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Force-Induced Turn-On Persistent Room-Temperature Phosphorescence in Purely Organic Luminogen

Jia Ren, Yunsheng Wang, Yu Tian, Zhenjiang Liu, Xiangheng Xiao, Jie Yang, Manman Fang, and Zhen Li**

Abstract: *Research of purely organic room-temperature phosphorescence (RTP) materials has been a hot topic, especially for those with stimulus response character. Herein, an abnormal stimulus-responsive RTP effect is reported, in which, purely organic luminogen of Czs-ph-3F shows turn-on persistent phosphorescence under grinding. Careful analyses of experimental results, coupled with the theoretical calculations, show that the transition of molecular conformation from quasi-axial to quasi-equatorial of the phenothiazine group should be mainly responsible for this exciting result. Furthermore, the applications of stylus printing and thermal printing are both successfully realized, based on the unique RTP effect of Czs-ph-3F.*

Recently, purely organic RTP luminogens have been attracting increasing attention due to their extensive applications in various fields, such as anti-counterfeiting, sensor, bioimaging and OLEDs.[1] For the further development of RTP materials, a deep understanding of the internal mechanism is of great importance. Accordingly, thanks to the great efforts of scientists, a series of corresponding mechanisms have been proposed, such as H-aggregation, strong intermolecular hydrogen bonds, π–π stacking, intermolecular n–π electron coupling, and so on.[2] Most of them are focusing on molecular stacking, while there are fewer researches on molecular conformation, regardless of its important role for the intermolecular interactions.

Phenothiazine is a well-known building block for luminescent materials, and its derivatives usually have quasi-axial (ax) and quasi-equatorial (eq) conformers that can convert to each other under the external stimulus (Figure 1 A). Accordingly, a series of stimulus-responsive emissive effects have been carried out based on the changed molecular conformation of phenothiazine derivatives. For example, Minakata and co-workers successfully realized the tricolor-changing mechanochromic luminescence through conformational change of phenothiazine upon grinding.[3] Li and co-workers utilized the unique conformation-dependent emission property of phenothiazine derivative in the development of dynamic mechanoluminescence, another kind of emission process excited by mechanical stimulus without UV irradiation.[4] Xu and co-workers reported the force-induced delayed fluorescence in two phenothiazine derivatives based on the transition of their conformations from quasi-axial to quasi-equatorial ones.[5] Thus, could the adjustable RTP emission be realized through changing the molecular conformation of phenothiazine derivatives with external stimulus? If it could, the stimulus-responsive RTP emission and the clarification of relationship between RTP effect and molecular conformation should be both achieved, and also the related information could be obtained for the further rational molecular design and deep understanding of the molecular behaviors in aggregated states.

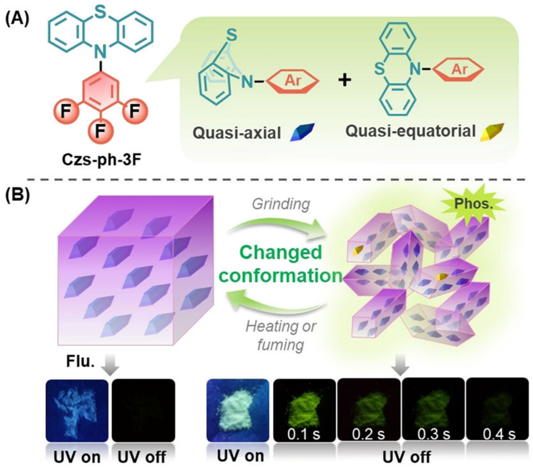

Figure 1. A) The molecular structure and two possible conformations of CzS-ph-3F. B) A proposed diagram for the stimulus-responsive RTP effect based on conformational change and photographs of Czs-ph-3F taken before and after turning off the 365 nm UV irradiation under ambient conditions.

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[*] J. Ren, Y. Wang, Y. Tian, Z. Liu, Dr. J. Yang, Dr. M. Fang, Prof. Z. Li
Institute of Molecular Aggregation Science, Tianjin University
Tianjin 300072 (China)
E-mail: manmanfang@tju.edu.cn
lizhentju@tju.edu.cn
Prof. Z. Li
Department of Chemistry, Wuhan University
Wuhan, Hubei 430072 (China)
and
Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University
Binhai New City, Fuzhou, Fujian 350207 (China)
and
Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, Tianjin University
Tianjin 300072 (China)
E-mail: lizhen@whu.edu.cn
Prof. X. Xiao
School of Physics and Technology, Wuhan University
Wuhan, Hubei 430072 (China)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.202101994.

Herein, a new organic luminogen of Czs-ph-3F was designed and synthesized, in which electron donor of phenothiazine and acceptor of trifluorobenzene were connected by C−N bond. For comparison, another analogue molecule of Czs-ph-F was also prepared, with only one F atom instead of three ones in Czs-ph-3F. With this molecular structure of Czs-ph-3F, three issues could be expected: 1) the existence of N/S heteroatoms could facilitate n–π* transition, to promote the RTP emission; 2) the multiple fluorine atoms could lead to the formation of effective hydrogen-bonding interaction, then contributing to the restricted non-radiative transition and the resultant emission; 3) the conformational change potential of phenothiazine group might give rise to the stimulus-responsive emission effect.[6] Upon excitation, the crystal of Czs-ph-3F just gave blue fluorescence emission, while a turn-on phosphorescence with obvious green afterglow appeared after grinding, showing the unique force-induced RTP effect (Supporting Information, Movie S1). To the best of our knowledge, this should be the first example of persistent RTP luminogen with mechano-responsive turn-on RTP effect, as the mechanical stimulus usually led to the quenched RTP emission for the damaged lattice.[7] Furthermore, the grounded powder would return to the non-RTP phase after heating or fuming stimulus, and the cycle process could be repeated for heaps of times, which were much beneficial for the practical applications.[8] Careful analyses of experimental results, coupled with the theoretical calculations, demonstrated that the transition of molecular conformation from quasi-axial to quasi-equatorial of partial molecules should be mainly responsible for these exciting results. Herein, we present the synthesis, photophysical property, crystal structure, and theoretical calculations of Czs-ph-3F in detail, to fully understand its abnormal force-induced RTP effect and summarize the molecular conformation–property relationship.

Czs-ph-3F was conveniently synthesized in just one step (Supporting Information, Scheme S1). In the photoluminescence (PL) process, Czs-ph-3F showed different emission behaviors in different phases. As shown in Figure 2A, its crystal just gave a blue fluorescence peaked at 437 nm with the PL quantum yield (Φ_{PL}) of 2.30 %, while no RTP emission could be detected. Interestingly, when the crystal was grounded, a new peak at about 505 nm appeared and gradually increased (Supporting Information, Figures S1,S2, Table S1). At last, the PL emission was changed to green with the Φ_{PL} of 4.27 %. At this time, the emission lifetimes for the peaks of 437 and 505 nm were measured to be 11.56 ns and 20.44 ms, respectively (Supporting Information, Figure S3). After turning-off the UV irradiation, the obvious green afterglow could last more than 0.5 s. Furthermore, the temperature-dependent PL behaviors were studied for grounded sample of Czs-ph-3F, it was found that the emission intensity and lifetime at 505 nm both increased with the decreased temperature, indicating that the new peak should be assigned to phosphorescence (Figure 2B,C; Supporting Information, Figure S4). Thus, the first example of persistent RTP luminogen with mechano-responsive turn-on RTP effect was demonstrated. Further on, the grounded sample of Czs-ph-3F could return to the non-RTP phase after heating at 75 °C for about 0.5 h or fuming with dichloromethane for about 0.5 h, showing the reversible stimulus-responsive RTP effect. Especially, after more than 10 times of cycles for both grinding-heating or grinding-fuming, the turn-on RTP effect could still be readily realized under mechanical stimulus, showing excellent stability and recyclability.

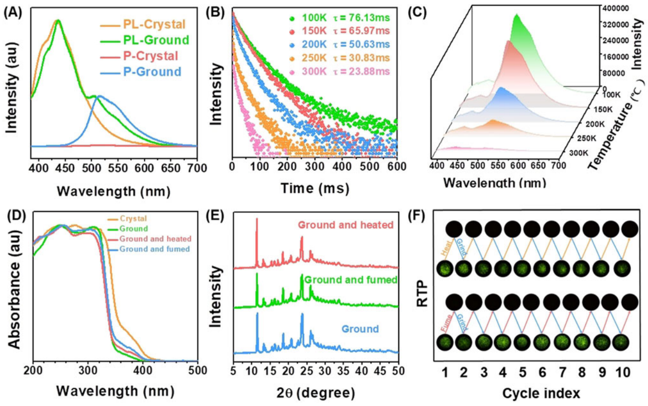

Figure 2. A) The steady-state PL and phosphorescence (P) spectra for the crystal and grounded samples of Czs-ph-3F. B) Temperature-dependent phosphorescence decays for the grounded sample of Czs-ph-3F from 100 K to 300 K. C) Temperature-dependent PL spectra for the grounded sample of Czs-ph-3F from 100 K to 300 K. D) The solid UV/Vis absorption spectra of Czs-ph-3F in different solid phases. E) The PXRD patterns of Czs-ph-3F in different solid phases. F) Stimulus-responsive RTP behaviors of Czs-ph-3F and the corresponding reversible cycle diagram.

To investigate the origin for this peculiar stimulus-responsive RTP effect, the powder X-ray diffraction (PXRD) measurements were carried out for Czs-ph-3F samples in different phases (Figure 2E). Interestingly, similar PXRD patterns with sharp peaks could be observed for the grounded sample with RTP and grounded-heated/grounded-fumed ones without RTP. This disclosed their similar molecular packing mode and crystalline degree. As the PL behavior for the same luminogen was mainly determined by the corresponding molecular conformation and packing, it could be expected that the changed molecular conformation, rather than packing, should be mainly responsible for the stimulus-responsive RTP effect. To further explore the changes that occurred during the grinding process, their solid UV/Vis absorption spectra were measured (Figure 2D). In comparison with Czs-ph-3F crystal, the UV/Vis absorption at about 350 nm to 400 nm was much weakened after grinding, then re-enhanced to some extent with heating or fuming stimulus. Thus, the changed molecular conformation as the main origin for stimulus-responsive RTP effect could be certified.

Then why didn't the conformational change influence the molecular stacking? It was deduced that the conformational change only happened in a small fraction of Czs-ph-3F molecules. As shown in the Supporting Information, Figure S5, little change was found for the solid ^{13}C NMR spectra of Czs-ph-3F crystal and grounded sample, indicating the negligible change of chemical environment for C atoms in Czs-ph-3F during the grinding process. On the other hand, the DSC measurements also showed the similar results that the melting points of the crystal and grounded samples were almost the same (Supporting Information, Figure S6). Therefore, during the grinding process, the conformational change only happened for a small fraction of molecules, which was not strong enough to influence the resultant packing mode. Accordingly, a self-doping system should be formed for the molecules with initial conformation as host and those with new conformation as guest.

The single crystal of Czs-ph-3F was cultured and the corresponding crystal structure was analyzed. The crystal of Czs-ph-3F gave a space group of P21/C1 (Supporting Information, Table S2), in which efficient intermolecular hydrogen bonds and π–π interactions were observed. To simplify the crystal analyses, eight dimers with close intermolecular interactions in the crystal were selected (Figure 3B). π–π interactions existed in dimer 1 and 2 with the central-central distances of 3.954 and 3.883 Å respectively, while C−H⋯S bonds were found in dimer 1 and 3 with distances of 3.128/3.950 and 3.193 Å respectively. Particularly, thanks for the introduction of the three fluorine atoms, there were many strong C−H⋯F bonds in crystal, especially in dimer 1 (distances of 2.968 Å), dimer 5 (distances of 2.732–2.993 Å), dimer 6 (distances of C−H⋯F 2.645 Å), dimer 7 (distances of 2.576–2.882 Å) and dimer 8 (distances of C−H⋯F 2.967 Å). With these strong intermolecular interactions, a rigid environment could be formed for Czs-ph-3F crystal, which could endow it good lattice stability.[9] Therefore, once stimulated by mechanical force, the crystal was just broken into micro-crystals. At this time, the resultant molecular stacking mode showed no difference, while a small number of molecules underwent conformational change, then leading to the resultant RTP emission.

Then the relationship between molecular conformation and RTP effect was further investigated. Although Czs-ph-3F presented a typical quasi-axial (ax) conformation in crystal phase, the optimized molecular structure in gas state by TD-DFT calculation gave a quasi-equatorial (eq) one (Supporting Information, Figure S7), indicating the existence of two possible conformations. Furthermore, these two conformations of Czs-ph-3F presented much different HOMO/LUMO orbital distributions (Supporting Information, Figure S8). Among them, Czs-ph-3F(ax) showed large overlap for their HOMO and LUMO, while obvious charge transfer could be found for Czs-ph-3F(eq). Accordingly, the much stronger spin orbit coupling between singlet and triplet states could be achieved in Czs-ph-3F(eq) (Figure 3C). Particularly, the spin orbit coupling constant (SOC) between S$_0$ and T$_1$ of Czs-ph-3F(eq) was calculated to be as large as 33.34 cm^{-1}, much larger than that (5.64 cm^{-1}) of Czs-ph-3F(ax), indicating the better phosphorescence emission ability of quasi-equatorial conformation. Based on it, the ground-induced RTP effect could be well understood: in crystal, Czs-ph-3F showed no RTP emission with quasi-axial (ax) conformation; then some of Czs-ph-3F molecules were converted into quasi-equatorial (eq) one after grinding, thus resulting in the appearance RTP emission.

Further on, the theoretical absorption spectra of Czs-ph-3F(ax) and Czs-ph-3F(eq) were calculated. As shown in Figure S9A, another shoulder peak could be observed in the long wavelength region for Czs-ph-3F(ax), while not for Czs-ph-3F(eq). This could be well consistent with the experimental results: a shoulder peak could be observed in the long wavelength region for Czs-ph-3F crystal with quasi-ax con-

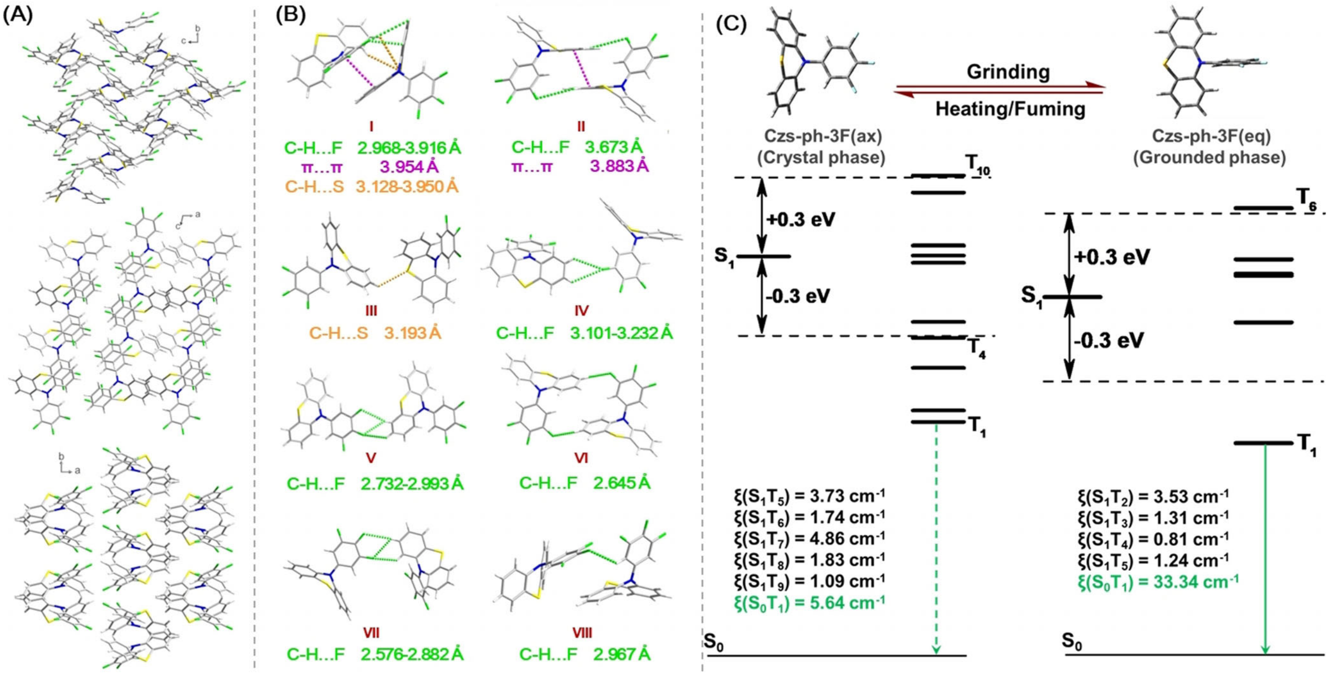

Figure 3. A) Molecular packing of Czs-ph-3F crystal observed from the a, b, and c directions, respectively. B) Dimers in Czs-ph-3F crystal and their intermolecular interactions. C) Calculated spin–orbit coupling constants (ξ) between the S$_0$/S$_1$ and T$_n$ ($\Delta E_{S1Tn} < 0.3$ eV) for Czs-ph-3F(ax) and Czs-ph-3F(eq).

former, while the grounded Czs-ph-3F sample was not (Supporting Information, Figure S9B). Thus, the existence of Czs-ph-3F(eq) in grounded phase could be further certified.

On the other hand, the measurement of Raman spectra was carried out for Czs-ph-3F crystal and grounded phases. As shown in the Supporting Information, Figure S10A, the Raman peaks centered at 162 and 191 cm^{-1} (central ring boat deformation) decreases obviously after grinding, which is consistent well with the decreased distortion of phenothiazine group from Czs-ph-3F(ax) to Czs-ph-3F(eq) (Supporting Information, Figure S10B).[10] Based on the Raman spectra, the conformation change from Czs-ph-3F(ax) to Czs-ph-3F(eq) under grinding could be further certified.

Then the photophysical properties of Czs-ph-3F in solution phase were studied carefully (Supporting Information, Figures S11–S13). As shown in Figure S11, Czs-ph-3F solution showed similar UV/Vis absorption spectrum to grounded phase, while that of crystal phase was much different with an additional shoulder peak ranging from 350 to 400 nm. This indicated that Czs-ph-3F molecules mainly showed the quasi-equatorial conformation (Czs-ph-3F(eq)) in solution phase, just like that after grinding. Also, the PL spectrum of Czs-ph-3F solution at 77 K is similar to the grounded sample at low temperature (Supporting Information, Figure S13), further certifying their similar molecular conformation. Besides, dominant phosphorescence emission could be achieved for Czs-ph-3F solution at 77 K, indicating the great phosphorescence emission ability for Czs-ph-3F(eq) when its non-radiative transition was restrained. Based on these experimental results, the existence of Czs-ph-3F(eq) with great phosphorescence emission ability could be well certified. Then, the transition of Czs-ph-3F(ax) to Czs-ph-3F(eq) could lead to the force-induced RTP effect.

To further prove that quasi-equatorial conformation favored RTP emission, one analogue, Czs-ph-F, consisting of phenothiazine and fluorobenzene units, was synthesized and studied (Supporting Information, Figures S14–S19). As shown in the Supporting Information, Figure S17, Czs-ph-F crystal gave fluorescence-phosphorescence dual emissions with lifetimes of 1.36 ns and 0.70 ms, respectively, just like that of Czs-ph-3F in grounded phase. The analysis of the single-crystal structure found that it presented typical quasi-equatorial conformation with fluorobenzene perpendicular to phenothiazine group in radial direction (Supporting Information, Figure S18). As just one fluorine atom existed in compound Czs-ph-F, the corresponding intermolecular interactions were much weaker than those of Czs-ph-3F, which might be the main reason for the much shorter RTP lifetime in Czs-ph-F crystal. With the experimental results from Czs-ph-F crystal, the significant role of quasi-equatorial conformation in RTP emission of phenothiazine derivatives could be further verified.

Further on, the cocrystal of Czs-ph-F/Czs-ph-3F with mass ratio of 1:100 was cultured, in which the small amount of Czs-ph-F with quasi-equatorial conformation acted as RTP emitter and the large one of Czs-ph-3F with quasi-axial conformation as rigid host. The measurement of single crystal structure found that the packing of cocrystal was almost identical to Czs-ph-3F crystal, regardless of the trace amounts of Czs-ph-F (Supporting Information, Table S2). Just as expected, the cocrystal showed green RTP with the lifetime of 36.90 ms (Supporting Information, Figure S20), which was longer than those of the Czs-ph-F crystal and the grounded phase of Czs-ph-3F, because of more C−H···F intermolecular interactions and better crystalline in cocrystal. The RTP spectrum of co-crystal could be well consistent with the that in doped PMMA film for Czs-ph-F, indicating the RTP emission in cocrystal was indeed from Czs-ph-F (Supporting Information, Figure S21). On the other hand, obvious overlap could be found between the PL spectrum of Czs-ph-3F crystal and UV/Vis absorption spectra of Czs-ph-F crystal/PMMA film, then the energy transfer could happen in the cocrystal (Supporting Information, Figure S22). Thus, Czs-ph-3F not only acted as a rigid host, but also an energy donor in the cocrystal, which might work together to promote the RTP emission. And this effect might also exist in Czs-ph-3F at grounded phase. Besides, when Czs-ph-3F was doped in the PMMA with mass ratio of 1:100, the resultant film also showed the green RTP with lifetime of 14.01 ms (Supporting Information, Figure S23), since Czs-ph-3F tended to show quasi-equatorial conformation in non-crystal phase, just like that after grinding. These experimental results further confirmed that the quasi-equatorial conformation of phenothiazine derivatives could promote RTP emission.

Inspired by the unique force-responsive RTP effect of Czs-ph-3F, the corresponding stylus printing was carried out, in which the stylus printer created a typeface by hitting carbon paper with a needle in the print head. Firstly, the typing paper was constructed with two layers, namely transparent encapsulation film and Czs-ph-3F layer, in which Czs-ph-3F layer has been fumed with dichloromethane to reach the non-RTP phase. When the typing paper was passed over the print head, the preset pattern was printed by hitting paper with a needle. As shown in Figure 4 A, the green pandas were successfully printed on the paper for the turn-on RTP effect of Czs-ph-3F after force stimulus. It was a pity that the afterglow of pandas was not so clear for the inferior force-stimulus sensitivity.

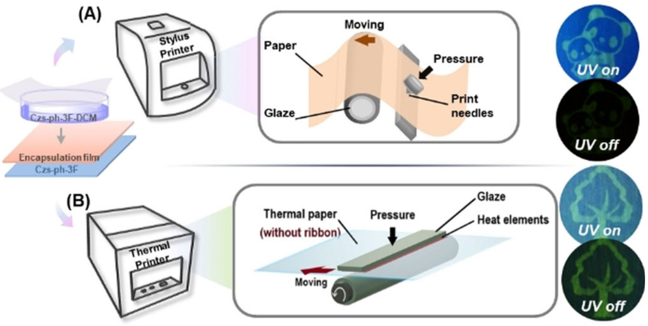

Figure 4. A) Application of stylus printing: First, the typing paper was made of Czs-ph-3F and transparent encapsulation film; then, it was passed over the print head, and the preset pattern was printed by hitting paper with a needle in the print head. B) Application of thermal printing: the preset pattern was printed under the combined actions of heating and pressure.

To further promote the RTP emission of the printed pattern, the thermal printer was utilized. Similar to a stylus printer, the thermal printer produces image by selectively heating the thermochromic paper, coupled with a certain force. Because of the advantages of fast speed, low noise, clear printing and easy to use, thermal printer has been widely used in receipt printers, mobile label printers, and fax machines.[11] In previous works, we have successfully realized the thermal printing based on the host-guest doping materials with stimulus-responsive RTP emission.[12] As multi-components were needed for the doping systems, the structure of thermal paper was a little bit complicated. In this work, the simplified structure of thermal paper with just two layers could be obtained. When it passed through the print heat, a green pattern of a tree with clear afterglow appeared due to the combined actions of heating and pressure.

In summary, we have demonstrated the first example of force-induced turn-on persistent RTP emission in a purely organic luminogen of Czs-ph-3F. Through measuring the changed solid UV/Vis spectra under external stimulus, coupled with theoretical calculations, the relationship between molecular conformation and RTP effect was clearly clarified. It was found the quasi-equatorial conformation of the phenothiazine derivatives was more likely to give RTP emission than the quasi-axial one, and the transition between them led to interesting stimulus-responsive RTP effect of Czs-ph-3F. This demonstrates that the tuning of molecular conformation is a good approach to modify the material properties, once again showing the molecular uniting set identified characteristic (MUSIC) proposed in 2018.[2b] Furthermore, with the unique force-induced RTP effect, this material was successfully utilized in thermal printing and stylus printing for the first time, which further extended the application of RTP materials. Thus, the control of molecular conformation should be considered during the rational molecular design for achieving excellent material performance.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: conformers · phenothiazine · phosphorescence · stimulus response

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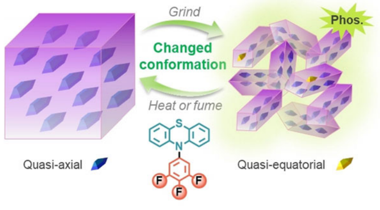
Communications

Phosphorescence

J. Ren, Y. Wang, Y. Tian, Z. Liu, X. Xiao, J. Yang, M. Fang,* Z. Li* ____ ▮▮▮▮–▮▮▮▮

Force-Induced Turn-On Persistent Room-Temperature Phosphorescence in Purely Organic Luminogen



Force-induced turn-on persistent room temperature phosphorescence (RTP) material

The first example of force-induced turn-on persistent RTP luminogen named Czs-ph-3F is reported. The abnormal stimulus-responsive RTP effect is attributed to the transition of molecular conformation from quasi-axial to quasi-equatorial of the phenothiazine group. This material was successfully applied in thermal printing and stylus printing.