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Precise peripheral design enables propeller-like squaraine dye with highly sensitive and wide-range piezochromism†

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Piezochromic fluorescent (PCF) materials that feature high sensitivity and wide-range switching are attractive in intelligent optoelectronic applications but their fabrication remains a significant challenge. Here we present a propeller-like squaraine dye SQ-NMe₂ decorated with four peripheral dimethylamines acting as electron donors and spatial obstacles. This precise peripheral design is expected to loosen the molecular packing pattern and facilitate more substantial intramolecular charge transfer (ICT) switching caused by conformational planarization under mechanical stimuli. As such, the pristine SQ-NMe₂ microcrystal exhibits significant fluorescence changes from yellow ($\lambda_{em} = 554$ nm) to orange ($\lambda_{em} = 590$ nm) upon slight mechanical grinding and further to deep red ($\lambda_{em} = 648$ nm) upon heavy mechanical grinding. Single-crystal X-ray diffraction structural analysis of two SQ-NMe₂ polymorphs provides direct evidence to illustrate the design concept of such a piezochromic molecule. The piezochromic behavior of SQ-NMe₂ microcrystals is sensitive, high-contrast, and easily reversible, enabling cryptographic applications.

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Introduction

Recently piezochromic fluorescent (PCF) materials with fluorescence properties changed under mechanical stimuli (pressure, grinding, stretching, or shearing) have garnered much interest from researchers in intelligent optoelectronic fields.^{1–5} Since the seminal work of 1957,⁶ the field of PCF materials has significantly flourished by exploiting purely organic luminophores.^{7–12} During this process, molecular packing rearrangements,^{13–15} molecular conformational changes,^{16,17} and bond breaking^{18,19} have been well assigned to cause their piezochromic behavior.²⁰ Nevertheless, due to small-shifted luminescence spectra upon mechanical stimuli, most PCF materials exhibit inconspicuous color switching.^{21,22} This is mainly attributed to the fact that a universal design principle of PCF materials is less well established and the pressure-induced severe π - π interaction in π -conjugated PCF molecules thus quenches their luminescence rather than luminescence spectra shifting.^{23,24}

The highly twisted π -conjugated stereogeometry intrinsically suppresses the π - π interaction and facilitates molecular conformational planarization under mechanical stimuli, thus being a privileged candidate in the fabrication of PCF materials.^{25,26} In this regard, the natural propeller shape of tetraphenylethylene (TPE) and triphenylamine (TPA) makes them highly suitable for the test of the molecular conformational effect on piezochromism,²⁷ despite requiring very high pressure on the order of GPa.²⁸ Subsequent research further found that the piezochromic behaviors of TPE/TPA derivatives can become more effortless and highly tunable when stimuli-sensitive intramolecular charge transfer (ICT) features are brought on the TPE/TPA skeleton.^{29–31} These findings tentatively establish a specific stereogeometry, that of highly distorted molecular conformations with ICT features, which may serve as a concise but more precise molecular design guideline for high-performance PCF materials.^{32,33}

Squaraine dyes (SQs), with strong absorption and emission in a wide-range spectrum region, are classical organic dyes applied in advanced optoelectronic fields.^{34–38} The SQ molecule bearing two diphenylamine moieties is documented as an aggregation-induced emission (AIE)-active luminogen,³⁹ adopting a centrosymmetric molecular conformation and propeller-like shape with intrinsic ICT features. With this in mind, here we present propeller-like SQ-NMe₂ with four peripheral dimethylamines that act as both electron donors and spatial obstacles (Fig. 1a). This precise peripheral design is expected to enhance its ICT effect further and cause multiple “soft

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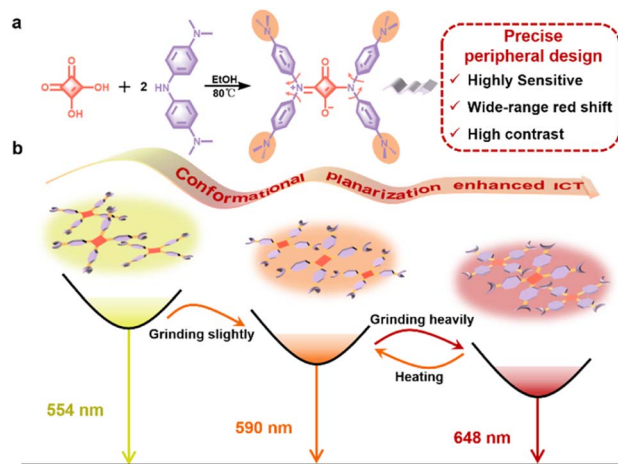


Fig. 1 (a) Synthesis route, molecular structure, and main advantages of PCF-active SQ-NMe₂. (b) Proposed mechanism of molecular conformation changes of SQ-NMe₂ microcrystals during the pressure-heating process.

interactions” (such as C–H⋯π and C–H⋯N/O interactions) to loosen the molecular packing pattern,^{40–42} which both are crucial to the sensitivity and switching range under mechanical stimuli. Eventually, we demonstrated the highly sensitive and wide-range piezochromic switching of SQ-NMe₂ microcrystals under mechanical grinding (Fig. 1b and Table S1†), and theoretical calculations and single crystal X-ray diffraction analyses directly proved the mechanism. Cryptographic applications

with good recovery and high contrast have also been demonstrated based on SQ-NMe₂ microcrystals.

Results and discussion

The synthesis route and structural characterization of SQ-NMe₂ are detailed in the ESI†. In common organic solvents, the UV-vis absorption spectra of SQ-NMe₂ were recorded with a maximum absorption peak (λ_{ab}) centered at 460 nm (Fig. S1†), and no fluorescence emission was observed. In *N,N*-dimethylformamide (DMF)/water mixtures, SQ-NMe₂ remains non-emissive with the increase of water fractions (f_w) from 0% to 40%; after that, the amorphism emissions with the maximum peak (λ_{em}) around 583 nm increased rapidly together with tiny nanoparticles appeared, suggesting a typical AIE characteristic (Fig. S2†).^{43,44}

SQ-NMe₂ has a high crystallization tendency, probably ascribed to its multiple intermolecular interactions (such as C–H⋯π and C–H⋯N/O interactions).⁴⁵ The SQ-NMe₂ microcrystals can be facilely obtained by recrystallization in DMF and methanol (for details see the ESI†). As shown in Fig. 2a and b, these microcrystals showed a strong yellow emission with λ_{em} at 554 nm and a fluorescence quantum yield (Φ_{PL}) of 36.9%. When scraping these pristine SQ-NMe₂ microcrystals with a spatula, apparent changes in the UV-vis and emission colors can be easily observed. As such, we then examined the complete PCF behaviors of these microcrystals. Upon being slightly ground with a pestle for only 1 min, the emission color of these

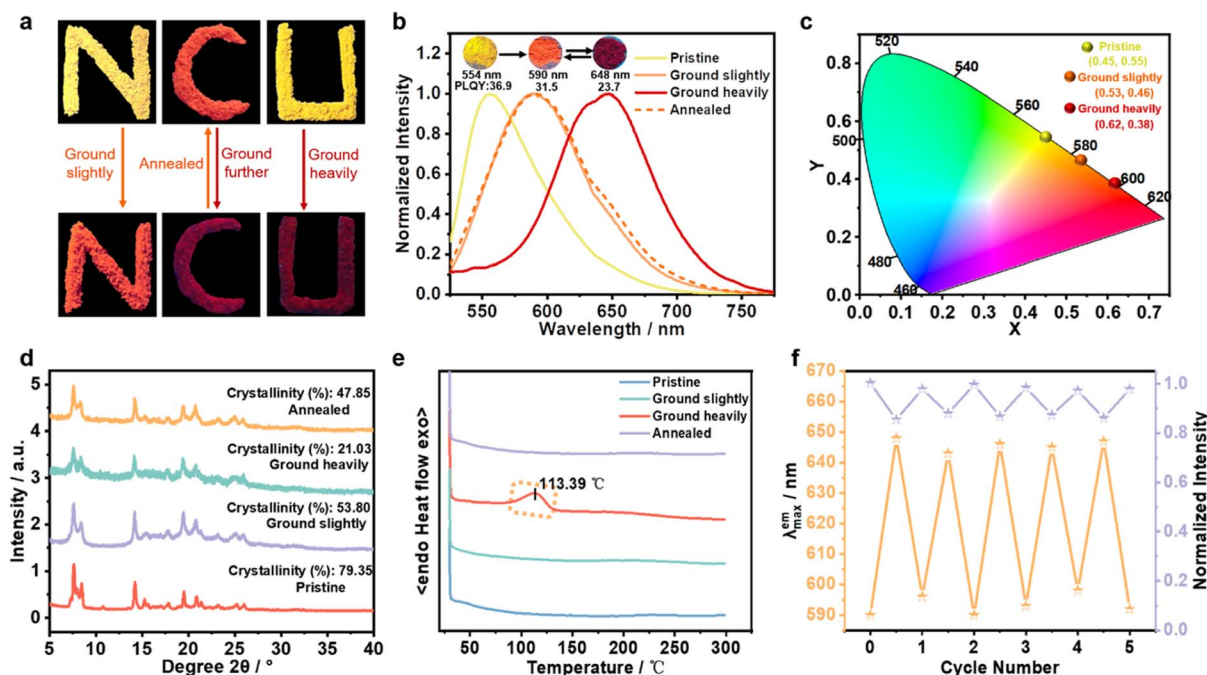


Fig. 2 (a) Fluorescence photographs of pristine and treated SQ-NMe₂ microcrystals under UV light illumination (365 nm). (b) Normalized PL spectra of pristine SQ-NMe₂ microcrystals during grinding (solid line) and subsequent annealing (dotted line) processes (inset: corresponding PL photographs). (c) CIE coordinate diagram of SQ-NMe₂ microcrystals during the gradual grinding process. (d) PXRD patterns and (e) DSC curves of pristine and treated SQ-NMe₂ microcrystals. The scan rate is 20 °C min⁻¹ under N₂. (f) Cyclic switch of the wavelength and intensity during the grinding–heating process.



microcrystals fully changed from yellow to orange with λ_{em} redshifted to 590 nm, and Φ_{PL} decreased a bit to 31.5%. Upon further grinding heavily for 5 min, deep red emission with λ_{em} at 648 nm appeared, and Φ_{PL} further lowered to 23.7%. After more than twenty minutes of continuous grinding, no new red-shifted peaks were recorded. Furthermore, after heating at 140 °C for only 1 min, the deep red emission of these heavily ground SQ-NMe₂ microcrystals was back to orange emission. At the same time, continuous heating did not restore its yellow emission any further. We plotted Commission International de L'Éclairage (CIE) 1931 coordinates (Fig. 2c), showing a wide-range redshift of the piezochromic process. The redshift in the λ_{ab} of pristine SQ-NMe₂ microcrystals further corroborated the red-shifted emission from grinding (Fig. S3†). The lifetime decay profiles of SQ-NMe₂ microcrystals in the piezochromic process were tested by single photo-counting, showing approximately short lifetimes of 1.65 ns, 1.32 ns, and 1.26 ns for the yellow, orange, and deep red ones, respectively (Fig. S4†). All the photophysical data of SQ-NMe₂ microcrystals are summarized in Table S2.†

To essentially understand their microstructure, powder X-ray diffraction (PXRD) measurement was performed on SQ-NMe₂ microcrystals that were treated under different conditions. The results show that SQ-NMe₂ microcrystals transitioned from well-order crystalline to amorphous during the gradual grinding. As shown in Fig. 2d, the number and intensity of diffraction peaks decreased with gradual grinding of pristine SQ-NMe₂ microcrystals, which can be revealed by tapering crystallinity from 79.35% to 53.8% to 21.03%. Not surprisingly, the annealed SQ-NMe₂ powders restored to the crystalline phase with crystallinity increasing to 47.85%, similar to slightly ground SQ-NMe₂ microcrystals. The differential scanning calorimetry (DSC) curves revealed that the heavily ground SQ-NMe₂ powders display a cold-crystallization transition peak at 113.39 °C (Fig. 2e), which supports the heat treatment temperature of 140 °C in the above recoverability testing. Meanwhile, the DSC curve of the slightly ground SQ-NMe₂ microcrystals showed no peak, which matched well with the fact that continuous heating cannot restore its orange emission to yellow any further. In other words, this DSC curve showed that the ground powders were in the metastable amorphous phase and converted into a stable crystalline phase *via* external thermal recrystallizing. Moreover, the grinding–heating rewritable test demonstrated that the SQ-NMe₂ emission cyclic process between orange and deep red could be repeated at least five times, which provides its practical possibility (Fig. 2f and S5†).

Fortunately, high-quality needle-like crystals were found in preparing pristine SQ-NMe₂ microcrystals, which is suitable for single-crystal XRD analysis (termed as Y-form). The PXRD patterns of pristine SQ-NMe₂ microcrystals coincided with their simulated XRD patterns, suggesting the same molecular packing modes (Table S3, Fig. S6 and S8†). In Fig. 3a(i), the torsion angles between the four-membered ring and diphenylamine moieties in SQ-NMe₂ Y-form were determined to be approximately 29° and 65°. There is a type of weak Ar–H⋯O hydrogen bonding interaction of 2.860 Å between Ar–H and carbonyl at the four-membered ring, which restrains one of the

dihedral angles to 65°. Two types of hydrogen bonding interaction that restrains the dihedral angles to 29° were observed, one was Ar–H⋯N of 3.004 Å and the other was Ar–H⋯π of 3.012 Å between adjacent SQ-NMe₂ molecules (Fig. 3a(ii)). There is no π – π overlap in SQ-NMe₂ Y-form, accounting for its efficient yellow emission.^{46–48} More importantly, such two types of hydrogen bonding interactions belong to the so-called “soft interactions” and good response to the sensitive PCF behaviors of SQ-NMe₂ Y-form.

By slow evaporation in dichloromethane, another orange needle-like SQ-NMe₂ single-crystal was cultured, termed O-form (Table S3, Fig. S6 and S8†). Single-crystal XRD analysis revealed that the torsion angles between the four-membered ring and diphenylamine moieties in SQ-NMe₂ O-form ranged from 33° to 43° (Fig. 3b(i)), which were smaller compared to that of the Y-form. There is also no π – π overlap in SQ-NMe₂ O-form (Fig. 3b(ii)), and simultaneously the emission spectrum of SQ-NMe₂ O-form turned out to be very similar to that of slightly ground SQ-NMe₂ microcrystals (Fig. S9 and S10†), implying their quite similar molecular conformations. As such, it was concluded that the red-shifted emission of pristine SQ-NMe₂ microcrystals was possibly derived from the molecular conformational planarization-induced ICT enhancement after slight grinding. Multiple Ar–H⋯ π and Ar–H⋯N hydrogen bonding interactions were observed with the distance ranging from 2.699 to 3.142 Å between adjacent molecules in SQ-NMe₂ O-form (Fig. 3b(ii)). These interactions, maintaining the dihedral angles of the four-membered ring and diphenylamine moieties, were richer and slightly more potent than the Y-form but still soft. These observations thus account for the deep red emission of orange SQ-NMe₂ microcrystals arising from further conformational planarization under heavy grinding. Detailed single-crystal analyses of these two SQ-NMe₂ polymorphs have been deciphered in the ESI (Fig. S11 and S12).†

In order to verify the significance of “soft interactions” in the piezochromic behaviors of SQ-NMe₂ microcrystals, we designed and synthesized SQ-H and SQ-OMe as the control group (for synthesis methods and characterization see the ESI†). Their corresponding single crystals were easily obtained and the single-crystal XRD analyses are further detailed in the ESI (Table S4, Fig. S13 and S15).† As shown in Fig. 3c and d, there are multiple moderate to strong Ar–H⋯O and Ar–H⋯ π interactions locking the phenyl rotations of SQ-H and SQ-OMe and subsequent ICT switching. These differences in their stereochemistry, compared to SQ-NMe₂, enhance their intramolecular rigidity in crystals and will suppress their piezochromism. Not surprisingly, SQ-H and SQ-OMe microcrystals exhibited no PCF behavior, and their PXRD patterns didn't show obvious change upon grinding and heating (Fig. S16 and S17†). All those crystal structure analyses indicate that the “soft interactions” caused by the peripheral dimethylamines loosen the molecular packing pattern in such propeller-like squaraine dye, thus triggering highly sensitive and wide-range piezochromism of SQ-NMe₂ microcrystals. Like SQ-NMe₂, the photophysical and structural characterization of SQ-H and SQ-OMe was also conducted, which is detailed in the ESI (Fig. S18, S22 and Table S5).†



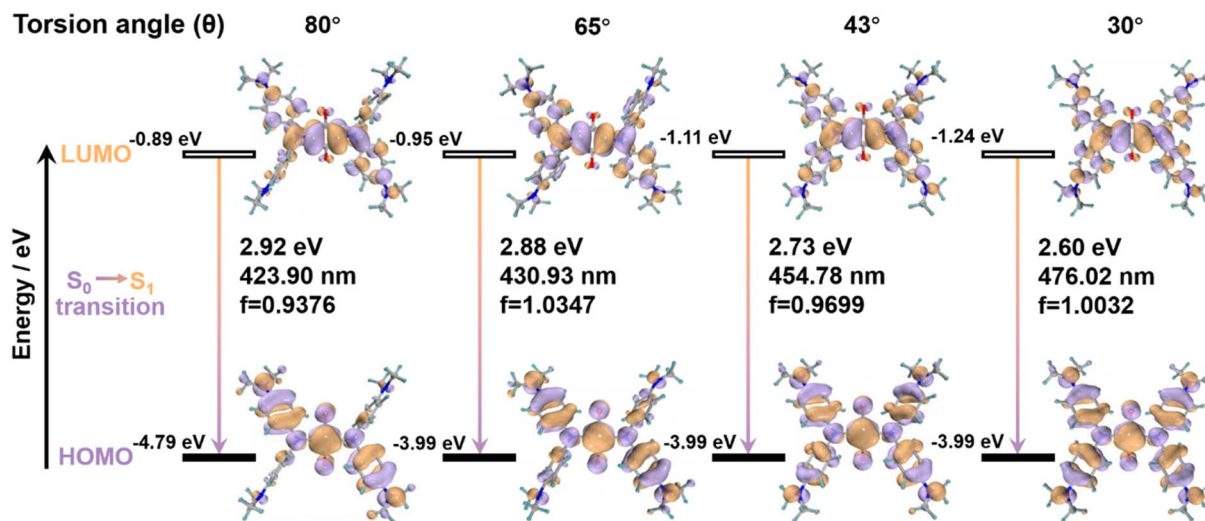


Fig. 4 Energy diagrams and the frontier orbital contribution of SQ-NMe₂ in a fixed conformation based on gradually decreased torsion angles (θ) between the central four-membered ring and diphenylamine rotors, together with their lowest-energy transitions estimated by theoretical calculations.

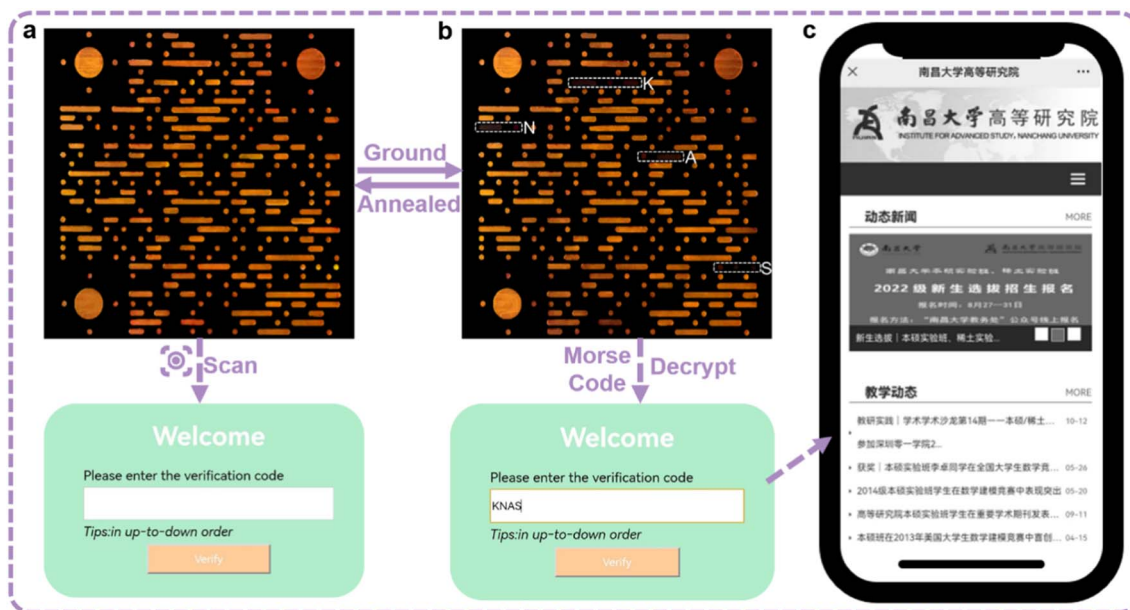


Fig. 5 A complicated QR code. (a) QR code with SQ-OMe and SQ-NMe₂ crystal phases is constructed, and a login window appears when scanning the code with a smartphone. (b) Grinding the QR code leads to the appearance of Morse signals, which are then translated into the letter sequence "KNAS". (c) The input of "KNAS" as the verification code allows access to the target website.

whole QR code, only part of the SQ-NMe₂ O-form became deep red, which demonstrated the Morse signals that can be translated into "KNAS" (Fig. S25[†]). Furthermore, the verification code "KNAS" was entered, and then the link automatically redirected to the target website (<https://ias.ncu.edu.cn/>). As the deep red emission of the obtained SQ-NMe₂ microcrystals can be annealed to orange and SQ-OMe has high thermal stability, the QR code can be recovered to the initial state after heating at 140 °C for only 1 min. The encryption and decryption of QR codes are just realized through the regulation of the crystal state under external mechanical stimuli, but not some complex

chemical reactions or fumigation with an organic solvent. This provides a good reference for the future green and rewritable applications of PCF materials.

Conclusions

In summary, based on propeller-like squaraine dye, a precise peripheral design for highly sensitive and wide-range PCF materials was consciously proposed. Peripheral dimethylamines, acting as electron donors and spatial obstacles, were introduced into this highly twisted π-conjugated molecule.



Such a design can loosen the molecular packing pattern and easily facilitate more substantial ICT switching caused by conformational planarization under mechanical stimuli. As a result, SQ-NMe₂ microcrystals showed a highly sensitive spectral shift of their emission from yellow ($\lambda_{em} = 554$ nm) to deep red ($\lambda_{em} = 648$ nm) upon grinding. Multi-level cryptographic applications with good recovery and high contrast have also been achieved based on SQ-NMe₂ microcrystals. Our research provided new design guidance for developing excellent PCF materials with high sensitivity, wide-range switching, and good recovery.

Data availability

Additional experimental data supporting this article are included in the ESI.†

Author contributions

Weihan Guo conducted formal analysis, performed experimental measurements, and prepared the initial version of the manuscript. Mingda Wang performed the theoretical calculations. Leilei Si performed experimental measurements. Yigang Wang helped with the revision of the manuscript. Hongming Wang helped with the revision of the manuscript. Guomin Xia: formal analysis, supervision, and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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