A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Loading Photochromic Molecule into Luminescent Metal-Organic Framework for Potential Information Anti-counterfeiting

Authors: Banglin Chen, Zhiqiang Li, Guannan Wang, Bin Li, Yingxiang Ye, and Huanrong Li

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.201910467
Angew. Chem. 10.1002/ange.201910467

Link to VoR: http://dx.doi.org/10.1002/anie.201910467
http://dx.doi.org/10.1002/ange.201910467

WILEY-VCH

Loading Photochromic Molecule into Luminescent Metal-Organic Framework for Potential Information Anti-counterfeiting

Zhiqiang Li,[ab] Guannan Wang,[a] Yingxiang Ye,[b] Bin Li,[a] Huanrong Li*[a] and Banglin Chen*[b]

Abstract: Stimuli-responsive photoluminescent materials have attracted particular attention due to their potential applications in security protection field, because the data or information recorded directly in materials with static luminescent outputs are usually visible under either ambient or UV light. Especially the ones with remote control over reversible luminescence ON-OFF switch behavior are extremely expected, as reversible visible/invisible information transformation can be achieved in a noninvasive manner. Herein, we realize reversible information anti-counterfeiting via loading photoswitchable diarylethene derivative into lanthanide metal-organic framework (MOF). The light triggers open and close isomerization of the diarylethene unit, which respectively regulates the inactivation and activation of the photochromic FRET process between diarylethene acceptor and lanthanide donor, resulting in reversible luminescence ON-OFF of lanthanide emitting center in MOF host. This photoresponsive host-guest system allows for reversible multiple information pattern visible/invisible transformation by simply alternating the exposure to UV and visible lights.

Introduction

Photoluminescent materials have attracted considerable attention due to their widely application in data recording, storage and security technologies.[1] However, materials with static luminescent outputs are adverse to their practical application in confidential information protection, because the data or information recorded directly in these materials are usually visible under either ambient or the excitation of NIR or UV light.[2] In this context, smart luminescent materials, which can change their luminescent outputs in response to external stimuli, and possess extra security features, have been regarded as ideal alternate candidates to prevent tampering or counterfeiting.[3] Amongst them, the ones with luminescence ON-OFF switch behavior are extremely interesting, as reversible visible/invisible information transformation can be achieved. In this case, the information pattern is usually invisible under normal condition, while only become visible when needed, making it nearly impossible to mimic and counterfeit. In recent years, thermal-responsive,[4] chemical-responsive,[5] mechanical-responsive[6] and electrochromic[7] luminescent materials have been explored. However, these stimuli-responsive luminescent materials either rely on constant addition of chemicals or require invasive stimuli, which are not only harmful to environment and humans, but also inconvenient for suppliers and consumers without professional chemistry knowledge to handle the anti-counterfeiting operation. On the other hand, some of these responses are irreversible.[8] As a result, the quenched luminescence cannot recover anymore.[2a] The encoded information is irreversibly destroyed, rather than temporarily hided. In contrast, photoresponsive luminescent materials are appealing candidates, because light irradiation has the possibility to remote trigger cleanly and spatiotemporally control over the action with high precision.[9] Moreover, photoswitchable materials can be reversibly interconverted between two discrete states with drastic different optical outputs upon alternative light trigger, showing much more convenience in displaying or erasing the encoded information in a noninvasive manner.[10]

In terms of emitting centers, lanthanides are widely believed to be ideal emitting sources because of their intriguing optical properties, such as high luminescence quantum yield, long excited lifetime, large Stokes shifts and characteristically narrow emissions.[11] As an emerging class of crystalline materials that combine the stability and porosity with the chemical tunability of traditional organic chemistry, metal-organic frameworks (MOFs) have attracted vast attention in various fields.[12] Lanthanide MOFs, assembled by lanthanide ions with organic bridging linkers are very promising platforms to explore versatile luminescent materials.[11d, 13] The emission colors, excitation bands as well as pores/channels can be finely tuned by varying the lanthanide ions and organic linkers.[14] Intelligent MOF materials with remote-controllable capacity can be achieved by incorporating photoswitchable molecules.[15] However, besides tedious synthesis of organic linkers, directly integrating photochromic units as part of the linker molecules and incorporating them into the backbone of MOF structures also usually lead to limited isomerization yield and slow isomerization speed, since isomerization are hindered in the rigid crystalline frameworks.[16] Recently, encapsulating functional guest molecules into porous MOFs has been proved to be a feasible strategy to boost the application of MOFs by us and other groups.[17] Several photoswitchable molecules were also encapsulated into the cavity of MOFs to adjust their flexibilities and adsorption behaviors, etc.[18] To the best of our knowledge, there is only one report about loading photochromic molecule into MOFs cavity for data storage. However, it still need the co-stimulation of light and heat with harsh condition for long time to realize transformation between two different emission wavelengths, rather than ON-OFF switch.[19] Therefore, photoswitch loaded luminescent MOFs with information protection property capable of being easily operated in a noninvasive manner are still highly desired.

Herein, we demonstrate an approach to realize reversible confidential information protection based on remote control over photoresponsive luminescence ON-OFF of photoswitch loaded lanthanide MOF. Diarylethene is chosen as photoswitch, since it is regarded as the shining star in photochromic realm due to its thermal irreversibility and excellent fatigue resistance, high

---

[a] Dr. Z. Li, G. Wang, B. Li, Prof. Dr. H. Li
Tianjin Key Laboratory of Chemical Process Safety, School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, P. R. China.
E-mail: lihuanrong@hebutedu.cn
[b] Dr. Z. Li, Y. Ye, Prof. Dr. B. Chen
Department of Chemistry, University of Texas at San Antonio, San Antonio, TX 78249, USA.
E-mail: banglin.chen@utsa.edu
Supporting information for this article is given via a link at the end of the document.

10.1002/anie.201910467

speed photoresponse, and good performances in both solution and solid phase.[20] To transfer the reversible ring-closing and ring-opening isomerization of diarylethene unit to the luminescence switching, Eu^{3+} ion possessing spectral overlapping with the diarylethene isomer is introduced to construct the host luminescent MOF. For example, there is no spectral overlap between the absorption band of the open form diarylethene and the emission band of Eu^{3+}, the host MOF exhibits characteristic emission of Eu^{3+} and the encoded information is readable. While there is perfect spectral overlap between the absorption of close form diarylethene and the emission of Eu^{3+}, leading to the luminescence quench of Eu^{3+} attributed to the activation of the photochromic fluorescence resonance energy transfer (FRET) between Eu^{3+} and diarylethene. As a result, the security code becomes invisible and unreadable. Hence, the photo triggers open and close isomerization of the diarylethene unit, and thus regulates the inactivation and activation of the FRET process, resulting in a reversible luminescence ON-OFF switch of Eu^{3+} emitting center in the diarylethene loaded lanthanide MOF, which is capable of conducting reversible multiple security data protection.

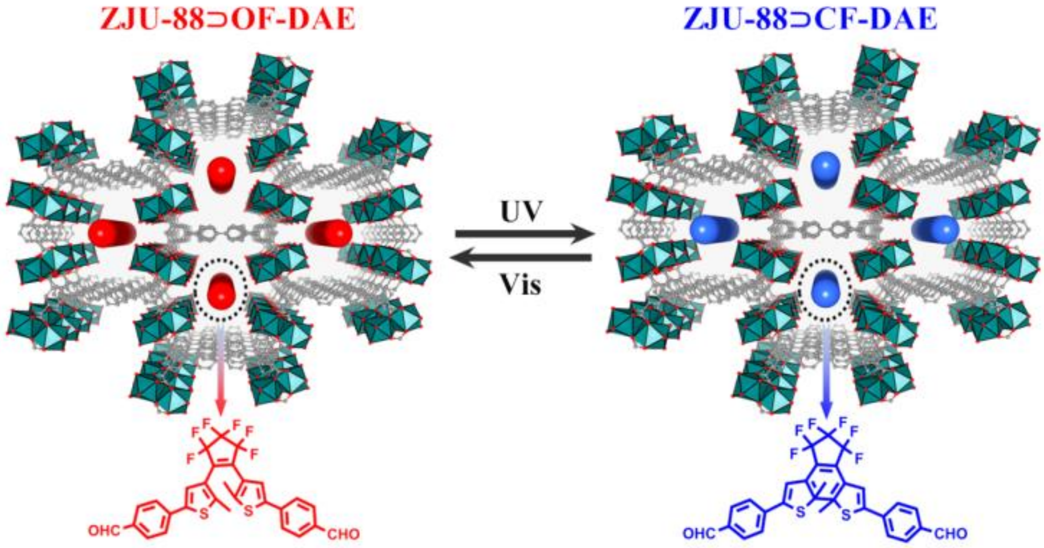


Figure 1. Schematic illustration of photochromic **DAE** chromophores incorporated into **ZJU-88**, and photoswitchable isomerization behavior of **ZJU-88⊃OF-DAE** under alternating UV and visible light irradiation.

Results and Discussion

Host MOF **ZJU-88** with a chemical composition of $[Eu_2(QPTCA)(NO_3)_2(DMF)_4]\cdot(CH_3CH_2OH)_3$ was prepared by reaction of 1,1′:4′,1″:4″,1‴-quaterphenyl-3,3‴,5,5‴-tetracarboxylic acid (H_4QPTCA) with $Eu(NO_3)_3$ according to our previous method.[21] The crystal of **ZJU-88** has one-dimensional channels along the *c*-axis of about 8 × 12 Å^2, which are large enough to encapsulate 1,2-Bis(2-methyl-5-(4-formylphenyl)-thiophen-3-yl)hexafluorocyclopentene (**OF-DAE**) (23.38 ×8.98 × 7.75 Å) molecules (Figure S1).[22] **ZJU-88⊃OF-DAE** was obtained as white powder after loading **OF-DAE** into **ZJU-88** (see Experimental Section in supporting information). Powder X-ray diffraction (PXRD) after loading showed that the 2θ positions of all characteristic reflections remain unchanged compare to **ZJU-88** (Figure 2), demonstrating the retention of crystalline MOF backbone. The PXRD signal/noise ratio became lower after loading, in addition to decreased size, this may be also attributed to partial framework defects induced by mechanical force. However, compare to **ZJU-88**, the PXRD peak intensity of **ZJU-88⊃OF-DAE** didn't decreased a lot, and all the characteristic peak of **ZJU-88** were maintained. This phenomenon revealed that the vast majority of frameworks were retained after loading. Besides, characteristic vibration peaks of **OF-DAE** was observed in the FT-IR spectra of **ZJU-88⊃OF-DAE** (Figure S2). S element was also detected in elemental analysis of **ZJU-88⊃OF-DAE** (Table S1). These results indicated that **DAE** had been successfully loaded into MOF host. To distinguish whether **DAE** was loaded into the MOF pores or adsorbed on the MOF surface, we carried out the following control experiment: **ZJU-88** and **OF-DAE** were individually ground for 2 h, and then mixed without further grinding, washed repeatedly with EtOH. We then monitored the UV-Vis absorption spectra of the wash filtrate of both **ZJU-88⊃OF-DAE** and the control group (Figure S3). The results revealed that the **DAE** in the eluate of **ZJU-88⊃OF-DAE** was in two states (in pores and surface adsorbed), while the **DAE** in that of the control group was in one state (surface adsorbed). In addition, the surface adsorbed **DAE** can be completely washed away in three times (Figure S3B and 3D). ^{1}H NMR spectra (Figure S4A) of acid digested **ZJU-88⊃OF-DAE** revealed the molar ratio of H_4QPTCA to **DAE** is about 7 (Eu^{3+}: **DAE** =14:1), which is consistent with that obtained by elemental analysis (Table S1). while no obvious **DAE** peaks were observed in the ^{1}H NMR spectra of the control group after washing for three times (Figure S4B). Meanwhile, compare to **ZJU-88**, the DMF content in **ZJU-88⊃OF-DAE** underwent an obvious decrease (about 53.3% according to the ^{1}H NMR integral data), implying that the included solvent had been partially squeezed out the channel of **ZJU-88** host by the guest molecules (Figure S5). In order to further obtain molecular level information of **ZJU-88⊃OF-DAE**, we measured the survey XPS spectra of both **ZJU-88** and **ZJU-88⊃OF-DAE** surface (Figure S6). The presence of F 1s and S 2p peaks in **ZJU-88⊃OF-DAE** XPS spectra confirmed the existence of **DAE** in the host-guest complex. We then etched **ZJU-88⊃OF-DAE** to 20 nm depth and collected the elemental composition of 20 nm depth, where F 1s and S 2p peaks were also detected. This result demonstrated that **DAE** also existed in the MOF pores, rather than simply adsorbed on the MOF surface. More importantly, the F and S contents at 20 nm depth were slightly higher compare to the **ZJU-88⊃OF-DAE** surface. This can be explained as follow: although the **DAE** at outer wall of MOF has been wash away, the surface XPS test usually penetrate and collect elemental information of the superficial several nanometers, rather than the outermost surface. However, **DAE** at the outer wall of MOF had been wash away, as a result, the F and S contents of the surface test is only slightly lower than that of 20 nm depth. These results also provided powerful evident that **DAE** had been successfully loaded into the MOFs host. Moreover, XPS scanning at different areas of **ZJU-88⊃OF-DAE** showed similar element composition, revealing that **DAE** guest distributed homogeneously in **ZJU-88⊃OF-DAE** crystal blocks. These results jointly confirmed that the **OF-DAE** molecules have been embedded within **ZJU-88**.

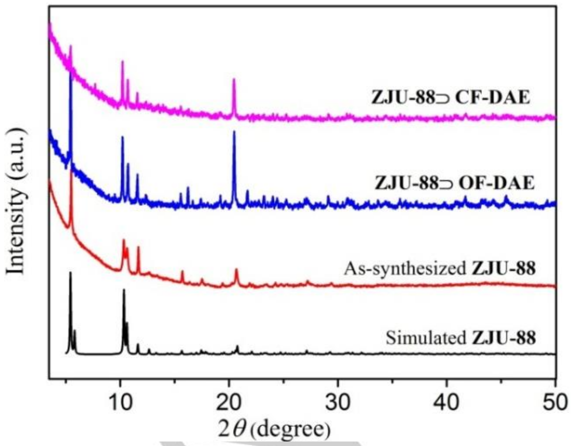


Figure 2. PXRD patterns of **ZJU-88**, and **ZJU-88⊃OF-DAE** before and after (**ZJU-88⊃CF-DAE**) irradiated with 300 nm UV light for 60 seconds.

We then investigated the photoluminescence behaviors of the host-guest system. The excitation spectrum of **ZJU-88⊃OF-DAE** by monitoring the $^5D_0\rightarrow{}^7F_2$ transition showed a broad band in the range of 250-400 nm, corresponding to the absorption of H_4QPTCA ligands, and thus indicates the occurrence of energy transfer from ligand to metal (Figure S7).[23] When excited at 350 nm, the emission spectrum of **ZJU-88⊃OF-DAE** powder displayed five sharp peaks at 579, 590, 613, 650, and 698 nm, attributing to the $^5D_0\rightarrow{}^7F_J$ (J = 0–4) transitions. Amongst these peaks, the $^5D_0\rightarrow{}^7F_2$ band at 613 nm is predominantly responsible for the emission color in red. The quantum yield of **ZJU-88⊃OF-DAE** was determined to be 7.16%, indicating sufficient brightness for luminescent applications.

Next, we investigated the photoresponse of **ZJU-88⊃OF-DAE** as a result of the isomerization of **DAE** moieties. Before loaded into **ZJU-88**, UV–Vis (Figure S8) and ^{1}H NMR spectra (Figure S9) revealed individual **DAE** underwent reversible open and close isomerization quantitatively upon alternating exposure to UV and visible light.[24] In the as-prepared **ZJU-88⊃OF-DAE** white powder, since **DAE** was in the open configuration and showed the absorption below 400 nm, there was no spectral overlap between the emission of **ZJU-88** and the absorption of **OF-DAE** (Figure 3A). As a result, **ZJU-88⊃OF-DAE** exhibited the characteristic color and brightness of Eu^{3+} ions under 365 nm light, as no FRET occurred. After irradiated with 300 nm UV light, the white host-guest inclusion complex turned to blue. This is because **DAE** switched from open form (**OF-DAE**) to close form (**CF-DAE**) with a new absorption band in the range of 500-700 nm, which is perfectly overlapped with the emission spectrum of **ZJU-88** host (Figure 3A). Meanwhile, the luminescence of **ZJU-88⊃CF-DAE** quenched gradually and reached to the equilibrium in 60 s (Figure 3B). The luminescence quenching followed a biexponential attenuation law (Figure S10), underwent a fast process, followed by a slow process to the photo steady state. At the end point, the luminescence intensity was quenched by 91% with concomitant decreases of the decay from 540 μs to 65 μs (Figure S11). These observations jointly indicated the occurrence of the FRET from the Eu^{3+} donor in **ZJU-88** to the **CF-DAE** acceptor. The FRET efficiency (*E*) was calculated to be 88% according to the reported methods.[25] To be noticed, the confinement of **DAE** within the **ZJU-88** is essential to draw the donor and acceptor in close proximity, which plays vital role in facilitating high efficiency FRET.[26] Non-porous Eu/2,6-pyridinedicarboxylic acid complex[27] Eu(PDA)$_3$, which also has spectral overlap with **CF-DAE**, was taken as a model compound and mixed with **OF-DAE** in EtOH. However, after irradiated with 300 nm UV light for 60 seconds, no effective FRET was observed in the mixture (Figure S12). Interestingly, upon subsequent irradiation with visible light (λ > 450 nm), the luminescence of quenched **ZJU-88⊃CF-DAE** recovered in 90 s and the PL intensity reached to 96% of the original value accompanied with the color change back to white, arising from the reverse photoisomerization back to **OF-DAE** (Figure 3C). The fatigue resistance of **ZJU-88⊃DAE** was further examined after 20 consecutive cycle irradiation of UV (300 nm, 60 s) and visible light (> 450 nm, 90 s), and the results are shown in Figure S13. Negligible decrease in PL intensity was observed, implying excellent fatigue resistance of our host-guest system, which are of utmost important for photochromic optical memory and data storage materials.

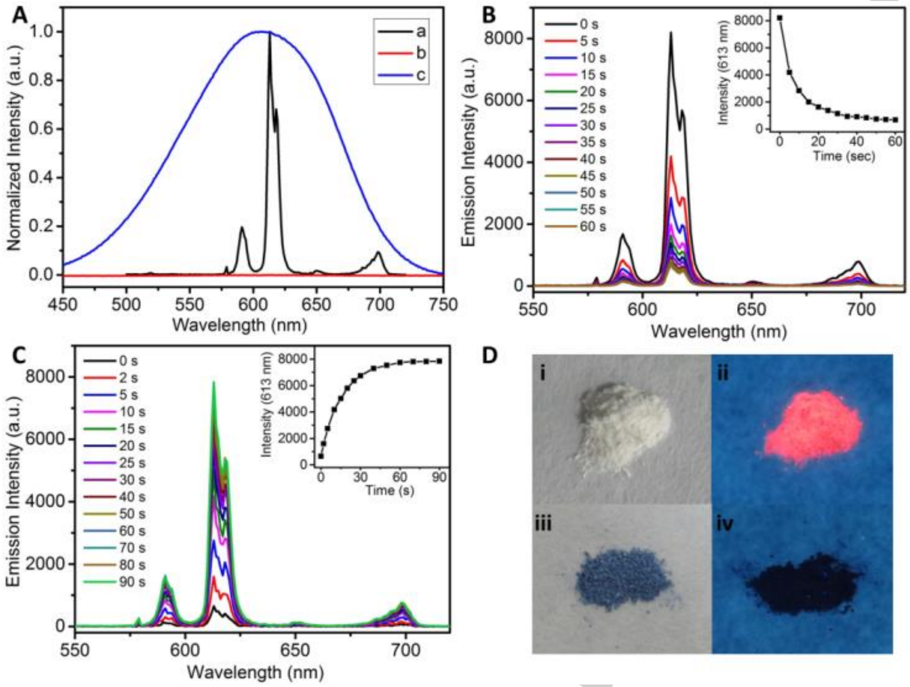


Figure 3. (A) Normalized emission spectra of **ZJU-88⊃OF-DAE** (a), as well as absorption spectra of **OF-DAE** (b) and **CF-DAE** (c). (B) Luminescence emission spectra (λ_{ex} = 350 nm) and emission intensity changes at 613 nm (inset) of **ZJU-88⊃OF-DAE** upon 300 nm UV light irradiation. (C) Luminescence emission spectral intensity and emission intensity changes at 613 nm (inset) of **ZJU-88⊃CF-DAE** upon subsequent irradiation with visible light (> 450 nm). (D) The photographs of **ZJU-88⊃OF-DAE** under daylight (i) and 365 nm UV lamp (ii), under daylight (iii) and 365 nm UV lamp (iv) after irradiated with UV light for 60s.

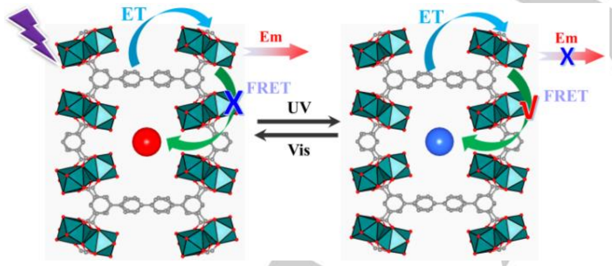


Figure 4. Schematic illustration of the photo triggered luminescent ON-OFF switch behavior of **ZJU-88⊃OF-DAE** under alternating UV and visible light irradiation

UV-Vis and ^{1}H NMR spectra provided important insight into the nature of the light-triggered luminescence ON-OFF switch of host-guest inclusion complex. After photo-irradiation of **ZJU-88⊃OF-DAE** with 300 nm UV light, the resulting blue powder was digested by hydrochloric acid and diluted by DMSO, then monitored by UV-Vis analysis (Figure S14). The absorption peak at 330 nm decreased and the absorption at 607 nm increased, which explained the color change from white to blue, indicating the successful transformation to inherently thermal and daylight stable **OF-DAE** (Figure S15). In the ^{1}H NMR spectra (Figure 5), after 300 nm UV light irradiation, the thiophene protons (H_b) showed drastic upfield shift from 7.74 ppm to 7.18 ppm, while the methyl protons (H_a) also showed downfield shift from 2.03 ppm to 2.13 ppm. Meanwhile, the aldehyde proton (H_e) underwent downfield shift from 10.01 ppm to 10.08 ppm. However, it was difficult to monitor the chemical shifts of H_c and H_d due to the signal overlap with H_3 and H_4 protons of H_4QPTCA. All these shifts were complete and negligible signals were observed in the original chemical shifts of **OF-DAE**, indicating quantitative transition from **OF-DAE** to **CF-DAE** in this solid host-guest inclusion complex. The open to close form photo-isomerization yield was calculated to be 95.2% according to the integral of ^{1}H NMR[24a], which is much higher than that directly integrating **DAE** as MOFs backbone[16b] and is as good as that of diarylethene derivative monomers in other host-guest system.[10a, 28]

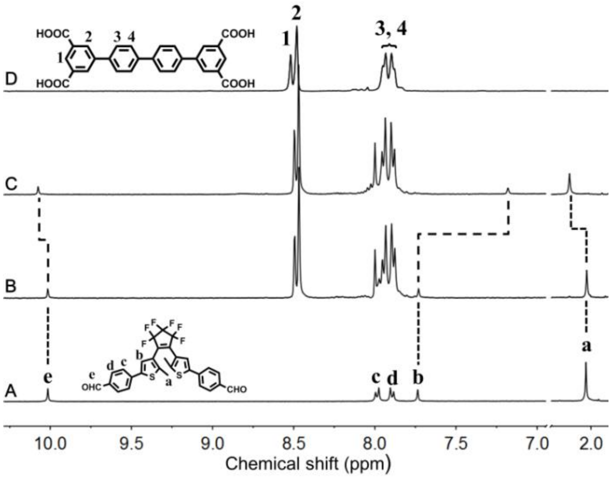


Figure 5. Partial ^{1}H NMR spectra of **OF-DAE** (A), **ZJU-88⊃OF-DAE** (B), **ZJU-88⊃CF-DAE** (C) and H$_4$QPTCA in DCl/DMSO-d_6 (1:10, v:v) at 25 °C.

Encouraged by the above findings, we designed a novel strategy for information coding and anti-counterfeiting by using this host-guest complex as invisible security ink. Various patterns with good resolution were obtained by spraying **ZJU-88⊃OF-DAE** ethanol suspension on filter paper with hollow out stencils, including the logo of Hebei University of Technology and QR code. For the sake of illustration, we programed the information in the QR code and loaded it to the website of our University. The logo was invisible under daylight (Figure S16A), and became visible under commercial portable UV lamp (365 nm), allowing for readout the stored information. Then we tried to erase the pattern with 300 nm UV light. After irradiating, the luminescence of the pattern quenched and cannot be read out anymore under the UV lamp, but the pattern turned to blue and became visible under daylight, failing in confidential information hiding (Figure S16C). In order to develop hidden label, we took blue filter paper with negligible auto fluorescence as the background (Figure 6 and Figure S17). The pattern was also invisible under daylight (Figure 6A and video S1) and readable under UV lamp by WeChat (Figure 6B and video S2), a commercially available smartphone app has more than one billion users in China, despite the luminescence intensity was lower than that on white filter paper. To be noticed, the main absorption band of **OF-DAE** peaked at 330 nm and the absorption at 365 nm was relatively weak (Figure S8). As a result, the light-triggered transformation process from **OF-DAE** to **CF-DAE** was slow under 365 nm UV lamp, which allowed enough time for the the coding information to be read out. Upon irradiated with 300 nm UV light, the quenched luminescence and blue background jointly promoted the really invisible (video S3) characteristic of **ZJU-88⊃CF-DAE** patterns (Figure 6C and 6D), which is essential and necessary for confidential information anti-counterfeiting. The erased pattern was very stable under daylight due to the thermal irreversibility nature of **DAE** derivatives, and remained unreadable even after several months. No obvious automatic recovery in UV–Vis spectra of both **ZJU-88⊃CF-DAE** (Figure S15) and **CF-DAE** (Figure S18) were observed after being placed under daylight for months. The quenched **ZJU-88⊃CF-DAE** pattern was also very stable, which was still invisible under both daylight and UV lamp during this period (Figure S19). Subsequent recognition process (video S4) can be conducted remotely by exposing the hidden pattern to visible light (>450 nm). This remote light-triggered reversible information hiding and recognition process showed good fatigue resistance and still remained unaffected even after 20 consecutive switching cycles (video S5), implying that our platform is suitable for multiple information anti-counterfeiting.

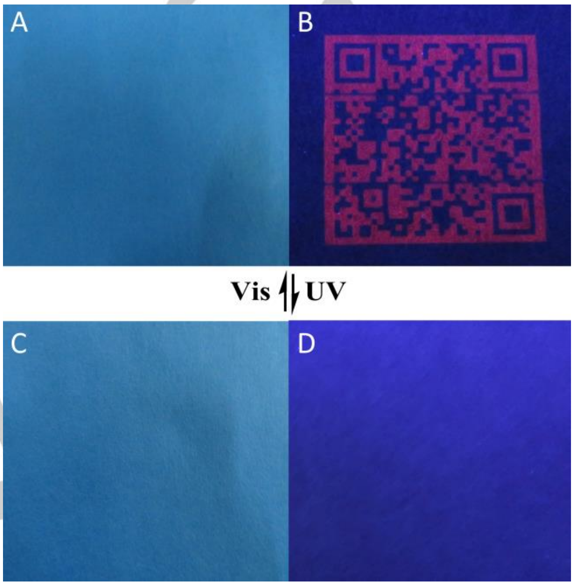


Figure 6. Light-triggered reversible information anti-counterfeiting behaviors of the host-guest complex. Photographs of the **ZJU-88⊃OF-DAE** luminescent QR code on blue filter paper (size: 6 × 6 cm) upon alternating UV (300 nm, 60 sec) and visible light (>450 nm, 90 sec) irradiation under daylight (A, C) and 365 nm UV lamp (B, D). Photographs of QR code before (Figure 6A, 6B) and after (Figure 6C, 6D) irradiated with 300 nm UV light.

Conclusion

In conclusion, we reported an approach to realize potential confidential information protection based on the solid state photoresponsive luminescence ON-OFF switch behavior of photochrome loaded lanthanide MOF. Owing to the FRET between Eu metal center and photochromic unit governed by the light triggered open and close isomerization of **DAE**, it was loaded into **ZJU-88** to produce photoswitchable luminescence host-guest complex. The information recorded in this anti-counterfeiting system could be precisely concealed and read out by simply alternating the irradiation with UV and visible light in a very short time, making it extremely attractive and suitable as the next generation of intelligent information protection material. As the emission and excitation wavelengths, pore sizes of MOFs host could be precisely tailored through the appropriate choice of various metal centers and organic linkers, this will nodoubt allow the MOFs host to load various photoswitchable molecules with diverse emission wavelengths. We believe this remote light triggered host-guest strategy will offer new insights in broadening the practical applications of MOFs.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (21871075, 21502039, 21771050), the Natural Science Foundation of Hebei Province (No. B2018202134, B2016202149, B2016202147 and B2017202048), and the Program for Top 100 Innovative Talents in Colleges and Universities of Hebei Province (No. SLRC2019023).

Conflict of interest

The authors declare no conflict of interest

Keywords: metal-organic framework • lanthanide • photoswitchable • host-guest system • information anti-counterfeiting

[1] a) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002,** *420*, 759-760; b) T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005,** *4*, 685-687; c) X. Hou, C. Ke, C. J. Bruns, P. R. McGonigal, R. B. Pettman, J. F. Stoddart, *Nat. Commun.* **2015,** *6*, 6884; d) P. Zijlstra, J. W. Chon, M. Gu, *Nature* **2009,** *459*, 410-413.

[2] a) X. Ji, R. T. Wu, L. Long, X. S. Ke, C. Guo, Y. J. Ghang, V. M. Lynch, F. Huang, J. L. Sessler, *Adv. Mater.* **2018,** *30*, 1705480; b) X. Chen, Q. Jin, L. Wu, C. Tung, X. Tang, *Angew. Chem., Int. Ed.* **2014,** *53*, 12542-12547; c) Q. Lou, S. Qu, P. Jing, W. Ji, D. Li, J. Cao, H. Zhang, L. Liu, J. Zhao, D. Shen, *Adv. Mater.* **2015,** *27*, 1389-1394; d) J. Wang, C. F. Wang, S. Chen, *Angew. Chem., Int. Ed.* **2012,** *51*, 9297-9301.

[3] a) Y. Sagara, S. Yamane, M. Mitani, C. Weder, T. Kato, *Adv. Mater.* **2016,** *28*, 1073-1095; b) K. Huang, N. M. Idris, Y. Zhang, *Small* **2016,** *12*, 836-852; c) S. J. Bradberry, A. J. Savyasachi, M. Martinez-Calvo, T. Gunnlaugsson, *Coord. Chem. Rev.* **2014,** *273*, 226-241; d) M.-K. Tsang, G. Bai, J. Hao, *Chem. Soc. Rev.* **2015,** *44*, 1585-1607; e) A. J. McConnell, C. S. Wood, P. P. Neelakandan, J. R. Nitschke, *Chem. Rev.* **2015,** *115*, 7729-7793.

[4] a) K. Jiang, Y. Wang, C. Cai, H. Lin, *Adv. Mater.* **2018,** *30*, 1800783; b) J. Yu, Y. Cui, C.-D. Wu, Y. Yang, B. Chen, G. Qian, *J. Am. Chem. Soc.* **2015,** *137*, 4026-4029.

[5] a) X. Li, Y. Xie, B. Song, H. L. Zhang, H. Chen, H. Cai, W. Liu, Y. Tang, *Angew. Chem., Int. Ed.* **2017,** *56*, 2689-2693; b) J. Hai, T. Li, J. Su, W. Liu, Y. Ju, B. Wang, Y. Hou, *Angew. Chem. Int. Ed.* **2018,** *57*, 6786-6790.

[6] a) H. Sun, S. Liu, W. Lin, K. Y. Zhang, W. Lv, X. Huang, F. Huo, H. Yang, G. Jenkins, Q. Zhao, *Nat. Commun.* **2014,** *5*, 3601; b) Y. Sagara, T. Kato, *Angew. Chem., Int. Ed.* **2011,** *50*, 9128-9132.

[7] a) K. Y. Zhang, X. Chen, G. Sun, T. Zhang, S. Liu, Q. Zhao, W. Huang, *Adv. Mater.* **2016,** *28*, 7137-7142; b) H. Xu, Q. Sun, Z. An, Y. Wei, X. Liu, *Coord. Chem. Rev.* **2015,** *293*, 228-249.

[8] X. Y. Xu, X. Lian, J. N. Hao, C. Zhang, B. Yan, *Adv. Mater.* **2017,** *29*, 1702298.

[9] a) M. M. Lerch, W. Szymański, B. L. Feringa, *Chem. Soc. Rev.* **2018,** *47*, 1910-1937; b) D.-H. Qu, Q.-C. Wang, Q.-W. Zhang, X. Ma, H. Tian, *Chem. Rev.* **2015,** *115*, 7543-7588; c) Z. Y. Li, J. W. Dai, M. Damjanović, T. Shiga, J. H. Wang, J. Zhao, H. Oshio, M. Yamashita, X. H. Bu, *Angew. Chem. Int. Ed.* **2019,** *58*, 4339-4344; d) Q. Yu, X. Yang, Y. Chen, K. Yu, J. Gao, Z. Liu, P. Cheng, Z. Zhang, B. Aguila, S. Ma, *Angew. Chem., Int. Ed.* **2018,** *57*, 10192-10196.

[10] a) H. Wu, Y. Chen, Y. Liu, *Adv. Mater.* **2017,** *29*, 1605271; b) Q. Qi, C. Li, X. Liu, S. Jiang, Z. Xu, R. Lee, M. Zhu, B. Xu, W. Tian, *J. Am. Chem. Soc.* **2017,** *139*, 16036-16039.

[11] a) J.-C. G. Bünzli, *Chem. Rev.* **2010**, *110*, 2729-2755; b) L. D. Carlos, R. A. Ferreira, V. de Zea Bermudez, B. Julian-Lopez, P. Escribano, *Chem. Soc. Rev.* **2011,** *40*, 536-549; c) K. Binnemans, *Chem. Rev.* **2009,** *109*, 4283-4374; d) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014,** *43*, 5815-5840.

[12] a) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013,** *341*, 1230444; b) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. R. Long, *Chem. Rev.* **2011,** *112*, 724-781; c) S. Kitagawa, R. Kitaura, S. i. Noro, *Angew. Chem., Int. Ed.* **2004,** *43*, 2334-2375; d) P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, *Nature* **2013,** *495*, 80-84; e) W. P. Lustig, S. Mukherjee, N. D. Rudd, A. V. Desai, J. Li, S. K. Ghosh, *Chem. Soc. Rev.* **2017,** *46*, 3242-3285; f) A. Lan, K. Li, H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. Hong, J. Li, *Angew. Chem., Int. Ed.* **2009,** *48*, 2334-2338; g) S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009,** *1*, 695-704; h) N. Zheng, X. Bu, B. Wang, P. Feng, *Science* **2002,** *298*, 2366-2369; i) L. Jiao, Y. Wang, H. L. Jiang, Q. Xu, *Adv. Mater.* **2018,** *30*, 1703663; j) H.-L. Jiang, Y. Tatsu, Z.-H. Lu, Q. Xu, *J. Am. Chem. Soc.* **2010,** *132*, 5586-5587; k) J. Della Rocca, D. Liu, W. Lin, *Acc. Chem. Res.* **2011,** *44*, 957-968.

[13] a) Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem. Rev.* **2011,** *112*, 1126-1162; b) Y. Cui, B. Chen, G. Qian, *Coord. Chem. Rev.* **2014,** *273*, 76-86; c) D. Ananias, A. D. Firmino, R. F. Mendes, F. A. A. Paz, M. Nolasco, L. D. Carlos, J. O. Rocha, *Chem. Mater.* **2017,** *29*, 9547-9554; d) L. Wang, H. Xu, J. Gao, J. Yao, Q. Zhang, *Coord. Chem. Rev.* **2019,** *398*, 213016.

[14] a) R. B. Lin, S. Y. Liu, J. W. Ye, X. Y. Li, J. P. Zhang, *Adv. Sci.* **2016,** *3*, 1500434; b) A. D. Firmino, F. Figueira, J. P. Tome, F. A. A. Paz, J. Rocha, *Coord. Chem. Rev.* **2018,** *355*, 133-149; c) J. Rocha, C. D. Brites, L. D. Carlos, *Chem. - Eur. J.* **2016,** *22*, 14782-14795; d) M. Pan, W.-M. Liao, S.-Y. Yin, S.-S. Sun, C.-Y. Su, *Chem. Rev.* **2018,** *118*, 8889-8935; e) W. J. Rieter, K. M. Taylor, W. Lin, *J. Am. Chem. Soc.* **2007,** *129*, 9852-9853.

[15] a) W. Danowski, T. van Leeuwen, S. Abdolahzadeh, D. Roke, W. R. Browne, S. J. Wezenberg, B. L. Feringa, *Nat. Nanotechnol.* **2019,** 14, 488-494; b) L. Heinke, C. Wöll, *Adv. Mater.* **2019,** *31*, 1806324; c) S. Garg, H. Schwartz, M. Kozlowska, A. B. Kanj, K. Müller, W. Wenzel, U. Ruschewitz, L. Heinke, *Angew. Chem., Int. Ed.* **2019,** *58*, 1193-1197; d) B. J. Furlong, M. J. Katz, *J. Am. Chem. Soc.* **2017,** *139*, 13280-13283.

[16] a) J. Park, D. Feng, S. Yuan, H. C. Zhou, *Angew. Chem., Int. Ed.* **2015,** *54*, 430-435; b) F. Luo, C. B. Fan, M. B. Luo, X. L. Wu, Y. Zhu, S. Z. Pu, W. Y. Xu, G. C. Guo, *Angew. Chem., Int. Ed.* **2014,** *53*, 9298-9301; c) D. E. Williams, C. R. Martin, E. A. Dolgopolova, A. Swifton, D. C. Godfrey, O. A. Ejegbavwo, P. J. Pellechia, M. D. Smith, N. B. Shustova, *J. Am. Chem. Soc.* **2018,** *140*, 7611-7622.

[17] a) J. Yu, Y. Cui, H. Xu, Y. Yang, Z. Wang, B. Chen, G. Qian, *Nat. Commun.* **2013,** *4*, 2719; b) H. He, E. Ma, Y. Cui, J. Yu, Y. Yang, T. Song, C.-D. Wu, X. Chen, B. Chen, G. Qian, *Nat. Commun.* **2016,** *7*, 11087; c) N. Yanai, K. Kitayama, Y. Hijikata, H. Sato, R. Matsuda, Y. Kubota, M. Takata, M. Mizuno, T. Uemura, S. Kitagawa, *Nat. Mater.* **2011,** *10*, 787-793; d) C. Zhang, B. Wang, W. Li, S. Huang, L. Kong, Z. Li, L. Li, *Nat. Commun.* **2017,** *8*, 1138; e) D. S. Zhang, Q. Gao, Z. Chang, X. T. Liu, B. Zhao, Z. H. Xuan, T. L. Hu, Y. H. Zhang, J. Zhu, X. H. Bu, *Adv. Mater.* **2018,** 30, 1804715; f) H. He, Y. Cui, B. Li, B. Wang, C. Jin, J. Yu, L. Yao, Y. Yang, B. Chen, G. Qian, *Adv. Mater.* **2019,** *31*, 1806897; g) J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen, G. Qian, *Angew. Chem. Int. Ed.* **2012,** *51*, 10542-10545; h) Y. Takashima, V. M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa, *Nat. Commun.* **2011,** *2*, 168; i) S.-T. Zheng, X. Zhao, S. Lau, A. Fuhr, P. Feng, X. Bu, *J. Am. Chem. Soc.* **2013,** *135*, 10270-10273; j) Z. Wang, C.-Y. Zhu, J.-T. Mo, P.-Y. Fu, Y.-W. Zhao, S.-Y. Yin, J.-J. Jiang, M. Pan, C.-Y. Su, *Angew. Chem. Int. Ed.* **2019,** DOI: 10.1002/ange.201905186.

[18] a) N. Yanai, T. Uemura, M. Inoue, R. Matsuda, T. Fukushima, M. Tsujimoto, S. Isoda, S. Kitagawa, *J. Am. Chem. Soc.* **2012,** *134*, 4501-4504; b) J. Park, D. Yuan, K. T. Pham, J.-R. Li, A. Yakovenko, H.-C. Zhou, *J. Am. Chem. Soc.* **2011,** *134*, 99-102.

[19] M. Tu, H. Reinsch, S. Rodríguez‐Hermida, R. Verbeke, T. Stassin, W. Egger, M. Dickmann, B. Dieu, J. Hofkens, I. F. Vankelecom, *Angew. Chem. Int. Ed.* **2019,** *58*, 2423-2427.

[20] a) M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010,** *132*, 14172-14178; b) C.-J. Carling, J.-C. Boyer, N. R. Branda, *J. Am. Chem. Soc.* **2009,** *131*, 10838-10839; c) C.-C. Ko, V. W.-W. Yam, *Acc. Chem. Res.* **2017,** *51*, 149-159; d) N. M. W. Wu, M. Ng, V. W. W. Yam, *Angew. Chem., Int. Ed.* **2019,** *58*, 3027-3031; e) J. Zhang, H. Tian, *Adv. Opt. Mater.* **2018,** *6*, 1701278; f) A. M. Asadirad, S. p. Boutault, Z. Erno, N. R. Branda, *J. Am. Chem. Soc.* **2014,** *136*, 3024-3027.

[21] Y. Cui, R. Song, J. Yu, M. Liu, Z. Wang, C. Wu, Y. Yang, Z. Wang, B. Chen, G. Qian, *Adv. Mater.* **2015,** *27*, 1420-1425.

[22] S. Yamamoto, K. Matsuda, M. Irie, *Chem. - Eur. J.* **2003,** *9*, 4878-4886.

[23] a) Z. Li, G. Wang, Y. Wang, H. Li, *Angew. Chem. Int. Ed.* **2018,** *57*, 2194-2198; b) Z. Li, Z. Hou, H. Fan, H. Li, *Adv. Funct. Mater.* **2017**, *27*, 160437.

[24] a) H.-B. Cheng, G.-F. Hu, Z.-H. Zhang, L. Gao, X. Gao, H.-C. Wu, *Inorg. Chem*. **2016**, *55*, 7962-7968; b) Z. Li, H. Chen, B. Li, Y. Xie, X. Gong, X. Liu, H. Li, Y. Zhao, *Adv. Sci*. 201901529.

[25] Z. Q. Li, Y. M. Zhang, D. S. Guo, H. Z. Chen, Y. Liu, *Chem. - Eur. J.* **2013,** *19*, 96-100.

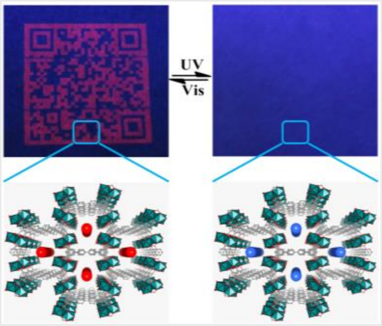
[26] a) Z.-Y. Gu, D.-S. Guo, M. Sun, Y. Liu, *J. Org. Chem.* **2010,** *75*, 3600-3607; b) H. Cai, W. Lu, C. Yang, M. Zhang, M. Li, C. M. Che, D. Li, *Adv. Opt. Mater.* **2019,** *7*, 1801149.

[27] Q. Xu, Z. Li, H. Li, *Chem. Eur. J.* **2016**, *22*, 3037-3043.

[28] H.-B. Cheng, H.-Y. Zhang, Y. Liu, *J. Am. Chem. Soc*. **2013**, *135*, 10190-10193.

RESEARCH ARTICLE

We realize reversible confidential information protection via loading photoswitchable molecule into lanthanide MOF. The light triggered open and close isomerization of the diarylethene unit regulates luminescence ON-OFF switch of lanthanide emitting center, allowing for reversible multiple information anti-counterfeiting by simply alternating the exposure to UV and visible lights.



Z. Li, G. Wang, Y. Ye, B. Li, H. Li and B. Chen**

Page No. – Page No.

Title