the same wavelength but different fluorescence intensity. General observation was that fluorescence intensity decreases as polarity of solvent increases. The most pronounced change in fluorescence intensity is observed for **5** and shown in Figure 5.



**Figure 5.** (A)Fluorescence intensity of **5** *vs.* ET(30) solvent polarity parameter; (B) Photographs of **5** after being exposed to vapours of tetrahydrofurane, dichloromethane, acetone, ethanol and methanol, observed in daylight and under UV lamp (*λ*exc = 365 nm).

To demonstrate the possible applications of investigated compounds, we present novel paper-based fluorescent materials. Filter paper strips are soaked in saturated ethanol solution of **2**-**5** and dried at room temperature. Paper strips with different colour are developed, while **5** retained orange-red emission (Figure 6a). Since mechanofluorochromic properties of **2**-**4** are not significantly expressed (Figure S12), demonstration of applicability is presented for **5** (Figure 6b). Patterns can be reversibly recorded simply by writing with spatula and subsequently erased by fuming with solvents within few minutes. Writing / erasing is reversible for several cycles. This simple demonstration implies potential of such simple and small organic molecule in optical recording, security printing or mechanochromic materials.



**Figure 6.** Different patterns written with a spatula on the sample casted on the filter paper and erased by keeping the paper strip in the acetone vapour atmosphere for a few minutes (365 nm UV light).

**4. Conclusions**

Five benzimidazole-based Schiff bases are presented as novel solid-state emitters. Different substituents on the *π*-conjugated backbone generate tuneable solid-state emission from blue to red. Fluorophores **4** and **5** can undergo the excited state proton transfer, which conjoined with the aggregation induced emission enable red fluorescence in solid-state emitter **5**.

Since AIE can be easily disrupted, spectral properties of solid-state fluorophores are sensitised to external stimuli, such as external mechanical stimuli or vapours of organic solvents. Reversible mechanochromic luminescence is observed for fluorophores **2**-**5** with wavelength shifts from 16 nm to 48 nm. Red fluorescence of fluorophore **5** is exploited in order to demonstrate a simple reversible mechanochromic paper-based material.

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**Appendix A. Supplementary data**

Supplementary data associated with this article can be found in the online version.

**References**

[1] A. Ekbote, S.H. Han, T. Jadhav, S.M. Mobin, J.Y. Lee, R. Misra, Stimuli responsive AIE active positional isomers of phenanthroimidazole as non-doped emitters in OLEDs, Journal of Materials Chemistry C, 6(2018) 2077-87.

[2] X. Hou, C. Ke, C.J. Bruns, P.R. McGonigal, R.B. Pettman, J.F. Stoddart, Tunable solid-state fluorescent materials for supramolecular encryption, Nature Communications, 6(2015) 6884.

[3] J.B. Arockiam, S. Ayyanar, Benzothiazole, pyridine functionalized triphenylamine based fluorophore for solid state fluorescence switching, Fe3+ and picric acid sensing, Sensors and Actuators B: Chemical, 242(2017) 535-44.

[4] T. Han, X.G. Gu, J.W.Y. Lam, A.C.S. Leung, R.T.K. Kwok, T.Y. Han, et al., Diaminomaleonitrile-based Schiff bases: aggregation-enhanced emission, red fluorescence, mechanochromism and bioimaging applications, Journal of Materials Chemistry C, 4(2016) 10430-4.

[5] R. Radhakrishnan, K.G. Sreejalekshmi, Fluorophores based on a minimal thienylthiazole core: towards multifunctional materials with solid state red emissions, solvatochromism and AIE behaviour, RSC Advances, 6(2016) 32705-9.

[6] Z. Zhang, B. Xu, J. Su, L. Shen, Y. Xie, H. Tian, Color-Tunable Solid-State Emission of 2,2′-Biindenyl-Based Fluorophores, Angew Chem Int Ed, 50(2011) 11654-7.

[7] J.H. Chen, D.Y. Li, W.J. Chi, G.T. Liu, S.H. Liu, X.G. Liu, et al., A Highly Reversible Mechanochromic Difluorobenzothiadiazole Dye with Near-Infrared Emission, Chem-Eur J, 24(2018) 3671-+.

[8] M. Shimizu, R. Kaki, Y. Takeda, T. Hiyama, N. Nagai, H. Yamagishi, et al., 1,4-Bis(diarylamino)-2,5-bis(4-cyanophenylethenyl)benzenes: Fluorophores Exhibiting Efficient Red and Near‐Infrared Emissions in Solid State, Angew Chem Int Ed, 51(2012) 4095-9.

[9] C. Carayon, S. Fery-Forgues, 2-Phenylbenzoxazole derivatives: a family of robust emitters of solid-state fluorescence, Photochemical & Photobiological Sciences, 16(2017) 1020-35.

[10] Y. Zhang, H. Li, G. Zhang, X. Xu, L. Kong, X. Tao, et al., Aggregation-induced emission enhancement and mechanofluorochromic properties of [α]-cyanostilbene functionalized tetraphenyl imidazole derivatives, Journal of Materials Chemistry C, 4(2016) 2971-8.

[11] C. Maeda, T. Todaka, T. Ueda, T. Ema, Color-Tunable Solid-State Fluorescence Emission from Carbazole-Based BODIPYs, Chem-Eur J, 22(2016) 7508-13.

[12] K. Sakai, H. Kawamura, N. Kobayashi, T. Ishikawa, C. Ikeda, T. Kikuchi, et al., Highly efficient solid-state red fluorophores using ESIPT: crystal packing and fluorescence properties of alkoxy-substituted dibenzothiazolylphenols, CrystEngComm, 16(2014) 3180-5.

[13] M. Pannipara, A.G. Al-Sehemi, A. Kalam, A.M. Asiri, Naphthalene based AIE active stimuli-responsive material as rewritable media for temporary communication, Opt Mater, 72(2017) 442-6.

[14] M. K. Bera, C. Chakraborty, S. Malik, Solid state emissive organic fluorophores with remarkable broad color tunability based on aryl-substituted buta-1,3-diene as the central core, Journal of Materials Chemistry C, 5(2017) 6872-9.

[15] V. S. Padalkar, S. Seki, Excited-state intramolecular proton-transfer (ESIPT)-inspired solid state emitters, Chem Soc Rev, 45(2016) 169-202.

[16] J. Wang, Z. Liu, S. Yang, Y. Lin, Z. Lin, Q. Ling, Large Changes in Fluorescent Color and Intensity of Symmetrically Substituted Arylmaleimides Caused by Subtle Structure Modifications, Chemistry - A European Journal, 24(2018) 322-6.

[17] K. Benelhadj, J. Massue, P. Retailleau, G. Ulrich, R. Ziessel, 2-(2 '-Hydroxyphenyl)benzimidazole and 9,10-Phenanthroimidazole Chelates and Borate Complexes: Solution- and Solid-State Emitters, Org Lett, 15(2013) 2918-21.

[18] A. Malakar, M. Kumar, A. Reddy, H.T. Biswal, B.B. Mandal, G. Krishnamoorthy, Aggregation induced enhanced emission of 2-(2'-hydroxyphenyl)benzimidazole, Photochemical & Photobiological Sciences, 15(2016) 937-48.

[19] Y. Zhan, Q. Wei, J. Zhao, X. Zhang, Reversible mechanofluorochromism and acidochromism using a cyanostyrylbenzimidazole derivative with aggregation-induced emission, RSC Advances, 7(2017) 48777-84.

[20] Y.B. Shen, P. Chen, J.X. Liu, J.P. Ding, P.C. Xue, Effects of electron donor on luminescence and mechanochromism of D-pi-A benzothiazole derivatives, Dyes and Pigments, 150(2018) 354-62.

[21] H. G. Lu, Y.D. Zheng, X.W. Zhao, L.J. Wang, S.Q. Ma, X.Q. Han, et al., Highly Efficient Far Red/Near-Infrared Solid Fluorophores: Aggregation-Induced Emission, Intramolecular Charge Transfer, Twisted Molecular Conformation, and Bioimaging Applications, Angew Chem-Int Edit, 55(2016) 155-9.

[22] C. X. Niu, Y. You, L. Zhao, D.C. He, N. Na, J. Ouyang, Solvatochromism, Reversible Chromism and Self-Assembly Effects of Heteroatom-Assisted Aggregation-Induced Enhanced Emission (AIEE) Compounds, Chem-Eur J, 21(2015) 13983-90.

[23] A. K. Srivastava, A. Singh, L. Mishra, Tuning of Aggregation Enhanced Emission and Solid State Emission from 1,8-Naphthalimide Derivatives: Nanoaggregates, Spectra, and DFT Calculations, The Journal of Physical Chemistry A, 120(2016) 4490-504.

[24] A. Maity, F. Ali, H. Agarwalla, B. Anothumakkool, A. Das, Tuning of multiple luminescence outputs and white-light emission from a single gelator molecule through an ESIPT coupled AIEE process, Chem Commun, 51(2015) 2130-3.

[25] Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, et al., Recent advances in organic mechanofluorochromic materials, Chem Soc Rev, 41(2012) 3878-96.

[26] Y. Gong, Y. Tan, J. Liu, P. Lu, C. Feng, W.Z. Yuan, et al., Twisted D-pi-A solid emitters: efficient emission and high contrast mechanochromism, Chem Commun, 49(2013) 4009-11.

[27] J. Xu, Z. Chi, CHAPTER 1 Mechanofluorochromism: An Overview, Mechanochromic Fluorescent Materials: Phenomena, Materials and Applications, The Royal Society of Chemistry2014, pp. 1-6.

[28] J. Y. Zhao, J.B. Sun, O. Simalou, H.R. Wang, J. Peng, L. Zhai, et al., Multi-stimuli-responsive fluorescent aminostyrylquinoxalines: Synthesis, solvatochromism, mechanofluorochromism and acidochromism, Dyes and Pigments, 151(2018) 296-302.

[29] Y. X. Hu, J. Zhang, Z. Li, X.Y. Wang, J. Yin, S.H. Liu, Novel scorpion-like carbazole derivatives: Synthesis, characterization, mechanochromism and aggregation-induced emission, Dyes and Pigments, 151(2018) 165-72.

[30] H.C. Zhu, J.Y. Huang, L. Kong, Y.P. Tian, J.X. Yang, Branched triphenylamine luminophores: Aggregation-induced fluorescence emission, and tunable near-infrared solid-state fluorescence characteristics via external mechanical stimuli, Dyes and Pigments, 151(2018) 140-8.

[31] C. Ma, X. Zhang, L. Yang, Y. Li, H. Liu, Y. Yang, et al., Alkyl length dependent mechanofluorochromism of AIE-based phenothiazinyl fluorophenyl acrylonitrile derivatives, Dyes and Pigments, 136(2017) 85-91.

[32] M. Shimizu, Y. Takeda, M. Higashi, T. Hiyama, 1,4-Bis(alkenyl)-2,5-dipiperidinobenzenes: Minimal Fluorophores Exhibiting Highly Efficient Emission in the Solid State, Angew Chem, 121(2009) 3707-10.

[33] M. Hranjec, K. Starčević, S.K. Pavelić, P. Lučin, K. Pavelić, G. Karminski Zamola, Synthesis, spectroscopic characterization and antiproliferative evaluation in vitro of novel Schiff bases related to benzimidazoles, European Journal of Medicinal Chemistry, 46(2011) 2274-9.

[34] E. Horak, P. Kassal, I. Murković Steinberg, Benzimidazole as a structural unit in fluorescent chemical sensors: the hidden properties of a multifunctional heterocyclic scaffold, Supramol Chem, (2017) 1-20.

[35] E. Horak, P. Kassal, M. Hranjec, I.M. Steinberg, Benzimidazole functionalised Schiff bases: Novel pH sensitive fluorescence turn-on chromoionophores for ion-selective optodes, Sensors and Actuators B: Chemical, 258(2018) 415-23.

[36] E. Horak, R. Vianello, M. Hranjec, I. Murković Steinberg, Colourimetric and fluorimetric metal ion chemosensor based on a benzimidazole functionalised Schiff base, Supramol Chem, (2018) 1-10.

[37] E. Horak, M. Hranjec, R. Vianello, I.M. Steinberg, Reversible pH switchable aggregation-induced emission of self-assembled benzimidazole-based acrylonitrile dye in aqueous solution, Dyes and Pigments, 142(2017) 108-15.

[38] H. Auweter, H. Haberkorn, W. Heckmann, D. Horn, E. Luddecke, J. Rieger, et al., Supramolecular structure of precipitated nanosize beta-carotene particles, Angew Chem-Int Edit, 38(1999) 2188-91.