Spiro-Structure: A Good Approach to Achieve Mechanoluminescence Property

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ABSTRACT: Following the development of organic mechanoluminescence (ML) materials, molecular packing was proved as the key point to the emission process under an external force. In this text, with the introduction of spiro-(fluorene-9′-xanthene) (SFX) unit as the building block, the molecular packing of the resultant compound (BSFXA) was optimized with the interlaced mode, directly leading to the efficient ML effect. The key role of SFX with a spiro-structure can be further confirmed by the ML inactivity of reference compound BFA with the replacement of SFX unit by dimethyl fluorene (MeF), which provided a novel strategy to construct organic ML luminogens.

INTRODUCTION

Mechanoluminescence (ML), the emission by the mechanical force without UV irradiation, offers a feasible and promising solution to satisfy the increasing need for sensors, displays, lighting, stress sensing, and security.1−3 Although ML phenomenon was first reported by Francis Bacon in 1605, the pure organic ML luminogens are extremely rare compared to inorganic compounds and organometallic complexes.4−8 Only a few examples have been reported to display observable ML even at cryogenic temperatures or in dark, which should be mainly due to the unclear inherent mechanisms and lack of effective material design concept.9 In recent years, with the combination of the characteristic of aggregation-induced emission (AIE), some organic ML materials have been explored with strong emissions in solid state, and the basic AIE units with twisted configuration act as the main building blocks (Chart S1), for instance, tetraphenylethene (TPE), diphenylamine (DPA), and so on.10−18 Following the investigation of various organic luminogens possessing the ML effect, the key role of molecular packing has been observed in addition to the chemical structure, which could be confirmed by opposite ML activities of two polymorphs based on a TPE derivative.19 Accordingly, the stuck packing is proved as the preferred molecular packing, since the suppression of molecular slippage as the energy loss was the key point to realize the ML process, in addition to the piezoelectric effect.20−28 Thus, the optimization of molecular packing is essential to enhance the ML activity of organic materials, which can be conducted by the tunable molecular configurations and electronic properties.

Spiro-(fluorene-9′-xanthene) (SFX) unit, which consists of xanthene and fluorene moieties with the connection by a sp3-hybridized carbon, exhibits the orthogonal geometry for the spiro-structure.29−31 The SFX-based organic small molecules have been widely used in organic optoelectronic materials with excellent photovoltaic performance for the special molecular conformation and charge-transporting property.32−35 Since the possible π−π interactions from the two kinds of planar fused rings (xanthene and fluorene) with a nearly perpendicular configuration, the interlocked packing mode can be formed in the aggregated state, as proven by the crystal structure (Chart S2), which is much different from that of the isolated fluorene unit with almost parallel arrangement and in accordance with the preferred molecular packing of ML luminogens.36,37 Also, the oxygen atom in SFX can tune the electron property of the whole unit and induce more intermolecular interactions in the aggregated state, favoring the possible emission process for the suppression of molecular motions as a nonradiative process.38

With the above considerations in mind, the SFX unit was incorporated into the organic ML molecule with the linkage of DPA and borate functional group to form the compound BSFXA. A similar molecule with the replacement of the SFX fragment by one-dimensional dimethyl fluorene (MeF) was also synthesized for comparison, with the structure presented in Chart 1. Really, as expected, BSFXA and BFA demonstrated a totally different ML property: BSFXA is ML-active, while BFA is not, which is mainly due to the varied molecular packing with the presence or absence of the spiro-structure. Herein, we would like to present the synthesis, character-
STRUCTION AND DISCUSSION

Design and Synthesis. The synthetic routes of target molecules are illustrated in Scheme 1. First, monobromide intermediates were synthesized by classical Buchwald–Hartwig C–N coupling reaction of the SFX/MeF dibromide and DPA. After monobromide intermediates in 1,4-dioxane solution had reacted with 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane), K₂CO₃ and Pd(dppf)₂Cl₂ at 85 °C, the target molecules were obtained and characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrum (HRMS), and elemental analysis (Figures S1−S12). Compound BFA and BSFXA exhibited a good thermal stability from the thermogravimetric analysis curves (Figure S13), and the decomposition temperature (T_d) of BSFXA is higher than 260 °C.

Optical Properties. The UV-vis absorption spectra of BFA and BSFXA were measured in tetrahydrofuran (THF) solutions (Figure 1a) with peaks located at 366 and 372 nm, respectively. The slight red-shifted absorption of BSFXA is mainly due to the possible spiro-conjugation of the SFX unit, which is in agreement with the trend of energy gap calculated by density functional theory (DFT) at the B3LYP/6-31G (d) level (Figure 1b and Table S1).59 Also, BSFXA exhibited a red-shifted emission peak located at 462 nm, in comparison with that of BFA at 451 nm (Figure 1c). Their photoluminescence (PL) quantum yields (Φ_F) and fluorescence lifetimes (τ) were measured in THF solutions (Figure 1d), and BSFXA showed a relatively higher PL efficiency (21.12%) than that of BFA (15.83%). However, the fluorescence lifetime of BSFXA (2.12...
force. These luminescence properties can be reversible or be related to the less molecular motions under mechanical exhibited little changes in diocrystallized (467 nm). However, the PL spectra of BSFXA 452 nm) after grinding and turned to cyan one upon as prepared, and after being ground. The changes for samples in different solid states, including crystal, as-prepared, and ground heavily). (d) Fluorescence decay curves of BSFXA crystal under different solid states (excited at 490, 469, and 464 nm for crystal, as-prepared, and ground heavily).

The emission in solution, the slightly broader spectra in the aggregated state might be due to the strong intermolecular interactions. However, the emissive behaviors exhibited subtle changes for samples in different solid states, including crystal, as prepared, and after being ground. The fluorescence of the as-prepared BFA could keep its original blue emission (448–452 nm) after grinding and turned to cyan one upon crystallized (467 nm). However, the PL spectra of BSFXA exhibited little changes in different solid states, which should be related to the less molecular motions under mechanical force.40 These luminescence properties can be reversible or semireversible by fuming processes (Figure S14). Furthermore, it showed a much stronger emission as a crystal with the value of 40.43%, compared to that of BFA (16.34%), mainly due to the higher radiation rates of BSFXA (144.23 × 10⁻⁷ S⁻¹) than that of BFA (37.94 × 10⁻⁷ S⁻¹); this trend can be kept irrespective whether the solid was as prepared or ground. The better luminescence property of BSFXA should be ascribed to the optimized molecular packing in the solid state. The values of the two luminogens increased during the grinding of the prepared solid, from 9.55 to 12.37% for BFA and from 38.86 to 42.60 × 10⁻⁷ S⁻¹ for BSFXA, as well as the radiation rates decreased from 105.13 × 10⁻⁷ to 77.80 × 10⁻⁷ S⁻¹ for BFA and from 15.18 × 10⁻⁷ to 17.42 × 10⁻⁷ S⁻¹ for BSFXA (Table S4).

**ML Behavior of BSFXA.** With the aim to estimate the possible ML property, we scraped the solid samples of BFA and BSFXA heavily at room temperature. Clearly, BSFXA was ML-active but BFA was not; in detail, obvious cyan light was observed for BSFXA under mechanical force, even under daylight (Figure 3a), while no emission can be generated from BFA. The ML spectrum of BSFXA matched well with its PL one (Figure 3b), meaning that the similar excitation state was achieved by mechanical force and UV irradiation. Subsequently, powder X-ray diffraction (PXRD) spectra were recorded to investigate different ML properties of these two luminogens (Figures 3c and S15), and BSFXA crystal exhibited a much better compressive resistance than that of BFA for the maintainable crystalline state even after grinding heavily, which was beneficial to the ML effect, and related to the molecular packing in the crystal, and their varied packing modes and intermolecular interactions have been further confirmed by the theory calculation with quantum mechanics/molecular mechanics (QM/MM) method (Figures S16 and S17).

**Crystal Structures and Molecular Packing.** Single crystals of BFA and BSFXA were cultured by slowly evaporating their solution in a solvent mixture of dichloromethane and ethanol, with the related information listed in Table S5. The unit cell of BFA was centrosymmetric with a space group of P12₁/c1, while that of BSFXA was non-centrosymmetric with the space group of P1. Normally, the non-centrosymmetric packing can be favorable to obtaining the piezoelectric property, which could generate the electronic discharge upon mechanical stimulation, directly resulting in the dye excitation and generation of ML phenomenon. In detail, as to the BFA crystal, the head-to-head and tail-to-tail packing modes were found, with the relatively loose parallel or antiparallel arrangement (Figure 4a). However, the tight packing existed in the BSFXA crystal with the interlaced mode (Figure 4b), and the locked function is mainly from the SFX unit bearing the perpendicular moiety to the conjugation skeleton. These two different packing modes then demonstrated varied responses under mechanical stimulus. For BFA.

![Figure 2](image1.png)  
**Figure 2.** PL spectra of BFA (a) and BSFXA (b) in different solid states. Images below the respective subparts are those of BFA (a) and BSFXA (b) in different solid states and the corresponding quantum efficiencies. (c) Fluorescence decay curves of BFA under different solid states (excited at 467, 448, and 452 nm for crystal, as-prepared, and ground heavily). (d) Fluorescence decay curves of BSFXA under different solid states (excited at 490, 469, and 464 nm for crystal, as-prepared, and ground heavily).

![Figure 3](image2.png)  
**Figure 3.** (a) ML images of BSFXA under daylight (right) and in dark (left) at room temperature. (b) PL spectra (top) and ML spectra (bottom) of the as-prepared BSFXA. (c) XRD patterns of BSFXA in different solid states. (d) Fluorescence decay curves of BSFXA crystal with excitation at 469 nm.
were found in the SFX2 form. As for SFX3 form, it showed the
as two types of strong C···H interactions mainly existed in the
with close distance (2.774 and 3.616 Å). However, in the BFA
intermolecular interactions were derived from the SFX unit
SFX1 and SFX3 forms, among which, two kinds of strong

in a parallel arrangement, it would lead to the molecular slippage under the action of a force, resulting in the energy loss. As a consequence, nearly no ML can be observed in this case. However, the molecular motions in the BSFXA crystal have been locked by the adjacent molecules with stuck packing mode in a large degree. Thus, the mechanical force was easy to be converted into light emission for largely reduced energy loss via nonradiative relaxation channels.

In addition, intermolecular interactions in the crystals also play a vital role in ML property. There were no \( \pi \cdots \pi \) interactions in these two crystals for the twisted molecular configurations with the incorporation of DPA moieties. However, many C–H···O and C–H···B interactions could be observed in these crystals. To simplify crystal analyses, only the strong intermolecular interactions with the distance shorter than 4.0 Å are emphasized, and the corresponding results are presented in Figure 4c,d and Tables S6 and S7. There were three kinds of dimers in the unit cell of BFA and BSFXA crystals, marked as F1, F2, and F3 and SFX1, SFX2, and SFX3, respectively. In the SFX1 form, there are three types of strong C–H···O interactions with the distance as short as 2.77 Å and two kinds of C–H···N interactions with the distance of 3.73 and 3.92 Å, respectively. Similarly, one type of C–H···O interaction (2.85 Å) and C–H···B interaction (3.61 Å), as well as two types of strong C–H···π interactions (3.82 and 3.83 Å), were found in the SFX2 form. As for SFX3 form, it showed the strongest intermolecular interactions; in detail, it contained three types of C–H···π ranging from 2.97 to 3.49 Å, two types of strong C–H···B interactions (3.58 and 3.94 Å) and one type of C–H···O interaction (3.45 Å). Thus, in the BSFXA crystal, the strong intermolecular interactions mostly existed in the SFX1 and SFX3 forms, among which, two kinds of strong intermolecular interactions were derived from the SFX unit with close distance (2.774 and 3.616 Å). However, in the BFA crystal, strong intermolecular interactions mainly existed in the F1 form, including one type of C–H···π interaction (3.36 Å) and five types of C–H···O bonds with distances ranging from 2.71 to 3.87 Å. Furthermore, one type of C–H···O bond (2.15 Å) existed in the F2 form and F3 form contained one type of C–H···O bond (3.60 Å) and three types of C–H···O bonds, with distances ranging from 2.31 to 3.95 Å. Obviously, the much stronger molecule–molecule interactions in the BSFXA crystal resulted in a more compact molecular packing with high rigidity, favoring the efficient conversion of mechanical force to light emission; also, the spiro-structure of the SFX unit plays the key role to popular interactions among adjacent molecules and optimize the molecular packing with stuck mode.

CONCLUSIONS

In summary, a new ML luminogen (BSFXA) bearing spiro-
(4-fluorene-9,9′-xanthene) (SFX) moiety was reported with an obvious blue emission by mechanical stimulus, while the similar compound (BFA) with dimethyl fluorene (MeF) instead of SFX was ML inactive. Through careful investigation of their optical property in different conditions, crystal structures, together with theory calculations, SFX with spiro-
structure was proved as the main contributor to the optimized molecular packing and strengthened intermolecular interactions of BSFXA in solid state, resulting in the efficient conversion of mechanical force to light emission by the suppression of possible molecular slippage under external force. This is the first time for the spiro-structure as the main building block to ML luminogens, possibly affording an efficient strategy to expand the ML family by the rational molecular design.

EXPERIMENTAL SECTION

Instruments and Materials. \(^1\)H and \(^13\)C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Mass spectra were recorded on a ZAB 3F-HF spectrophotometer. High-resolution mass spectra were recorded on an LTQ-Orbitrap Elite high-resolution mass spectrometer (Thermo-Fisher Scientific, Waltham, MA) equipped with an electrospray ionization (ESI) source and a Dionex Ultimate 3000 UPLC system (Thermo-Fisher Scientific, Waltham, MA). Full MS scans were acquired in the positive-ion mode at a resolution of 60 000, the fragments were acquired with a high mass range of \(m/z\) 200–2500 at a resolution of 60 000. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a CARLOERBA-1106 microanalyzer. UV–vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Fluorescence quantum yields and lifetimes were determined with a FLS980 spectrometer. The powder X-ray diffraction patterns of crystals were recorded by Rigaku MiniFlex 600 with an X-ray source of Cu K\(\alpha\) (\(\lambda = 1.5418\) Å) at 25 °C at 40 kV and 15 mA at a scan rate of 5° (2\(\theta\))/min (scan range: 2°–50°). The single-crystal X-
ray diffraction data were collected in a Bruker Smart Apex CCD diffractometer. The ML spectra were measured on a spectrometer of Acton SP2750 with CCD (SPECT-10, Princeton) as a power detector. The quantum chemistry calculation was performed at the B3LYP/6-31G (d) level using the DFT method in Gaussian 09 software.

Toluene was dried over and distilled from K–Na alloy under an atmosphere of argon. All other reagents and compounds of DPA and BrMeF were purchased and used directly as received. 2,7-Dibromoisop[4-fluorene-9,9′-xanthene] (BrBSFX) was prepared according to literature procedures.\(^{40,41}\)
Synthetic Procedures. Synthesis of 7-Bromo-N,N-bis(4-methoxyphenyl)-9,9-dimethyl-9H-fluoren-2-amine (Br-MeFmDA). A mixture of BrMeF (3.17 g, 6.00 mmol), DPA (0.46 g, 2.00 mmol), (1,1′-bis(diphenylphosphino)ferrocene) (DPPF) (44 mg, 0.08 mmol), Pd(OAc)₂ (9 mg, 0.04 mmol), and sodium tert-butoxide (0.29 mg, 3.00 mmol) was placed in a nitrogen-flushed round-bottom flask. Toluene (20 mL) was then added and the solution was bubbled with nitrogen for 15 min. The mixture was stirred at 110 °C for 12 h before quenching by water. Then, the solution was extracted by dichloromethane for three times and the organic layer was dried over Na₂SO₄ for two hours. After the removal of solvent, the crude product was purified by column chromatography on a silica gel to yield a pale yellow powder as the desired product (0.65 g, 65% yield).¹H NMR (400 MHz, DMSO-d₆): 7.52 (d, J = 1.3 Hz, 1H, −ArH), 7.49–7.45 (m, 2H, −ArH), 7.42–7.40 (m, 1H, −ArH), 7.09–7.04 (m, 5H, −ArH), 6.86 (d, J = 8.9 Hz, 5H, −ArH), 3.80 (s, 6H, −OCH₃), 1.38 (s, 6H, −CH₃). ¹³C NMR (100 MHz, CDCl₃): 156.51, 156.05, 155.13, 141.47, 138.95, 136.55, 131.12, 130.42, 127.08, 126.43, 123.44, 120.91, 120.29, 119.88, 115.16, 55.94, 47.44, 27.29; MS (EI), [M⁺]: 547.78, calcd, 547.2894; anal. calcd for C₃₅H₃₈BN₃O₄: C, 76.94; H, 6.82; N, 2.33.

**Synthesis of 7-Bromo-N,N-bis(4-methoxyphenyl)spiro[fluorene-9,9′-xanthen]-2-amine (BSFXA).** A mixture of Br-SFXDA (0.51 g, 0.80 mmol), bis(pinacolato) diboron (0.23 g, 0.90 mmol), potassium acetate (0.24 g, 2.40 mmol), and Pd(dppf)₂Cl₂ (17 mg, 0.02 mmol) in anhydrous dimethyl sulfoxide (20 mL) was stirred at 80 °C under argon for 12 h, and then water (20 mL) was added. The crude product was extracted into ethyl acetate, washed with water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography on a silica gel to yield a pale yellow powder as the desired product (0.54 g, 74% yield).¹H NMR (400 MHz, DMSO-d₆): 7.82–7.77 (m, 2H, −ArH), 7.64–7.62 (d, J = 7.7 Hz, 1H, −ArH), 7.27–7.22 (m, 4H, −ArH), 7.18 (s, 1H, −ArH), 6.94–6.88 (m, 6H, −ArH), 6.80–6.78 (m, 5H, −ArH), 6.49–6.48 (d, J = 2.0 Hz, 1H, −ArH), 6.39–6.37 (d, J = 7.3 Hz, 2H, −ArH), 3.68 (s, 6H, −OCH₃), 1.19 (s, 12H, −CH₃). ¹³C NMR (100 MHz, THF-d₆): 156.80, 156.18, 154.47, 151.28, 149.71, 142.43, 140.56, 134.58, 132.32, 131.00, 127.86, 127.78, 126.09, 124.96, 122.97, 120.72, 120.21, 118.02, 117.31, 116.47, 114.31, 83.28, 54.52, 54.04, 29.41; HRMS (ESI), m/z [M + H⁺]: 868.3057, calcd, 868.3000; anal. calcd for C₃₅H₃₈BN₃O₄: C, 78.83; H, 5.88; N, 2.04. Found: C, 79.32; H, 5.58; N, 1.98.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02416.

NMR and mass spectra of new compounds; QM/MM model for BFA and BSFXA; detailed optical properties; PL lifetime and quantum yield parameters of BFA and BSFXA; and single-crystal data of BFA and BSFXA (PDF)

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (nos. 51673151 and 21734007), Hubei Province (2017CFA002), and Special funds for basic scientific research services in central colleges and Universities (2042017kf0247).

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