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Dancing Brightly Under Light: Intriguing Photomechanical Luminescence in Constructing Through-Space Conjugated AIEgens

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Abstract: Transforming molecular motions into macroscopic scale is a topic of great interest to nanoscience. Photomechanical effect is a promising strategy to realize this purpose but remains challenging to design molecular materials with superior photomechanical effect that can be visually monitored under UV light. Herein, we wish to report intriguing photomechanical luminescence driven by photodimerization of 2-phenylbenzo[b]thiophene 1,1-dioxide (P-BTO) in molecular crystals, and elucidate working mechanism and substituent effect via crystallography analysis and theoretical calculation. Striking splitting, hopping and bending mechanical behaviors accompanied by significant blue fluorescence enhancement are observed for P-BTO crystals under UV light, which is attributed to the formation of photodimer 2P-BTO. Although 2P-BTO is poorly π -conjugated because of the central cyclobutane ring, it exhibits prominent throughspace conjugation and aggregation-induced emission (AIE) characters, affording strong solid-state blue fluorescence at 415 nm with an excellent quantum yield of up to 96.2%. This work not only provides novel molecular crystals with photomechanical luminescence but also explores a new kind of AIE luminogens (AIEgens) based on a tailored through-space conjugated framework.

Photomechanical-responsive materials, such as photoactive polymers, elastomers, liquid crystals and molecular crystals, hold great potentials in light-driven artificial actuators,^[1] and have achieved remarkable progresses in recent years.^[2] In particular, considerable efforts have been devoted to exploring photomechanical crystals owing to their rapid energy transfer with less energy dissipation and higher Young's modulus. They can effectively amplify microscopic molecular motions into macroscopic scale, and the ordered molecular structures provide an opportunity to decipher the related processes. Various mechanical motions, such as jumping, bending, curling, crawling and twisting, have been realized in photomechanical crystals.^[3] With the desire to visually monitor and continuously characterize morphological changes of the crystals especially in dark background, photomechanical luminescence is a promising

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alternative, which means the photomechanical movements can be lit up by a simultaneous fluorescence "turn-on" phenomenon under UV light irradiation. Therein, the highly efficient photomechanical luminescence, driven by photochemical reactions using UV light as the excitation source, plays an important role in monitoring the process.

In general, the mechanical motions of photoactive crystals originate from structural transformations during mainly reactions, photochemical such isomerization as of azobenzene,^[3a,3b] [2 + olefins.[3c,3d] 2] cycloaddition of photocyclization of diarylethenes,[3e,3f] and [4 41 + photodimerization of anthracenes.[3g] Among diverse reported photochemical reactions, the topochemical [2 2] photodimerization has received most attention because of large structural variation and easy monitoring via NMR spectroscopy. But the formation of cyclobutane ring breaks the original π -conjugation of the precursor, causing severe damage to the luminescence of the product. So, efficient photomechanical luminescence is rarely achieved from molecular crystals involving photodimerization. In this work, we report the intriguing photomechanical luminescence based on photodimerization of 2phenylbenzo[b]thiophene 1,1-dioxide (P-BTO) in molecular crystals. The relevant working mechanism and substituent effect on the reaction are investigated. Although the generated photodimer 2P-BTO is poorly π -conjugated because of the presence of cyclobutane ring, they exhibit prominent aggregationinduced emission (AIE)^[4] property with strong deep blue fluorescence in solid powder, owing to the synergistic effect of efficient intramolecular through-space conjugation and restriction of intramolecular vibration. The formation of new robust AIE luminogens (AIEgens) is considered to contribute significantly to intense photomechanical luminescence.

The photodimerization of benzo[b]thiophene 1,1-dioxide (BTO) can date back to the 1950s,^[5] and the related photodimers structures and reaction mechanisms were subsequently reported.^[6] But all of these reactions were only performed in solutions. Until very recently, Resendiz et al.[7] reported the photodimerization of BTO derivatives in solid and elucidated the impact of reaction conditions on the structures of the photodimers. In comparison with BTO derivatives reported by Resendiz et al., P-BTO has a bulky phenyl substitute. In crystals, two adjacent P-BTO molecules can align in an antiparallel and head-to-tail manner (Figure 1), and the intermolecular distance between the reactive double bonds is 3.629 Å, shorter than 4.2 Å (Figure S8), well meeting the criteria of Schmidt for photodimerization in solid state.^[8] In the transition state, the two P-BTO molecules approach each other by maintaining the initial packing mode and the distance between the reactive carbons is shortened to 3.241 Å, as revealed by the calculation (Figure S18), which is beneficial for the formation of anti head-to-tail (anti-ht) conformation of the product.

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As expected, upon exposure to UV light (365 nm), the microcrystalline powder of P-BTO (Figure S2) undergoes topochemical photodimerization to generate 2P-BTO (Figure 1). The progress of photodimerization can be well monitored by using ¹H NMR spectroscopy (Figure S1). The singlet peak of H_a of BTO at 8.01 ppm is gradually decreased with the increase of irradiation time. Meanwhile, a new singlet peak appears at 5.96 ppm and intensifies progressively along with the irradiation, which is assigned to H_b in the newly formed cyclobutane ring, validating the concomitant formation of the photodimerization product. By calculating the related integral peaks in ¹H NMR spectrum, almost 86% photoconversion is achieved within a short exposure time of 2 hours, indicative of a high efficiency of the reaction. Single crystals of 2P-BTO can be obtained from a solution of P-BTO in dichloromethane/hexane mixture exposed under sunlight for a few days. The X-ray crystallography reveals that 2P-BTO only holds an anti-ht conformation, which is further confirmed by the single crystal grown by sublimation at 260 °C (Figure S3). The formation of sole anti-ht symmetrical photodimer undoubtedly demonstrates the excellent region- and stereo-selectivity of the photodimerization of P-BTO.



Figure 1. Synthetic routes of 2P-BTO, 2NP-BTO and 2MOP-BTO, the distance between two adjacent antiparallel P-BTO molecules, and crystal structure of 2P-BTO obtained in P-BTO solution.

Bulky substituents can effectively influence crystal stacking of the molecules, and thus can be used to tune the topophotochemical reactions and photophysical properties of the

generated photodimers. Hence, two new precursors of NP-BTO and MOP-BTO with more bulky naphthyl and 4-methoxyphenyl, respectively, are prepared and adopted for the photodimerization. However, their microcrystalline powders are photochemically inert under the same conditions. By carefully surveying the crystal packing, it is found that the distance between the reactive double bonds of two adjacent NP-BTO molecules is 4.949 Å, which is larger than 4.2 Å (Figure S9). For MOP-BTO crystals, although the distance of two reactive double bonds is short enough (3.852 Å), other important geometrical parameter θ_1 (the rotational angle of one double bond with respect to the other) is 54.17°, greatly deviating from the ideal value of 0° (Table S1, and Figure S10). Since the molecules are almost immobile in crystalline state, it is understandable that the photodimerization of these two precursors can hardly proceed in solid. On the contrary, the photodimerization can happen with high regioselectivity and high vields for NP-BTO, MOP-BTO as well as P-BTO in solution state, because the molecules have large freedom to adjust their relative positions. The generated photodimers 2NP-BTO and 2MOP-BTO also adopt anti-ht conformations, as determined by NMR spectroscopy or single crystal structures (Figure S4). Actually, the anti-ht conformations are the thermodynamically most stable conformations for these photodimers, as disclosed by the calculation (Figure S19). All the photodimers are very stable under ambient conditions in solid, and possess good thermal stability with high decomposition temperatures of 358-419 °C at 5% weight loss (Figure S12).



Figure 2. Fluorescence microscopy images of P-BTO single crystals during irradiation with 365 nm UV light for 1 min (A and I: under daylight; B-H: under UV light). Scale bar: $10 \ \mu$ m.

The photodimerization of P-BTO can also occur in its bulky single crystals, results in significant morphological evolution (Figure 2, Figure S13 and Video S1-3). It is found that bulky crystals rapidly split into small pieces, some of which can move and even jump out of the visual field under UV light irradiation, within a very short response time of 10 seconds. Moreover, some crystals can be divided into small belts, and become bent apparently. The obvious surface cracks of crystals can also be observed in scanning electron microscope (SEM) images (Figure

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S14). Along with the photomechanical effect, an impressive fluorescence "turn-on" phenomenon is observed. The P-BTO crystals show weak blue fluorescence (446 nm), but the fluorescence significantly intensifies after UV light irradiation for 1 h (Figure 3A). The vigorous photoinduced motions and fluorescence enhancement are also true for P-BTO microcrystalline powders under the same conditions, with noticeably increased fluorescence quantum yield (Φ_F) from 1.7% to 92.3% (Figure 3B and Table S2). More importantly, the photomechanical phenomena can be directly caught by naked eyes (Video S4-6), thanks to the fluorescence "turn-on" phenomenon.

To explore the driving force for the above photomechanical motions in depth, the photoinduced changes in cell parameters and crystal structures are analyzed by X-ray crystallography. Upon UV light irradiation for 1 minute, the unit cell of P-BTO crystal expands by 65.0% along a-axis and 46.4% along b-axis, but shrinks by 16.9% along c-axis (Table S3). On the other hand, the bond length of C-C single bond in cyclobutane ring of 2P-BTO is 1.583 Å, which means P-BTO molecules need to get closer by ~2.046 Å during photodimerization. And the distance between the outermost hydrogen atoms spreads to 7.562 Å in 2P-BTO molecule, disclosing obvious photo-triggered structural transformation (Figure 1C). Eventually, the space group is altered from $\overline{P1}$ for P-BTO crystals to C2/c for 2P-BTO crystals to accommodate these structural changes. Thus, photomechanical behaviors occur on account of instantaneous release of the accumulated strain during the photodimerization.



Figure 3. (A) PL spectra and (B) $\Phi_{\rm E}$ values of P-BTO microcrystalline powders under irradiation with 365 nm UV light for different time. Inset: fluorescent photos of P-BTO before and after UV light irradiation. (C) PL spectra of 2P-BTO in DMSO/water mixture with different water fractions (f_w) (10⁻⁵ M). (D) Plots of relative PL intensity (1//₀) versus f_w (I_0 = intensity at f_w = 0%). Inset: fluorescent photo of pure 2P-BTO under UV light irradiation.

To gain in-depth insights into the photomechanical luminescence, the photophysical property of 2P-BTO is carefully investigated. In dimethylsulfoxide (DMSO), 2P-BTO shows a maximum absorption band at ~277 nm, apparently blue-shifted than that of P-BTO (~341 nm). The fluorescence of 2P-BTO is also blue-shifted by 31 nm relative to that of P-BTO in solid powder (Figure S16 and S17). The blue shifts in absorption and fluorescence spectra are due to the non-conjugated cyclobutane ring, which greatly undermines the π -conjugation of 2P-BTO. Meanwhile, a large Stokes shift (12005 cm⁻¹) is observed for 2P-BTO in solid. And the onsets of absorption and emission are also apparently separated. These results demonstrate the conformation change between the ground state and excited state of 2P-BTO (Figure S17) under photoexcitation.^[9] Actually, 2P-BTO is a very faint emitter in DMSO, as evidenced by a $\Phi_{\rm F}$ as low as 0.8%, which is understandable in view of the poorly π -conjugated structure and vigorous intramolecular motion in solution.^[10] What surprised us is that its fluorescence becomes much stronger upon aggregate formation by adding a large amount of water to DMSO solution (Figure 3C and D). The solid powder of 2P-BTO can fluoresce strongly at 415 nm with an excellent $\phi_{\rm F}$ of up to 96.2%, unveiling the prominent AIE property. 2NP-BTO and 2MOP-BTO with different substituents display the similar AIE behaviors (Table 1).

 Table 1. Photophysical properties of 2P-BTO, 2NP-BTO and 2MOP-BTO.

Compound	λ _{abs} [nm] ^[a]	λ _{em} [nm] ^[b]	$oldsymbol{\Phi}_{F} [\%]^{[c]}$		a [d]
Compound			soln	solid	- UAIE
2P-BTO	277	415	0.8	96.2	120.3
2NP-BTO	279	439	0.5	50.6	101.2
2MOP-BTO	276	451	0.7	66.4	94.9

^[a]Absorption maximum in DMSO solution (10⁻⁵ M). ^[b]Emission maximum in solid powder. ^[c]Fluorescence quantum yields of DMSO solution (soln) and solid powder, determined by a calibrated integrating sphere (λ_{ex} = 340 nm). ^[d]AIE activity, calculated by σ_{F} (solid)/ σ_{F} (solin).

The strong fluorescence of 2P-BTO in solid powder obviously differs from those of P-BTO. To figure out the origin of the strong fluorescence, the crystal structure of 2P-BTO is studied. There are two pairs of phenyl rings (ϕ_1 and ϕ_2) aligning in close proximity with a shortest interplane distance of 3.147 Å (Figure 1C), which is short enough to engender noncovalent intramolecular interactions. To visualize such intramolecular interactions, the independent gradient model (IGM) method is used on the basis of single crystal structure.[11] The obvious green sections between two phenyl rings clearly validate that through-space interaction exist in 2P-BTO crystal (Figure 4A). Similar interaction is also found in 2MOP-BTO crystal (Figure S11). Such kind of throughspace interaction is conducive to stabilizing molecular structure and strengthening intramolecular electronic communication, and can result in a radiative channel for dissipating excited state energy.[10b,12]

Theoretical simulations are also carried out to decipher the mechanism of the efficient solid-state fluorescence. The large geometric change occurs between the ground state (S_0) and the lowest energy-excited state (S_1) . The two aromatic rings employ an almost parallel and closer stacking manner in the excited state (Figure S20, Table S4-S6). which is more favorable for interplane

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electronic communication and orbital overlap. Taking 2P-BTO as an example, the two phenyl rings (φ_1 and φ_2) get much closer in S₁ state, and stronger through-space interaction is visualized between two stacked phenyl rings (Figure 4B). In addition, apparent electronic delocalization of the lowest unoccupied molecular orbital (LUMO) is found between the two stacked phenyl rings, which confirms through-space conjugation character (Figure 4D).^[13] For 2NP-BTO and 2MOP-BTO, the interplane distances are slightly longer than that of 2P-BTO in S₁ state due to steric hindrance, but short enough for a large overlap degree of frontier orbitals. The through-space conjugation characters can be clearly observed in LUMOs as well (Figure S21 and S22). These results definitely manifest that these photodimers are governed by eminent through-space conjugation.



Figure 4. Visualization of through-space conjugation in (A) crystal and (B) lowest energy-excited state of 2P-BTO. The frontier orbital amplitude plots of 2P-BTO in (C) the ground state and (D) the lowest energy-excited state, calculated based on M06-2X with Grimme's empirical dispersion correction^[14] and the basis set 6-31G(d,p).

Furthermore, the formation of through-space conjugation in the excited state is also validated for 2P-BTO in solid. As shown in Figure 5A, the fluorescence intensity increases as the temperature rises from 77 to 298 K, which is opposite to the common observations of decreased fluorescence along with the increase of temperature due to the nonradiative decay caused by molecular motion. But in the case of 2P-BTO in solid, certain molecular motion can induce minor conformational adjustment and facilitate the formation of an intramolecular cofacial conformation in the excited state. Consequently, the intramolecular electronic coupling of 2P-BTO is reinforced, accounting for the increased fluorescence.[15] The ultrafast piconanosecond fluorescence transients monitored at different emission wavelengths further reveal the corresponding relaxation dynamics (Figure 5B). At the blue side of the emission (375 nm), the fluorescence lifetime is determined to be 5.50 ns. By monitoring at 415 nm (the fluorescence peak of 2P-BTO in solid), the lifetime becomes shorter (1.65 ns), which can be attributed to the enhancement of radiative decay rate. Therefore, the formation of energy-minimized geometry in S1 state with obvious throughspace conjugation (Figure 4D) can be further confirmed.



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Figure 5. (A) PL spectra of 2P-BTO in solid at 77 and 298 K, and (B) the ultrafast pico-nanosecond fluorescence transients of 2P-BTO in solid monitored at various wavelengths.

The calculation by the combined quantum mechanics and molecular mechanics (QM/MM) method with two-layer ONIOM approach^[16] on the basis of a solid-phase computational model of 2P-BTO crystal structure shows that the radiative decay rate from S_1 to S_0 is increased from gas (3.96 x 10⁶ s⁻¹) to solid (2.00 x 10⁷) s⁻¹) by about 5 times, partially owing to the reinforced throughspace conjugation in solid. On the other hand, the nonradiative decay rate in solid $(1.09 \times 10^9 \text{ s}^{-1})$ is decreased by about 3 orders of magnitude than that in gas $(1.28 \times 10^{12} \text{ s}^{-1})$, indicating the nonradiative decay has been remarkably blocked upon aggregation. The Huang-Rhys (HR) factors and reorganization energies (λ) which are crucial parameters to evaluate the nonradiative decay processes are determined by DUSHIN program (Figure 6 and Table S7).^[17] They are much smaller in solid than in gas, especially in low frequency region ($<100 \text{ cm}^{-1}$), disclosing the vibrational motions of phenyl rings are successfully restricted in solid relative to in gas, which suppresses nonradiative decay and contributes to through-space conjugation, rendering strong fluorescence in solid.





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Figure 6. Calculated reorganization energies of 2P-BTO in (A) gas and (C) solid and HR factors of 2P-BTO in (B) gas and (D) solid versus normal mode frequencies. Inset: representative vibration modes.

In summary, the photodimerization reactions of BTO derivatives with bulky substituents are studied, based on which a new kind of dynamic crystal photoactuator is explored. Photoinduced splitting, hopping and bending behaviors, as well as significant fluorescence enhancement are observed for P-BTO crystals, owing to the formation of photodimer 2P-BTO under UV light irradiation. Although 2P-BTO is poorly π -conjugated because of the central cyclobutane moiety, it exhibits prominent AIE property with strong blue fluorescence at 415 nm and a remarkable $\Phi_{\rm F}$ of 96.2% in solid powder, owing to efficient intramolecular through-space conjugation and restriction of intramolecular vibration. This work provides a new method to construct AIEgens based on through-space conjugation, with unequivocal working mechanism. And the presented photomechanical luminescence is to the benefit of visually monitoring morphological changes of crystals in high resolution, and offers great potential for the applications in smart devices and bionic science.

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Keywords: photodimerization • photochemical reaction • photomechanical luminescence • aggregation-induced emission • through-space conjugation

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Layout 1:

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Intriguing photomechanical luminescence is observed for P-BTO crystals, driven by photodimerization reaction under UV light irradiation. The generated photodimer 2P-BTO exhibits prominent through-space conjugation and aggregation-induced emission characters with an excellent fluorescence quantum yield of up to 96.2% in solid.



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Dancing Brightly Under Light: Intriguing Photomechanical Luminescence in Constructing Through-Space Conjugated AIEgens