ELSEVIER

Contents lists available at ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

Sectional intramolecular charge transfer manipulating in a D-A-D' coumarin derivative for recessive rewritable paper

Lian Duan^a, Shu Wang^a, Huijun Zhao^a, Tong Wu^a, Da Li^b, Li Guo^a, Xiaozhong Liang^b, Yue Sun^{a,*}, Kunpeng Guo^{b,**}, Jie Li^{b,***}

^a School of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, 030024, China

^b Ministry of Education Key Laboratory of Interface Science and Engineering in Advanced Materials, Research Center of Advanced Materials Science and Technology,

Taiyuan University of Technology, Taiyuan, 030024, China

ARTICLE INFO

Keywords: BF₃ fluorescent probe Sectional intramolecular charge transfer manipulating Recessive rewritable paper Encryption

ABSTRACT

External-stimuli-responsive rewritable paper has attracted significant attention for application in secure information. However, to encrypt information on papers which can not be read out under visible light is still challenging. In this work, recessive rewritable paper for security information handling was realized via sectional intramolecular charge transfer (SICT) manipulating in a delicately designed coumarin derivative CMNT. By rational arranging a thiophenyl group and a diethylamino group as electron donors at the 3- and 7-position of coumarin skeleton, respectively, CMNT exhibited obvious fluorescence switching upon BF₃ and trimethylamine stimuli. After impregnating a filter paper into CMNT solution with low concentration (1×10^{-6} M), no color change of the paper could be observed under visible light. Meanwhile, when writing and erasing the information on the paper by BF₃ ink and trimethylamine eraser, respectively, the process can only be witnessed under UV light. Studies revealed the ICT effect from diethylamino group to chromen-2-one was retained, thus producing such unique phenomenon.

1. Introduction

Confidential communication is vitally important in information transmission in fields of economic development, military and national security [1,2]. At present, many kinds of materials, including poly-oxometalates, transition metal oxides, nanomaterials, organic fluorescent compounds and inorganic-organic composite materials show response to external stimuli such as light, heat, mechanical stress and magnetism [3–9], and the molecular structure and absorption wavelength changed after stimulation. The emergence of rewritable paper has brought a huge change in the way of communication. Among them, the rewritable paper based on fluorescence effect on which the information is not visible by naked eyes has received extensive attention in data encryption for its simple operation, convenient use, low cost, quick and intuitive detection [10–12].

Recent studies on the media of rewritable paper focus on the compounds that respond to specific ions, for example, using CN^- as the ink to

leave notes on rewritable paper, when it was overwritten by trifluoroacetic acid (TFA), the fluorescence was "off", thus making a simple rewritable paper, the specific mechanism is that when hydrogen bonds are formed, both π conjugation and ICT effects are blocked [13]; The Khazi group developed an erasable paper based on mechanically induced fluorescence discoloration. The force-induced crystal structure changes from a crystalline to an amorphous state [14,15]. A new type of rewritable paper was developed based on the tetraphenyl ethylene Schiff base derivative media, which used 410 nm ultraviolet light that could promote the conversion of the compound structure from enol type to ketone type as a pen, and 420-590 nm visible light or white light that could speed up the recovery process as an eraser [16–18]; Chen's group developed a thermochromic material that changed its color from blue to colorless when the temperature was higher than 65 $^\circ$ C, remained colorless at room temperature, and returned to blue when the temperature was lower than -10 °C [19,20]. In addition, some acidic, alkaline or photochromic molecules were also designed, of which their chemical

https://doi.org/10.1016/j.dyepig.2021.109605

Received 3 May 2021; Received in revised form 23 June 2021; Accepted 25 June 2021 Available online 29 June 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.

^{*} Corresponding author.

^{**} Corresponding author.

^{***} Corresponding author.

E-mail addresses: sunyue@tyut.edu.cn (Y. Sun), guokunpeng@tyut.edu.cn (K. Guo), lijie01@tyut.edu.cn (J. Li).

and physical structures were changed by external stimuli to achieve the purpose of color conversion, enabling a variety of erasable writing [21]. Although these rewritable papers have realized rewritable functions in various ways, there are few rewritable papers that can be used for encryption [22–24]. Recessive rewritable paper refers to potential handwriting that cannot be directly observed by naked eyes after writing, including secret handwriting, automatically faded magic handwriting can only be colored and read out under certain conditions to realize information encryption application.

Herein, a D-A-D' structured coumarin derivative **CMNT** was developed with diethylamino (D) and thiophenyl (D') substituted on position 7 and 3 of the coumarin skeleton (A), respectively (Scheme 1). The intramolecular charge transfer (ICT) effect was rationally controlled by BF₃. It was demonstrated that the ICT effect from diethylamino group to chromen-2-one was suppressed by adding BF₃, while the ICT channel from thiophenyl group to chromen-2-one was retained, which leading to an obvious ratiometric fluorescence change. In comparison, a control compound **CMT** without the diethylamino group was synthesized to demonstrate the supposed sensing mechanism. Additionally, the color and fluorescence change of **CMNT** caused by BF₃ could be recovered by TEA. More importantly, there is no color change of the paper during this writing and cleaning process under visible light. Therefore information transmission confidentially on a recessive rewritable paper was realized by using BF₃ as ink and TEA as eraser under UV light.

2. Results and discussion

2.1. Crystal analysis

The molecular packing pattern in crystal was analyzed through X-ray diffraction experiments (Fig. 1) and the corresponding crystallographic data was summarized in Table S1. CMNT (CCDC: 2060124) crystallized in triclinic P-1 symmetry, and the planar molecules formed herringbone packing in a face to edge pattern without any π - π overlap between two adjacent molecules which would activate nonradiative pathways of excited states [29,30]. Several O…H hydrogen bonds with distances of 2.547 and 2.659 Å were observed between the carbonyl groups and the aromatic H of adjacent molecules. The existed O…H hydrogen bonds, as well as S…H hydrogen bonds between the adjacent molecules, rigidified the molecular conformation of CMNT in the solid. The stable conformation, as well as the face-to-edge packing, suppress the nonradiative pathways, resulting in strong emission in the crystals.

2.2. Photo-luminescence and UV-vis spectra in solution

The UV–visible and fluorescent spectra of the **CMNT** treated with BF_3 were shown in Fig. 2. **CMNT** exhibited a maximum absorption peak centered at 427 nm with a color of light yellow under visible light. Upon adding BF_3 , the intensity of the original absorption peak was decreased,

and a new peak centered at 368 nm appeared with intensity increased gradually. The reaction between **CMNT** and BF₃ got equilibrium when 11 equiv. of BF₃ were added. Similar phenomenon was observed in the fluorescent spectra. The solution of **CMNT** exhibited cyan color under UV light centered at 485 nm with a moderate fluorescence quantum yield (Φ) of 25.3%. With the addition of BF₃, a new emission peak centered at 431 nm emerged with the intensity increased, and the solution color turned to dark blue (fluorescence quantum yield Φ = 53.68%) (Fig. 2b). The spectra were recorded in less than 90 s after the addition of BF₃, implying the rapid response of CMNT to BF₃. (Fig. S1). The intensity ratio I₄₃₁/I₄₈₅ exhibited a good linear relationship with the BF₃ concentration between 1 × 10⁻⁵ M to 4 × 10⁻⁵ M (Fig. S2). The detection limit was determined to be 9.7 × 10⁻⁸ M based on LOD = $3\sigma_{bi}/m$ [31]. " σ_{bi} " is the standard deviation of 11 blank samples; "m" is the slope of the linear relationship obtained.

Moreover, as one of the important properties of a chemosensor, reversibility was also investigated. Interestingly, when another Lewis base triethylamine (TEA) was added to a mixture of **CMNT** and BF₃, the fluorescent spectra, as well as the solution color was recovered to the original state (Fig. 2c and d). The process could be repeated at least 8 times without any attenuation (Fig. S3).

In order to evaluate the selective property of **CMNT** to BF₃, other acids (20 equiv.) including boric acid, benzoic acid, salicylate acid, acetic acid and formic acid were added to the solutions of **CMNT**, respectively. As shown in Fig. S4, except for their characteristic absorption at 273 and 309 nm of benzoic acid and salicylate acid, no evidence-based change in both absorption and emission spectra of CMNT were observed after these analytes were added. Furthermore, competitive experiments with these species in the same environment were also carried out, and the signaling of **CMNT** toward BF₃ (1 equiv.) was not affected by the presence of 20 equiv. of coexisting species (Fig. S5). All of the results suggested that **CMNT** was an efficient specialized and ratiometric signaling probe for BF₃ detection in DCM solution.

2.3. Sensing mechanism

To illustrate the sensing process of **CMNT** to BF_3 , ¹⁹F NMR spectra were performed. As shown in Fig. 3a, in comparison with BF_3 signaling at -153 ppm, a new signal peak at -132 ppm appeared with the addition of insufficient amount of **CMNT**, suggesting that BF_3 was indeed reacted with **CMNT**, producing a new molecule. To further manifest the exact binding site of **CMNT** to BF_3 , a control molecule **CMT** without diethylamino substituent was synthesized (Scheme 1). Despite electronic-rich oxygen in the structure which can potentially form borate complexes, there was no influence on the fluorescence spectra when **CMT** was treated with BF_3 (Fig. 3b). As a result, it proved the binding site for BF_3 was the nitrogen in diethylamino rather than oxygen in carbonyl group, resulting in form a new borate complexe.

Based on the results above, the sensing mechanism was deduced and



Scheme 1. Synthetic routes of CMNT and the control compound CMT.



Fig. 1. ORTEP diagram, weak interactions in the crystal and molecular pattern of CMNT.



Fig. 2. UV–visible (a) and fluorescence (b) spectra of CMNT in DCM with addition of BF₃. Inset of b: fluorescence change photograph under illumination using a 365 nm UV lamp. CMNT: 2×10^{-5} M. The equivalent of BF₃ in the UV–visible spectra are: 0, 0.5, 1, 1.5, 2, 3, 5, 7, 9 and 11. The equivalent of BF₃ in the fluorescence spectra are: 0, 0.5, 1, 1.5, 2, 3, 5, 7, 9, 11 and 13. UV–Visible (c) and fluorescence (d) spectra of CMNT in DCM with the addition of BF₃ and TEA. Inset: Visual fluorescence change photograph under illumination using a 365 nm UV lamp. CMNT: 2×10^{-5} M, BF₃: 2.2×10^{-4} M, TEA: 1×10^{-3} M.

illustrated in Fig. 3c. CMNT was constructed as a D-A-D' molecule with the coumarin skeleton as the electron acceptor, and the diethylamino and thiophenyl substitutes as the electron donors, respectively. When excited by UV light, intramolecular charge transfer (ICT) occurred from both of the electron donor sites to the central electron acceptor, leading to green fluorescence peaking at 485 nm. With the addition of BF₃, the diethylamino substituent as a Lewis base was reacted with BF3 to form a new borate complex, and the sectional intramolecular charge transfer (SICT) within the molecule would be cut off in this process. However, the other part of ICT process from thiophenyl group to carbonyl moieties was not affected. It plays as the dominant role in fluorescence regulation after the interaction of CMNT with BF₃, leading to the remarkable blueshifts in both UV-visible and fluorescence spectra after the formed Lewis acid-base complexes between BF3 and the diethylamino group blocked the ICT process. As much as we know, most of the published work of BF₃ detection are based on the same mechanism, that is the ring forming process of B with N or O [32-34], and inevitably this type of probes tends to be bulky and complex. The BF3 chemosensor reported here is a novel smart ICT molecule, and the detection is based on a novel mechanism.

2.4. Rewritable paper and encryption application

CMNT powder showed yellow fluorescence peaking at 558 nm under UV irradiation (Fig. S6). To expand the practical application of **CMNT**, a preliminary paper strip testing system was developed by dipping the test strip into the solution of **CMNT** (1×10^{-3} M) and then dried at room temperature. The yellow colored test strip emitted yellowish green fluorescence at 493 nm under UV irradiation. After contacting to the vapor of BF₃, the paper was faded and the fluorescence wavelength was blue-shifted to 450 nm with emitting color of bright blue (Fig. 4a). Just like in solution, the color could be recovered when the test paper was contacted with TEA vapor. The fully reversible process guaranteed the paper to be reused over at least 5 cycles (Fig. 4b).

When the white strip was dipped into the **CMNT** solution of different concentrations, the yellow color on the paper faded gradually with the concentration decreased (Fig. S7). Finally, no color change was observed before and after interaction with BF₃ by naked eyes under visible light at a concentration of 1×10^{-6} M. However, the test strip exhibited obvious fluorescent color switching between cyan and blue under a UV lamp, implying the potential application ability of recessive erasable paper for



Fig. 3. (A) ¹⁹F NMR spectra. Red: BF₃ only, and cyan: CMNT with exceed BF₃. (b) Fluorescence spectra of CMNT and CMT treated with BF₃. CMNT: 2×10^{-5} M, CMT: 2×10^{-5} M, BF₃: 2.2×10^{-4} M. (c) The mechanism of SCIT manipulating in CMNT.



Fig. 4. (A) Fluorescence of CMNT (1×10^{-3} M) on the test strip. (b) The ratio intensity of the **CMNT** test strip recorded after adding BF₃·Et₂O and TEA for continuous 5 cycles.

encryption (Fig. 5a). A dilute concentration of **CMNT** (1×10^{-6} M) was chosen to carry out the recessive rewritable test. Some paper masks were made and overlaid on the white strips treated with **CMNT** as described above. And then treated them with BF₃ vapor. As was expected, there is nothing on the strip under the visible light. However, once put the strip under the UV light, a fine picture appeared with abundant details. Moreover, the picture would vanished when the strip treated with TEA vapor. It is noted that the paper can be reused at least 5 times (Fig. 5b).

3. Conclusion

In summary, a D-A-D' coumarin derivative CMNT was developed

with thiophenyl group and diethylamino group as the electron donors substituted at the 3- and 7- positions of coumarin skeleton, respectively. Based on the Lewis acid-base reaction between diethylamino group of **CMNT** and BF₃, **CMNT** showed high selectivity and sensitivity to BF₃ in dichloromethane solution with a detection limit to be 9.7×10^{-8} M. The ICT effect from diethylamino group to chromen-2-one was suppressed after adding BF₃, while the ICT channel from thiophenyl group to chromen-2-one was retained, leading to an obvious ratiometric fluorescence change. Contributed from this, recessive rewritable paper impregnated with **CMNT** was realized under UV light by using BF₃ as ink and TEA as eraser. More importantly, the color of the paper didn't change during this writing and cleaning process under visible light,



Fig. 5. (A) The impregnated paper of different CMNT concentrations treated with BF₃ under the visible light and 365 nm UV lamp. (b) Writing-erasing-rewriting process of one filter paper circularly treated with CMNT, BF₃, and TEA, displayed under 365 nm UV lamp.

enabling this rewritable paper as media for security information handling in portable way.

4. Experimental section

4.1. Materials and instruments

All the reagents and starting materials were purchased from commercial suppliers and used without further purification unless otherwise noted. NMR spectra measurements were carried out on a Bruker Avance 400 MHz for ¹H NMR, 100 MHz for ¹³C NMR and 376 MHz for ¹⁹F NMR. Fluorescence and UV–vis absorption spectra were recorded on a Hitachi F-4700 fluorescence spectrophotometer and a Shimadzu UV-1800 UV spectrophotometer, respectively. High resolution mass spectra were obtained on a Thermo Scientific Q Exactive Mass spectrometer. X-ray single-crystal diffractions was carried out on a Bruker SMART APEX II diffractometer with Mo Ka radiation ($\lambda = 0.71000$ Å). The structures were solved with direct method (SHELX-97) and refined with full-matrix least-squares technique. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were geometrically placed. Relevant crystal collection data, refinement data for the crystal structures were listed in the electronic supporting information (ESI).

4.2. Synthesis of CMNT [3-thienyl-7-diethylamino coumarin]

An acetic anhydride (10 mL) solution of compound 4-(diethylamino)-2-hydroxy-benzaldehyde (0.50 g, 2.60 mmol), 2-thiophene acid (0.47 g, 2.80 mmol) and several drops of triethylamine (3 mL) were charged sequentially into a three-necked flask. The reaction mixture was stirred for 8 h at 139 °C. After cooling to room temperature, the reaction mixture was poured into water and NaHCO₃ was added to neutralize the acetic anhydride. The water phase was extracted with dichloromethane. The organic extracts were combined and dried over anhydrous MgSO₄. After filtration and concentration under reduced pressure, the crude product was purified using a silica column with petroleum: ethyl acetate (20: 1, v: v) as eluent to afford **CMNT** as a yellow powder (0.55 g, yield 71%). ¹H NMR (400 MHz, DMSO d_6) δ 8.37 (s, 1H), 7.74–7.65 (m, 1H), 7.61–7.47 (m, 2H), 7.13 (dd, J = 5.0, 3.8 Hz, 1H), 6.76 (dd, J = 8.9, 2.4 Hz, 1H), 6.59 (d, J = 2.2 Hz, 1H), 3.45 (q, J = 7.0 Hz, 4H), 1.14 (t, J = 7.0 Hz, 6H). ¹³C NMR (100 MHz, DMSO) δ 172.6, 160.6, 156.1, 151.4, 138.3, 137.7, 130.5, 128.0, 127.4, 125.1, 113.9, 110.5, 109.0, 97.1, 45.1, 13.3 (Fig. S8). FTMS + p ESI: m/z [M + H]⁺ cacld: C₁₇H₁₈NO₂S, 300.10528, found: 300.10535.

4.3. Synthesis of CMT [3-thienyl coumarin]

An acetic anhydride (10 mL) solution of 2-hydroxybenzaldehyde (0.32 g, 2.6 mmol), 2-thiophene acid (0.47 g, 2.80 mmol) and triethylamine (3 mL) were charged sequentially into a three-necked flask. The reaction mixture was stirred overnight at 110 °C. After cooling to room temperature, the reaction mixture was poured into water and neutralize by NaHCO₃. The water phase was extracted with dichloromethane. The organic extracts were combined and dried over anhydrous MgSO₄. After filtration and concentration under reduced pressure, the product **CMT** was obtained as a yellow powder by a silica column with hexane/EtOAc (9: 1, v: v) as eluent (0.55 g, yield 71%). ¹H NMR (400 MHz, CDCl₃): δ 7.99 (s, 1H), 7.80 (dd, J = 3.8, 1.1 Hz, 1H), 7.56–7.48 (m, 2H), 7.42 (dd, J = 5.1, 1.1 Hz, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.30 (td, J = 7.6, 1.1 Hz, 1H), 7.12 (dd, J = 5.1, 3.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 159.4, 152.6, 135.9, 135.5, 131.2, 127.7, 127.5, 127.1, 124.7, 121.8, 119.3,

116.4, 77.3, 77.0, 76.7.(Fig. S9). FTMS + p ESI: m/z [M + H]⁺ cacld: C₁₃H₉O₂S, 229.03178, found: 229.03181.

4.4. Spectra measurements

The stock solution of **CMNT** was prepared in anhydrous dimethyl sulfoxide (DMSO) to afford a concentration of 1×10^{-3} M stock solution, and then diluted to 2×10^{-5} M with DCM. BF₃·Et₂O was used as the source of BF₃, and diluted with anhydrous Et₂O to concentrations of 1×10^{-3} M and 2×10^{-5} M, respectively. Other analytes (1×10^{-3} M and 2×10^{-5} M) were prepared with anhydrous ethanol. The titrations were performed in 10-mm quartz cuvettes at room temperature. The excitation and emission slit widths were 5.0 nm and 5.0 nm, respectively.

4.5. Preparation of test strip and rewritable paper

Test strips were prepared by soaking neutral filter paper to the solution of CMNT in dichloromethane (1 \times 10⁻³ or 1 \times 10⁻⁶ M) and drying in air at room temperature.

CRediT authorship contribution statement

Lian Duan: Conceptualization, MethodologyMeodology, Writing – review & editing. Shu Wang: Experiment, Paper revising, Writing – review & editing. Huijun Zhao: Data curation, Writing – original draft. Tong Wu: Experiment, Data collecting. Da Li: Devices testing. Li Guo: Experiment, Data collecting. Xiaozhong Liang: Devices testing. Yue Sun: Supervision, Funding acquisition. Kunpeng Guo: Conceptualization, Supervision. Jie Li: Writing – review & editing, English polishing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (21301126), the Natural Science Foundation of Shanxi Province (2013021009–3, 201701D221038) and Scientific and Technological Innovation Programs of Higher Education and Institutions in Shanxi (STIP) (2017128).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109605.

References

- [1] Fang WY, Zhao W, Pei P, Liu R, Zhang YY, Kong L, Yang JX. A-shaped cyanostilbene derivative: multi-stimuli responsive fluorescence sensors, rewritable information storage and colour converter for w-LEDs. J Mater Chem C 2018;6: 9269–76. https://doi.org/10.1039/C8TC02973C.
- [2] Abdollahi A, Zangabad KS, Mamaqani HR. Rewritable anticounterfeiting polymer inks based on functionalized stimuli-responsive latex particles containing spiropyran photoswitches: reversible Photopatterning and Security Marking. ACS Appl Mater Interfaces 2018;10:39279–92. https://doi.org/10.1021/ acsami.8b14865.
- [3] Zeinali E, Asl VH, Mamaqani HR. Synthesis of dual thermo- and pH-sensitive poly (N-isopropylacrylamide-co-acrylicacid)-grafted cellulose nanocrystals by reversible additionfragmentation chain transfer polymerization. J Biomed Mater Res 2018; 106:231–43. https://doi.org/10.1002/jbm.a.36230.
- [4] Ji YC, Peng Z, Tong B, Shi JB, Zhi JG, Dong YP. Polymorphism-dependent aggregation-induced emission of pyrrolopyrrole-based derivative and its multistimuli response behaviors. Dyes Pigments 2017;139:664–71. https://doi.org/ 10.1016/j.dyepig.2016.12.061.

- [5] Bhat A, Boadu JMA, Elie AG. Toward impedimetric measurement of acidosis with a pH-responsive hydrogel sensor. ACS Sens 2020;5:500–9. https://doi.org/10.1021/ acssensors.9b02336.
- [6] Echeverri M, Ruiz C, Valenzuela SG, Navarro MA, Puebla EG, Serrano JL, Delgado MCR, Lor BG. Stimuli-responsive benzothiadiazole derivative as a dopant for rewritable polymer blends. ACS Appl Mater Interfaces 2020;12:10929–37. https://doi.org/10.1021/acsami.9b21209.
- [7] Wang Y, Xiang HK, Zhao RR, Huang CS. A renewable test strip combined with solid-state ratiometric fluorescence emission spectra for the highly selective and fast determination of hydrazine gas. Analyst 2018;143:3900–6. https://doi.org/ 10.1039/C8AN00903A.
- [8] Kumar P, Ghosh A, Jose DA. Simple colorimetric sensor for the detection of moisture in organic solvents and building materials: applications in rewritable paper and fingerprint imaging. Analyst 2019;144:594–601. https://doi.org/ 10.1039/C8AN01042K.
- [9] Liu YC, Yin ZR, Jin LY, Yin BZ. Monopyrrolotetrathiafulvalene-based supramolecular organogels: multi-stimuli responsiveness and formation of chargetransfer salt gels. Dyes Pigments 2017;140:500–11. https://doi.org/10.1016/j. dyepig.2016.10.025.
- [10] Yang XF, Zhu FQ, Li YX, Yan M, Cui Y, Sun GX. Three indole derived azoazomethine dyes as effective chemosensors for F⁻ ion and trace water detection. Bull Chem Soc Jpn 2020;93:870–9. https://doi.org/10.1246/bcsj.20200003.
- [11] Yang W, Yang YY, Zhan LS, Zheng KL, Chen ZX, Zeng X, Gong SL, Yang CL. Polymorphism-dependent thermally activated delayed fluorescence materials with diverse three dimensional supramolecular frameworks. Chem Eng J 2020;390: 124626. https://doi.org/10.1016/j.cej.2020.124626.
- [12] Urano Y, Asanuma D, Hama Y, Koyama Y, Barrett T, Kamiya M, Nagano T, Watanabe T, Hasegawa A, Choyke PL, Kobayashi H. Selective molecular imaging of viable cancer cells with pH-activatable fluorescence probes. Nat Med 2009;15: 104–9. https://doi.org/10.1038/nm.1854.
- [13] Dong ZM, Ren H, Wang JN, Wang Y. A new naphthopyran-based chemodosimeter with aggregation-induced emission: selective dual-channel detection of cyanide ion in aqueous medium and test strips. Microchem J 2020;155:104676. https://doi. org/10.1016/j.microc.2020.104676.
- [14] Khazi MI, Jeong W, Kim JM. Functional materials and systems for rewritable paper. Adv Mater 2018;30:15. https://doi.org/10.1002/adma.201705310.
- [15] Dong YB, Zhang J, Li AS, Gong JY, He BZ, Xu SP, Yin J, Liu SH, Tang BZ. Structuretuned and thermodynamically controlled mechanochromic self-recovery of AIEactive Au(i) complexes. J Mater Chem C 2020;8:894–9. https://doi.org/10.1039/ C9TC06297A.
- [16] Sun H, Li JY, Han FF, Zhang R, Zhao Y, Miao BX, Ni ZH. Reversible photochromic tetraphenylethene-based Schiff base: design, synthesis, crystal structure and applications as visible light driven rewritable paper and UV sensor. Dyes Pigments 2019;167:143–50. https://doi.org/10.1016/j.dyepig.2019.04.025.
- [17] Li D, Wei J, Dong S, Li HN, Xia YG, Jiao XL, Wang T, Chen DR. Novel PVP/HTA hybrids for multifunctional rewritable paper. ACS Appl Mater Interfaces 2018;10: 1701–6. https://doi.org/10.1021/acsami.7b15483.
- [18] Gao ZP, Liu LT, Tian Z, Feng ZY, Jiang BL, Wang WS. Fast-response flexible photochromic gels for self-erasing rewritable media and colorimetric oxygenindicator applications. ACS Appl Mater Interfaces 2018;10:33423–33. https://doi.org/10.1021/acsami.8b09825.
- [19] Chen LZ, Weng MC, Huang F, Zhang W. Long-lasting and easy-to-use rewritable paper fabricated by printing technology. ACS Appl Mater Interfaces 2018;10: 40149–55. https://doi.org/10.1021/acsami.8b14625.
- [20] Hariharana PS, Pitchaimanib J, Madhu V, Anthonya SP. A halochromic stimuliresponsive reversible fluorescence switching 3, 4, 9, 10-perylene tetracarboxylic acid dye for fabricating rewritable platform. Opt Mater 2017;64:53–7. https://doi. org/10.1016/j.optmat.2016.11.036.
- [21] Wang J, Li DQ, Qiu Y, Liu XY, Huang L, Wen HM, Hu J. An europium functionalized carbon dot-based fluorescence test paper for visual and quantitative point-of-care testing of anthrax biomarker. Talanta 2020;220:121377. https://doi. org/10.1016/j.talanta.2020.121377.
- [22] Wu LL, Li XL, Huang CS, Jia NQ. Dual-modal colorimetric/fluorescence molecular probe for ratiometric sensing of pH and its application. Anal Chem 2016;88: 8332–8. https://doi.org/10.1021/acs.analchem.6b02398.
 [23] Delavari S, Ziadzadea S, Rad JK, Hamrang V, Mahdavian AR. Anticounterfeiting
- [23] Delavari S, Ziadzadea S, Rad JK, Hamrang V, Mahdavian AR. Anticounterfeiting and photoluminescent cellulosic papers based on fluorescent acrylic copolymer nanoparticles containing coumarin, Carbohydrate Polymers. Carbohydr Polym 2020;247:116756. https://doi.org/10.1016/j.carbpol.2020.116756.
- [24] Zhang GH, Zheng H, Guo MY, Du L, Liu GJ, Wang P. Synthesis of polymeric fluorescent brightener based on coumarin and its performances on paper as light stabilizer, fluorescent brightener and surface sizing agent. Appl Surf Sci 2016;367: 167–73. https://doi.org/10.1016/j.apsusc.
- [25] Abdollahi A, Sharif HA, Mamaqani HR, Herizchic A. Photoswitchable fluorescent polymer nanoparticles as high-security anticounterfeiting materials for authentication and optical patterning. J Mater Chem C 2020;8:5476–93. https:// doi.org/10.1039/D0TC00937G.
- [26] Wang DC, Qiu CW, Hong MH. Coupling effect of spiral-shaped terahertz metamaterials for tunable electromagnetic response. Appl Phys A 2014;115:25–9. https://doi.org/10.1007/s00339-013-7928-4.
- [27] Hernández JO, Portilla J. Synthesis of Dicyanovinyl-substituted 1-(2-Pyridyl) pyrazoles: design of a fluorescent chemosensor for selective recognition of cyanide. J Org Chem 2017;82:13376–85. https://doi.org/10.1021/acs.joc.7b02460.
- [28] Macharia DK, Ahmed S, Zhu B, Liu ZX, Wang ZJ, Mwasiagi JJ, Chen ZG, Zhu MF. UV/NIR-light-triggered rapid and reversible color switching for rewritable smart

L. Duan et al.

fabrics. ACS Appl Mater Interfaces 2019;11:13370–9. https://doi.org/10.1021/acsami.8b22443.

- [29] Li NN, Liu WB, Shi NN, Yang D, Zong Z, Zhang X, Wu RX, Xu CG, Bi SY, Fan YH. Multiple naphthalimide dimers polymorphs triggered solvatofluorochromism, solid-state emission and aggregation-induced emission by different interaction and its application in fluorescence ratiometric sensing of dichloromethane and 1,4dioxane. Dyes Pigments 2021;188:109172. https://doi.org/10.1016/j. dyepig.2021.109172.
- [30] Duan L, Yan XY, Guo L, Wu T, Zhang F, Gao L, Guo KP, Sun Y, Miao YQ. Slight substituent modification in coumarin molecular structures for strong solid emission and application in light-emitting devices. Dyes Pigments 2020;174:108117. https://doi.org/10.1016/j.dyepig.2019.108117.
- [31] Jhun BH, Ohkubo K, Fukuzumi S, You Y. Synthetic control over intra- and intermolecular charge transfer can turn on the fluorescence emission of non-

emissive coumarin. J Mater Chem C 2016;4:4556–67. https://doi.org/10.1039/C6TC00639F.

- [32] Choi MG, Lee SH, Jung YU, Hong JM, Chang SK. Fluorescence signaling of BF₃ species by transformation of an ESIPT dye to its difluoroboron adduct. Sens Actuators, B 2017;251:713–9. https://doi.org/10.1016/j.snb.2017.05.098.
- [33] Wang YZ, Yang Y, Qiu FZ, Feng Y, Song XR, Zhang GL, Liu WS. A reversible and colorimetric fluorescence probe for highly sensitive detection of toxic BF₃ in air. Sens Actuators, B 2018;276:166–72. https://doi.org/10.1016/j.snb.2018.08.095.
- [34] Wang ZL, Zhang Y, Song J, Wang YY, Li MX, Yang YQ, Xu X, Xu HJ, Wang SF. Two ultrafast responsive isolongifolanone based fluorescent probes for reversible and sensitive visualization of toxic BF₃ in solution and in gas phase, Sens. Actuators B 2020;304:127083. https://doi.org/10.1016/j.snb.2019.127083.