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Frustrated Element-Blocks: A New Platform for Constructing Unique Stimuli-Responsive Luminescent Materials

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ABSTRACT

An element-block, which is the heteroatom-containing functional minimum unit, is a versatile building block for constructing functional polymers. In this focus review, we explain the new concept for developing stimuli-responsive luminochromic materials based on “the frustrated” element-block. When the element-blocks which show relatively larger degree of structural relaxation in the excited state are structurally restricted, we regarded that these molecules are in “the frustrated state”. Recently, we discovered unique stimuli-responsive luminochromic behaviors from “the frustrated element-blocks”. As a representative example, stimuli-responsive properties of “the frustrated boron clusters” are initially illustrated. The series of luminochromic properties, such as mechano- and thermochromism are described. Next, we designed the fused complexes for suppressing intramolecular motions to obtain “frustrated boron complexes”. Not only constant emission in solution and solid but also mechanochromic luminescent materials have been obtained. Finally, “the frustrated state” by the polymerization is explained. Unique luminochromic behaviors, such as thermochromism in solution, mechanochromism in solid and vapochromism were observed from the polymers. Mainly from our recent works, stimuli-responsive luminochromic behaviors of “the frustrated element-block”-containing polymers and their mechanisms are illustrated.

INTRODUCTION

As a next-generation technology of organic light-emitting devices, many researchers have devoted tremendous efforts to develop chemical sensors, and stimuli-responsive polymers are regarded as one of versatile platforms. Owing to flexibility and film-formability of polymeric materials, advanced organic electronic devices, such as wearable and stretchable sensors, have been accomplished with stimuli-responsive polymers. In particular, because of superior light-absorption and luminescent properties and carrier-transport ability, conjugated polymers have attracted attention for constructing film-type sensors.¹ By incorporating functional units into the polymer-main chains, it is possible not only to tune optoelectronic properties but also to enhance sensitivity and selectivity for monitoring specific targets. For developing further sensing technologies, heteroatom-containing polymers are a promising scaffold. Because heteroatoms often show specific reactivity and environmental sensitivity, heteroatom-containing materials are applicable for realizing unique sensing systems. However, as is often the case with polymeric materials, it is difficult to combine heteroatoms with the main-chain conjugation and induce significant electronic properties from loaded elements. Additionally, stability is occasionally lowered by incorporating heteroatoms into polymers. Therefore, only the limited kinds of heteroatoms, such as boron and silicon, have been conventionally utilized for developing sensing materials based on conjugated polymers.^{2,3}

An element-block is defined as a minimum functional unit containing heteroatom.^{4,5} Functional conjugated polymers can be obtained by the connection, combination and assembly with element-blocks according to the preprogrammed designs. By employing element-blocks, several advantages are proposed for preparing stimuli-responsive

polymeric materials. First, even from the single type of element-blocks, various functions can be obtained by changing the connection manners. As summarized in the recent review and mentioned later, different stimuli-responsive luminescent properties were inducible by altering the connection points at the emissive element-block in the conjugated polymers.^{6,7} Second, additional functions can be loaded by combining different types of element-blocks. Simply by connecting a luminescent element-block with the guest unit which can capture the target host molecule, optical sensors for the host molecule can be readily obtained. Third, by changing chain assembly and morphology, optical properties can be controlled with some extent. Emission intensity and/or color of luminescent polymer solutions are varied when the polymer forms aggregation.

As a new aspect on the design for stimuli-responsive materials, we have recently focused on the element-blocks involving the distorted structure and unstable state of element. Owing to the development of organic synthetic tactics for stabilizing these unstable structures and electronic states of element, such as tricoordinate boron, new electronic properties have been revealed.⁸ In particular, if we can realize such energetically-unfavorable structures into the element-block, environment-sensitive materials with higher sensitivity than those of conventional ones can be obtained. Thus, exploration of such unstable element-blocks is a promising approach for developing advanced sensing materials.

In this focus review, we explain the new concept for developing stimuli-responsive materials based on “the frustrated element-block”. According to the previous studies, we found that some of boron complexes, named “excitation-driven complexes”, show slight

emission in solution due to excitation deactivation through structural transformation for stabilization in the excited state.⁹ Meanwhile, significant emission can be obtained by suppressing structural transformations with solidification or introduction into polymer main-chains. In particular, it was found that their emission properties are very sensitive toward environmental changes and external stimuli. Because of structural restriction in solid and polymer chains, emission properties can be preserved by considerably suppressing energy-consumable structural transformation (Figure 1). If the room is generated around the complex, transformation would be partially allowed. Then, although emission properties are maintained, different luminescent color corresponded to partially-transformed conformation in the excited state should be induced. It should be noted that the room in the atomic scale is large enough to show luminescent color changes. Thus, stimuli-responsive luminochromic behaviors with high sensitivity can be obtained. In this scenario, we named structurally-restricted states as “the frustrated state” (Figure 1). The word of “frustration” is already used in physics on the specific spin state¹⁰ and in chemistry on “frustrated Lewis pairs”¹¹ which Lewis acid and base are separated in the single molecule. In this paper, when structural relaxation in the excited state is insufficient to induce emission annihilation because of structural restriction, we regard that the molecule should be in “the frustrated state”.

Figure 1

“The frustrated element-blocks” of boron clusters

Aryl-modified *o*-carboranes (Figure 2) are one of typical examples of “excitation-driven element-blocks”.⁹ By suppressing molecular motions in the excited state, “the

frustrated state” at the boron cluster can be realized. Initially, “the frustrated state” of *o*-carboranes by suppressing these motions in solid and their stimuli-responsive luminochromic properties are explained. According to the recent studies, two types of molecular motions in the excited state of aryl-modified *o*-carboranes, such as the extension of the C–C bond in the cluster (Figure 2a)¹² and intramolecular rotation at the connecting bonds between the *o*-carborane unit and the aryl moiety (Figure 2b),¹³ are proposed. *o*-Carborane has an icosahedral structure composed of ten boron and two carbon atoms. Owing to electron delocalization through the cluster, high thermal stability is generally observed. When the aryl moiety is connected at the carbon atom in the cluster, *o*-carborane would work as a strong electron acceptor.¹⁴ As a result, significant emission from the electronic transition from the intramolecular charge transfer (ICT) state is observed. Interestingly, the ICT emission can be observed only in the solid state from the molecules in which the C–C bond in the cluster is not fixed. This emission enhancement by solidification is called aggregation-induced emission (AIE) properties.¹⁴ Since constant emission both in solution and solid states was observed by introducing the fixed structure at the C–C bond in the cluster, it has been proved that emission quenching in solution should be induced during the extension of the C–C bond in the *o*-carborane unit.¹² Therefore, it is likely that the transformation of the cluster would be disturbed in the solid state. Thus, “the frustrated state” can be readily prepared by solidification. Furthermore, it can be expected that diverse “frustrated states” can be induced in crystal and amorphous states.

Figure 2

It is proposed that the sphere structure of *o*-carborane should play an important role in avoiding aggregation-caused quenching (ACQ). Thus, some of aryl-modified *o*-carboranes show efficient solid-state luminescent properties.¹⁴ Because the progress of the C–C bond extension, followed by emission intensity changes (Figure 2a), is critically influenced by local environment, chemical sensors can be constructed for monitoring environmental factors. In the hydrogel matrices, the degree of the suppression of the bond extension is strongly dependent on the swelling/shrinking ratios.¹⁴ Although environment-sensitive luminescent enhancements were observed, similar behaviors can be readily obtained by using other conventional AIE dyes instead of *o*-carborane derivatives. Further, precisely speaking, sensing properties are originated from the formation of “frustrated state”. Next, representative examples regarding sensitive stimuli-responsiveness of *o*-carboranes in “the frustrated state” are demonstrated.

The unique feature of the *o*-carborane-based “frustrated element-blocks” are stimuli-responsive luminochromic properties. In particular, various behaviors can be observed from solid-state luminescent *o*-carborane dyads and triads. The degree of electron-accepting ability of *o*-carborane toward the aryl moiety is greatly enhanced by rotation (Figure 2b).¹³ In the planar conformation, where the direction of the C–C bond in the *o*-carborane unit is included on the π -plane of the aryl moiety, electronic interaction is negligible. Therefore, emission is observed originated from the transition from the locally-excited (LE) state of the aryl moiety. By the formation of the perpendicular conformation, the electronic interaction should be maximized, and intense ICT emission can be observed. According to quantum calculations, energy levels of the planar conformation are often lower than those of the perpendicular conformation in the ground

state, meanwhile the perpendicular conformation is more stable than the planar one in the excited state. Originating from the switch of the most stable conformation from the planar to the perpendicular one after photoexcitation, molecular rotations at the connecting point with the aryl moiety and the *o*-carborane unit can be induced in the excited state. It should be emphasized that this molecular rotation can occur even in solid as well as crystal.¹³ Because of the sphere structure of the boron cluster, molecular rotation, followed by luminescent color changes, should be allowed. Next, we explained these luminochromic behaviors by changing the degree of suppression of molecular rotation, in other words, the magnitude of “frustration”.

As mentioned above, emission color of the aryl-modified *o*-carboranes is significantly depended on the angle of the *o*-carborane unit toward π -plane. Additionally, molecular rotation can proceed in solid. Based on these facts, we expected to control the degree of rotation by the substituent groups, followed by regulation of thermochromic luminescent properties. We prepared three kinds of triphenylamine-tethered *o*-carboranes with or without substituents around the connection with *o*-carborane (Figure 3).¹⁵ The pristine triphenylamine-modified and mono-methyl-substituted *o*-carboranes showed intense ICT emission. In contrast, by introducing dimethyl groups at the triphenylamine moiety, dual emission properties consisted of LE and ICT emission bands were observed in solid. Especially, by changing temperature, intensity ratios were varied, following thermochromic luminescent behaviors between 77 K and 298 K. As another instance, the molecular rotation can be tuned by hydrogen bonding between the aryl moiety and *o*-carborane.¹⁶ Temperature-sensitive dual-emission properties were observed. In these studies, the interaction caused by the methyl substituents and hydrogen bonds should

contribute to enlarging the height of energy barrier in the rotation, and “the highly-frustrated state” should be realized by disturbing molecular rotation. Hence, tuning of temperature ranges in thermochromic luminescence was achieved.

Figure 3

Various element-blocks with mechanochromic luminescent properties have been reported, and it is suggested that intermolecular interaction could be the major factor for modulating luminescent color in solid.^{17,18} Actually, since molecular distribution and subsequently degree of intermolecular interaction would be considerably different between crystal and amorphous, mechanochromic luminescent behaviors appear when regular structures in the solid-state luminescent crystalline materials are collapsed by mechanical forces. On the other hand, in order to avoid ACQ usually caused by intermolecular interaction in the condensed state, the introduction of bulky substituents is one of conventional strategies. Therefore, in principle, it is difficult to design highly-sensitive mechanochromic luminescent materials for monitoring very weak mechanical forces.

More recently, stimuli-responsiveness toward tiny environmental changes or weak mechanical forces was accomplished by developing the modified aromatic compounds with dual *o*-carborane units. It is commonly difficult to realize luminochromism in polymer matrices, while the dual *o*-carborane-tethered conjugated triad can thermochromic luminescent properties.¹⁹ Owing to high sensitivity toward environmental changes, the peak shifts of the emission band with the ICT character were accomplished.

As another example, it was found that bis-*o*-carborane-tethered pyrene showed the multi-step luminescent color change (Figure 4).²⁰ By gently tapping the pristine crystal sample with a spatula, initial luminochromism can be induced. Subsequently, the further luminochromic behavior can be observed by grinding the sample. We detected reversible changes by heating and vapor fuming. It is proposed that defects should be generated by tapping in crystalline packing at the initial tapping treatment. Owing to high environmental sensitivity, optical properties of the surrounding molecules around defects should be drastically affected. Furthermore, it was shown that excimer emission was detected after grinding. Then, two-steps luminochromic behaviors were accomplished. The sparse crystal packing was obtained because of dual substitution of *o*-carboranes. Thereby, the collapse of regular structures can be readily induced in crystal packing.

Figure 4

In addition to the above example, the switching between ICT and excimer emission have been observed. Except for it, *o*-carborane-substituted aromatic derivatives also showed stimuli-responsive luminochromic behaviors originating from the switching of emission mechanism between excimer and ICT emission in solid (Figure 5).^{21–25} In particular, the modified *o*-carboranes with the ethynyl linker often showed solid-state excimer emission.^{22–25} By inserting the ethynyl linker, the energy barrier between LE and ICT states is lowered. As a result, both energy states should be formed after photoexcitation. In the condensed state, the formation of excimer can proceed between the excited molecules at the LE state. Thus, the switching of emission mechanism between LE and ICT can occur triggered by changing environmental factors. Indeed,

thermochromic luminescent behaviors based on the switching of emission mechanism without structural transition were also detected from the ethynyl-*o*-carboranes.^{22–25} Because of small energy barrier, reversible transitions can proceed.

Figure 5

In summary, by suppressing molecular motions in the excited state of aryl-modified *o*-carboranes intrinsically in the solid state, “the frustrated state”, in which structural relaxation is prohibited, is realized. Consequently, highly-sensitive stimuli-responsiveness is obtained. Fortunately, the *o*-carborane substitution contributes to avoiding ACQ. Therefore, a variety of luminochromic behaviors triggered by tiny external stimuli can be observed. Since multiple molecular motions in the excited state are clarified, various types of “the frustrated state” are presumable. Hence, *o*-carborane is a promising element-blocks for constructing further stimuli-responsive luminescent materials.

“The frustrated element-blocks” of boron complexes

Next, we mention “the frustrated state” induced by polymerization. By inserting excitation-driven complexes into polymer main-chains, molecular motions can be suppressed. In particular, by changing the connection points at the complex, we can selectively suppress the mobility in the substituent or atomic scale.^{6,7} Therefore, it can be expected that different types of stimuli-responsiveness might be observed from each polymeric structural isomer. In this section, we explained the stimuli-responsive polymers consisted of “the frustrated” boron complexes.

We have previously demonstrated the transformation of conventional boron complexes with ACQ behaviors to AIE-active ones based on the ketoiminate (ketiminate) ligand skeleton (Figure 6).²⁶ By replacing one of oxygen at the dative bonds to nitrogen in boron diketonate (BDK) which shows ACQ, AIE-active boron ketoiminate (BKI) and polymers can be obtained.²⁷ According to the mechanistic studies including theoretical calculations, it is suggested that molecular tumbling could be caused around the B–N dative bond which is weaker bond energy than B–O in the excited state. Therefore, emission annihilation in solution occurs. In aggregate, molecular tumbling would be effectively suppressed. Additionally, it is proposed from theoretical calculations that distribution of the highest occupied molecular orbital is localized in the ketoiminate ligand. Thus, intermolecular interactions followed by ACQ could be inhibited. By the combination with emission annihilation in solution and suppression of molecular motions, AIE behaviors can be achieved by the nitrogen substitution. Based on this finding, we designed “the frustrated element-block” based on the ketoiminate skeleton.

Figure 6

By introducing BKI into the hydrogel, emission intensity changes were also observed during swelling and shrinking processes, similarly to *o*-carborane-containing gels.²⁸ In the case of BKI, much higher environmental sensitivity was observed. Hydrogels are generally shrunk in organic solvents. When BKI-containing hydrogels were soak into polar organic solvents such as dimethyl sulfoxide and dimethyl formamide, which are a poor solvent toward BKI, blue luminescence was observed from the shrunk gel (Figure

7).²⁹ In contrast, by using tetrahydrofuran and dioxane which are a good solvent toward BKI, yellow luminescence was detected. In the polar solvents, molecular tumbling at the BKI units should be highly restricted by adsorbing hydrogel matrices. Therefore, emission was observed in the relatively shorter wavelength region because structural relaxation should be highly suppressed. This aggregation-induced luminochromic properties were also observed in the presence of proteins. By altering the degree of gel shrinking, the extent of “frustration” should be varied. As a consequence, luminochromic behaviors should be induced.

Figure 7

To realize “the frustrated state” by fixing potentially-mobile points, we introduced the fused structure involving the nitrogen moiety. It was presumed that molecular tumbling can be suppressed by the fused structure (Figure 6).³⁰ Therefore, not only solid-state emission but also environment-sensitive luminescent properties in the AIE behavior can be preserved both in solid and solution. Based on this idea, we prepared four types of fused boron ketoiminates (FBKI) and investigated their luminescent properties.³⁰ Accordingly, AIE properties were no longer observed, meanwhile dual-state emission in solution and crystal was detected. In particular, mechanochromic luminescent properties, which were not observed from boron ketoiminates, were detected. As we designed, the solid-state luminescent molecules with stimuli-responsiveness were obtained.

In order to detect luminochromic behaviors triggered by weak stimuli, similarly to dual-substituted molecule with *o*-carboranes, we elaborated the chemical structure of the

ligand moiety. By replacing benzene to thiophene, electron density in π -conjugation and molecular planarity should be improved (Figure 8).³¹ These features are beneficial for improving environmental sensitivity. The designed boron complex, thio-FBKI, was synthesized, and crystal polymorphs were obtained by changing the type of solvent in the recrystallization step. Notably, one of polymorphs displayed multi-step mechanochromic behaviors. In particular, the initial luminochromism was able to be initiated by very weak physical forces. These data represent that electronic properties of the molecules in “the frustrated state” can be tuned by chemical modification. Next, based on these data, we designed and synthesized conjugated polymers with FBKI and thiophene.

Figure 8

We synthesized conjugated polymers with FBKI and the bithiophene comonomer by changing the substitution point at the fused unit.³² The linear (*l*-PBT) and zigzag-type (*z*-PBT) polymers were obtained, and their optical properties were examined. Accordingly, *l*-PBT and *z*-PBT present unique luminochromic behaviors in solution and solid, respectively. Initially, we examined luminescent properties of *l*-PBT and interestingly thermochromic behaviors were observed from the chloroform solution (Figure 9). Yellow luminescence with the peak around 580 nm was observed at 30 °C, while luminescence color was tuned to be green at 60 °C. By cooling to 30 °C, the yellow luminescence was recovered. From UV–vis absorption spectra, the new absorption band with the peak around 550 nm was detected at 30 °C and disappeared at 60 °C. The data from dynamic light scattering measurements indicated that aggregation should form in solution and can be released by heating. These results suggest that *l*-PBT can form chain assembly even

in fluid around room temperature, and self-absorption of luminescence around 550 nm proceeds. By heating, these chain assembly should be released, and correspondingly the absorption band disappear. Therefore, luminochromic behaviors can be induced. In THF which is a good solvent for *l*-PBT, molecular assembly followed by luminochromism was hardly observed.

Figure 9

In general, amorphous states are obtained from the solids of conjugated polymers. Therefore, it is difficult to induce mechanochromic luminescent properties with conjugated polymers because environmental changes are too small to perturb electronic properties of main-chain conjugation by the mechanical treatment. In contrast, from *z*-PBT in solid, mechanochromic luminescent properties were obtained (Figure 10).³² Orange emission was tuned to yellow by grinding in solid. According to the data from differential scanning calorimetry, the significant endothermic peak was observed only before the treatment. It is implied that regular structures could be locally formed in the solid sample of *z*-PBT. By the mechanical treatment, amorphous state should be enlarged, and the luminescent color change is obtained. This result is one of clear examples to demonstrate the applicability of “the frustrated element-blocks” for constructing sensitive stimuli-responsive materials.

Figure 10

By replacing another oxygen to nitrogen in boron ketoiminate, diiminate complexes

are obtained (Figure 11).^{27,33,34} Boron ketoiminates can show emission enhancement in amorphous and crystal, while emission enhancement can be detected only in crystal from boron diiminate complexes (crystallization-induced emission, CIE). It is likely that far more structural restriction should be required for suppressing emission annihilation caused by molecular motions because of high mobility in the excited state. By introducing dual iodine groups into the phenyl groups with variable positions in the tetra-phenyl-substituted complex, we observed different mechanochromic luminescent behaviors (Figure 11).³⁵ When the iodine groups were introduced into the ring A and D, luminochromic properties were hardly observed by the mechanical forces. On the other hand, other complexes showed mechanochromic luminescent properties. According to the X-ray structural analyses, it was shown that tight packing should be formed in the crystalline sample presenting insensitivity toward the mechanical treatments. When drastic collapses are induced by the mechanical treatment, luminochromic behaviors are obtained. These data represent that environmental sensitivity can be tuned by modulating the substitution positions.

Figure 11

By introducing boron diiminate into the polymer main-chains, luminochromic properties were obtained by morphology changes in film. We synthesized the regioregular homopolymer with boron diiminate (Figure 12).³⁶ By using the AB-type monomer, the head-to-tail polymer can be obtained. As a comparison, we also prepared random polymers. In the THF and chloroform vapors, we annealed the film samples, and luminescent properties were monitored. Accordingly, vapo-chromic luminescent

behaviors were observed only from the regioregular polymer. By the annealing treatment with solvent vapor, polymer chains should locally form regular structures especially at the alkyl side chains. As a result, molecular planarity of the polymer main-chains is lowered, followed by blue-shifted emission bands. In the case of the random polymer, amorphous state can be preserved after the vapor annealing treatment. Therefore, significant changes in luminescent properties were hardly observed.

Figure 12

Vapochromic luminescent properties were also observed from the conjugated polymers composed of boron azomethine complexes (Figure 13). Boron azomethine and azobenzene complexes are also classified as an excitation-driven complex.^{37–45} Because of intrinsic structural distortion caused by boron complexation, the bending motion originating from elongation at the imine bond is proposed according to quantum calculation for estimating the most stable conformation in the ground and excited states. Indeed, boron azomethine complexes also show CIE properties and its polymers have constant luminescent properties in solution and film (Figure 13).⁴⁶ Similarly to above AIE- and/or CIE-active molecules, emission annihilation caused by molecular motions should be suppressed by connecting with comonomer units. Further, solid-state emission properties can be induced through the preservation of solid-state emission of CIE by inserting the polymer main-chains (Figure 14).^{37–45} By fuming the film of boron azomethine polymers with relatively-shorter alkyl chains, peak shifts were detected from the deep-red to the near-infrared region.⁴⁷ By replacing alkyl side-chains to longer ones, luminochromic behaviors were spoiled, meaning that partial crystallization and assembly

of side-chains should be responsible for luminochromic behaviors by vapor annealing.

Figures 13 and 14

CONCLUSION

“The frustrated state” can be realized by suppressing molecular motions in the excited state from the molecular scale to bulk states. When the complexes possess solid-state emission properties, stimuli-responsive luminochromic properties can be often obtained in film. As a result, film-type sensing materials are obtained. As is often the case with polymers, environmental sensitivity of each monomer unit is often lowered or spoiled by polymerization because influence on electronic properties is too small to induce optical changes in the random distributions in amorphous films, whereas significant stimuli-responsive luminochromic behaviors were obtained from the polymers containing “the frustrated element-blocks”. High sensitivity toward environmental changes plays a key role in optical changes. As a consequence, mechano- and vapochromic behaviors can be observed from the polymer films. In the polymer design, we have various options for modulating optical properties, such as changing comonomer units, side-chains and connecting points with the commoner units. We believe the idea of “the frustrated element-blocks” is a potential strategy for constructing advanced stimuli-responsive and environment sensitive materials, which can be a scaffold for next generation of chemical sensors.

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FIGURES

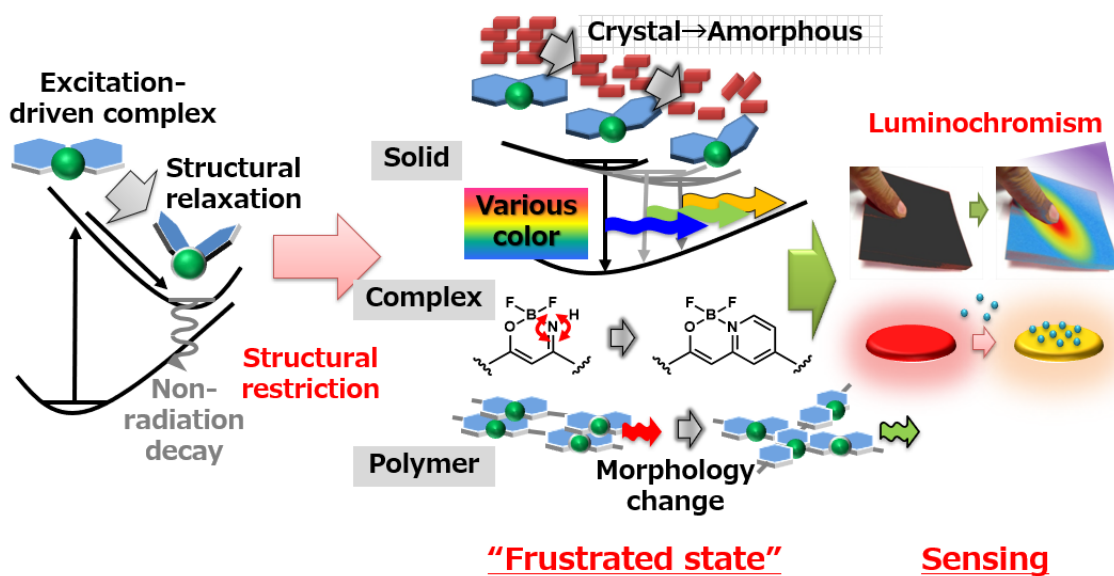


Figure 1. Schematic illustration on the concept of “the frustrated element-block” materials and their applications for stimuli-responsive luminescent materials.

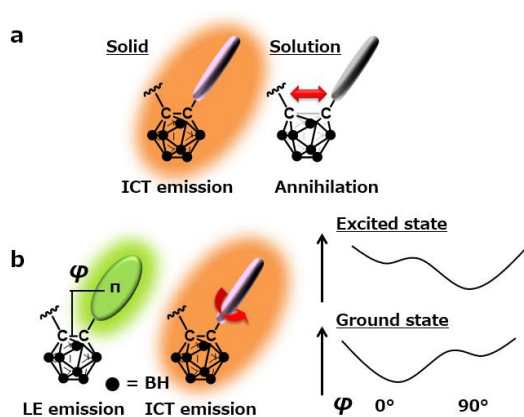


Figure 2. Molecular motions of aryl-modified *o*-carborane in the excited state. (a) Emission annihilation mechanism of the ICT emission triggered by the extension of the C–C bond in the *o*-carborane unit. (b) The switching of emission mechanisms between the LE and ICT emission by intramolecular rotation.

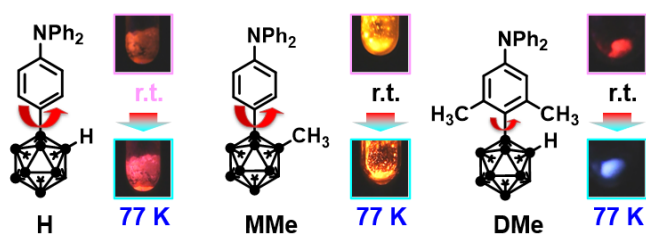


Figure 3. Modulation of thermochromic luminescent properties by intramolecular rotation barriers with the substituents. Reprinted with permission from ref 15. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA.

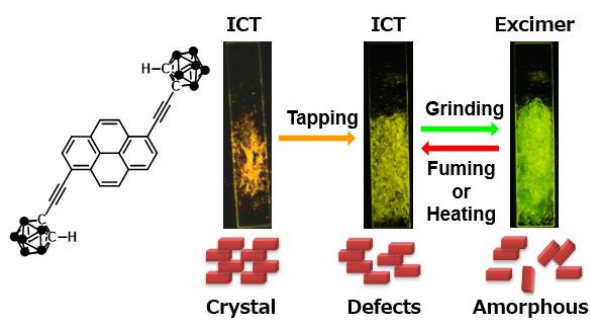


Figure 4. Multi-step mechanochromic luminescent properties of the modified pyrene with dual *o*-carborane substituents. Adapted with permission from ref. 20. Copyright 2022 Elsevier.

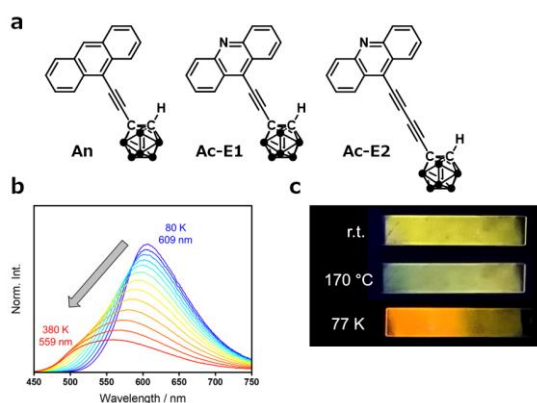


Figure 5. (a) Examples of the *o*-carboranes having the ethynyl linker which can exhibit solid-state excimer and ICT. (b) Variable temperature emission spectra and (c) appearances under UV irradiation of **Ac-E1**. Adapted with permission from ref. 22. Copyright 2021 American Chemical Society.

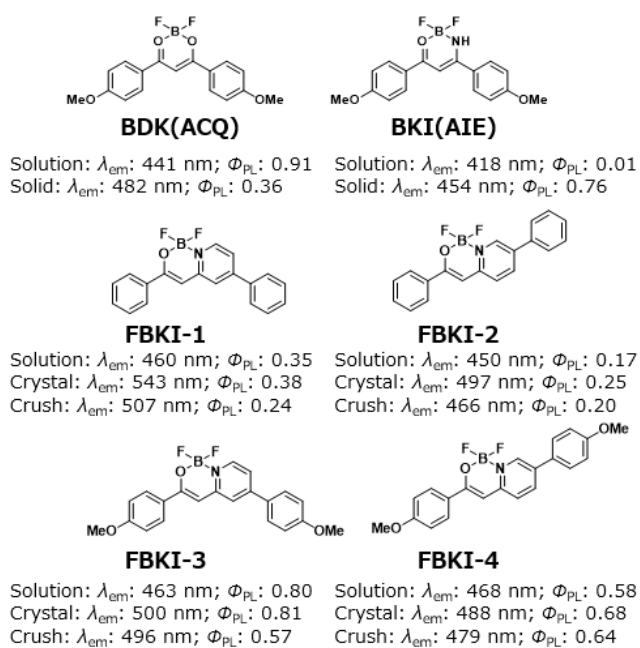


Figure 6. Luminescent properties of boron diketonate, ketoiminate and fused ketoiminate complexes.

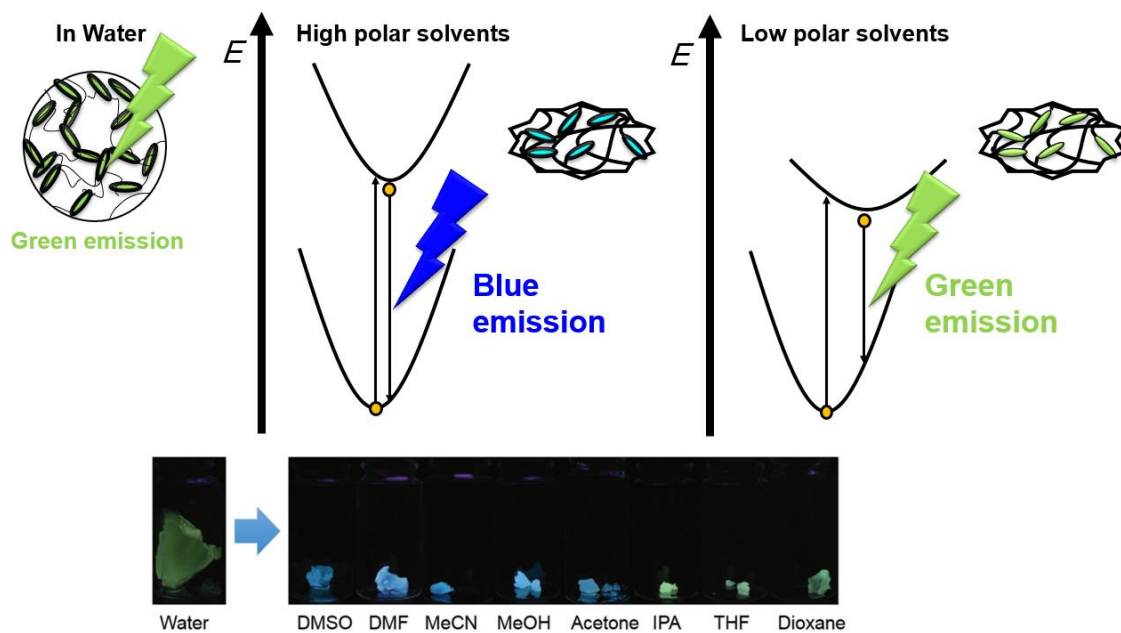


Figure 7. Emission of the BKI-modified shrunk hydrogels with various solvents and the plausible mechanisms on aggregation-induced emission color changes. Reprinted with permission from ref 29. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA.

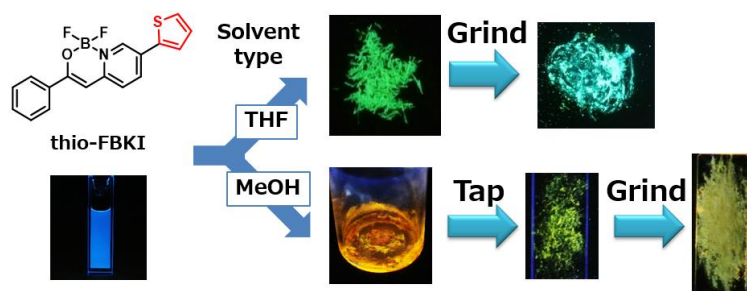


Figure 8. Mechanochromic luminescent properties of thio-FBKI. Reproduced from Ref. 31 with permission from The Royal Society of Chemistry.

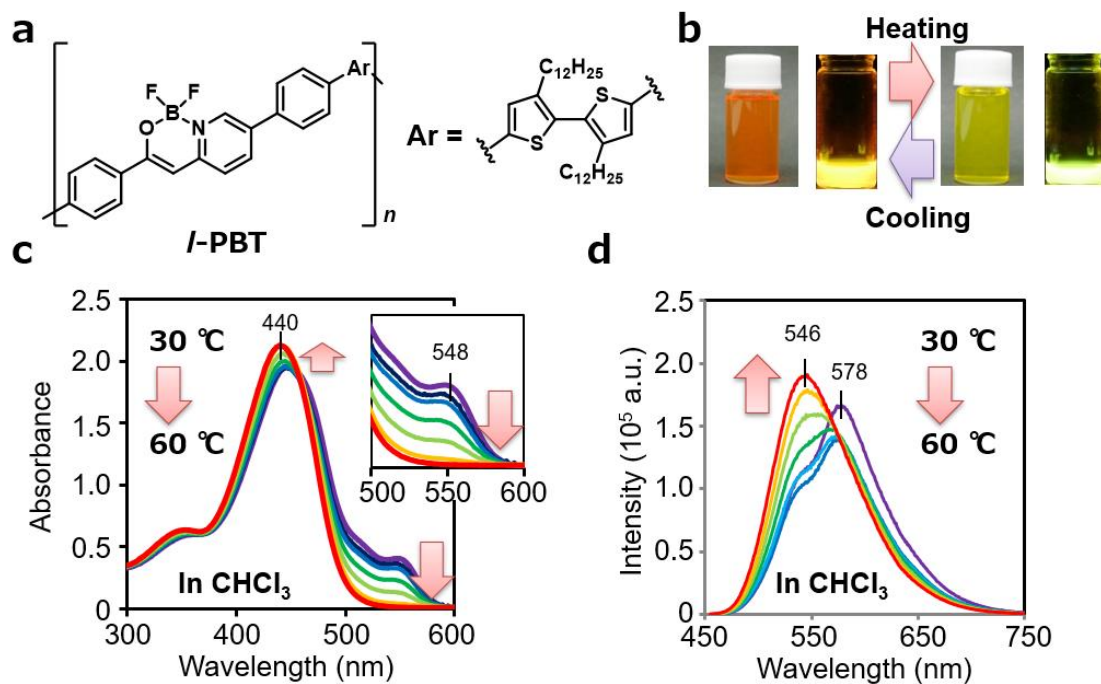


Figure 9. (a) Chemical structure of *l*-PBT and (b) solution appearances and (c) UV-vis absorption and (d) photoluminescence spectra of the chloroform solutions. Reproduced from Ref. 32 with permission from The Royal Society of Chemistry.

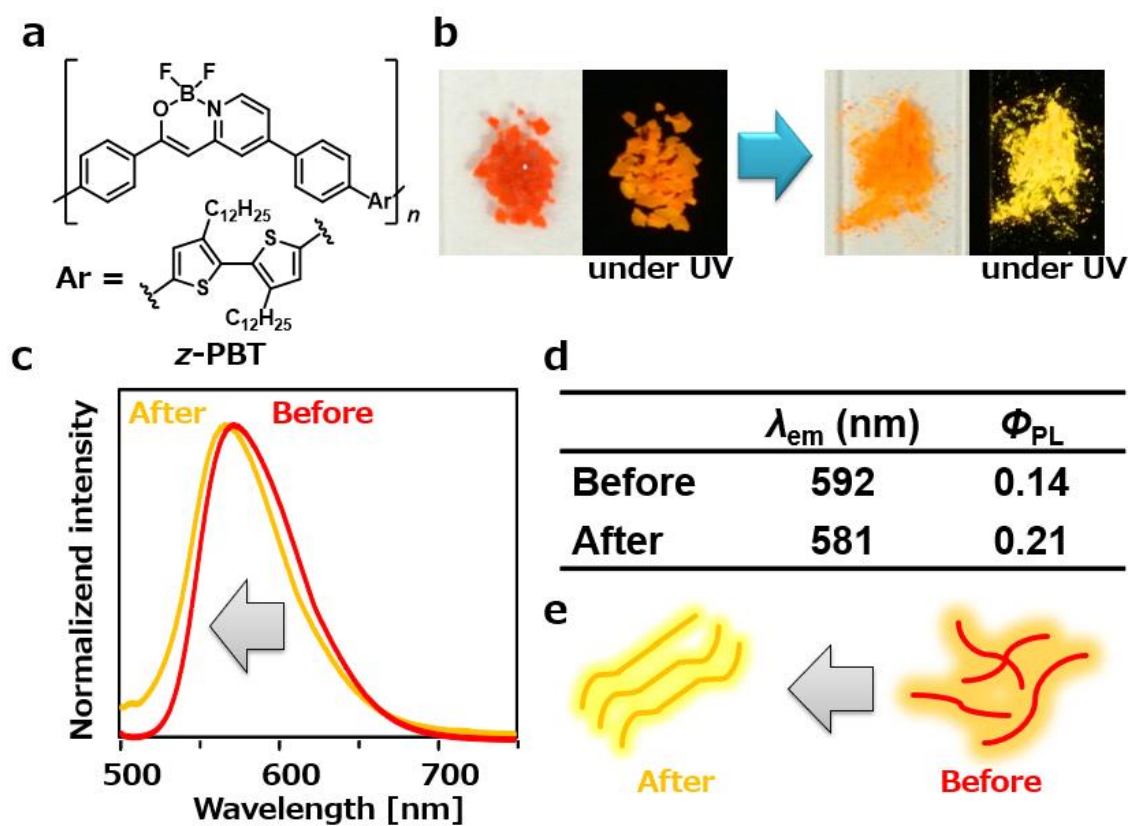


Figure 10. (a) Chemical structures of **z-PBT** and (b) appearances, (c) photoluminescence, (d) photochemical properties and (e) the proposed model of mechanochromic luminescent behaviors of **z-PBT**. Reproduced from Ref. 32 with permission from The Royal Society of Chemistry.

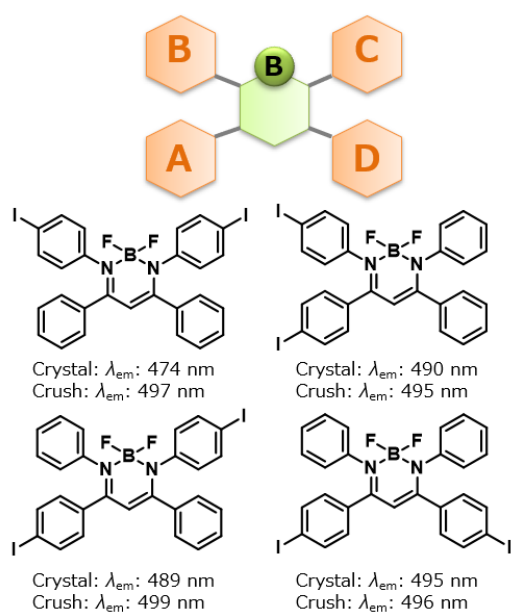


Figure 11. Luminescent properties of diiodo boron diiminate complexes before and after the mechanical treatments.

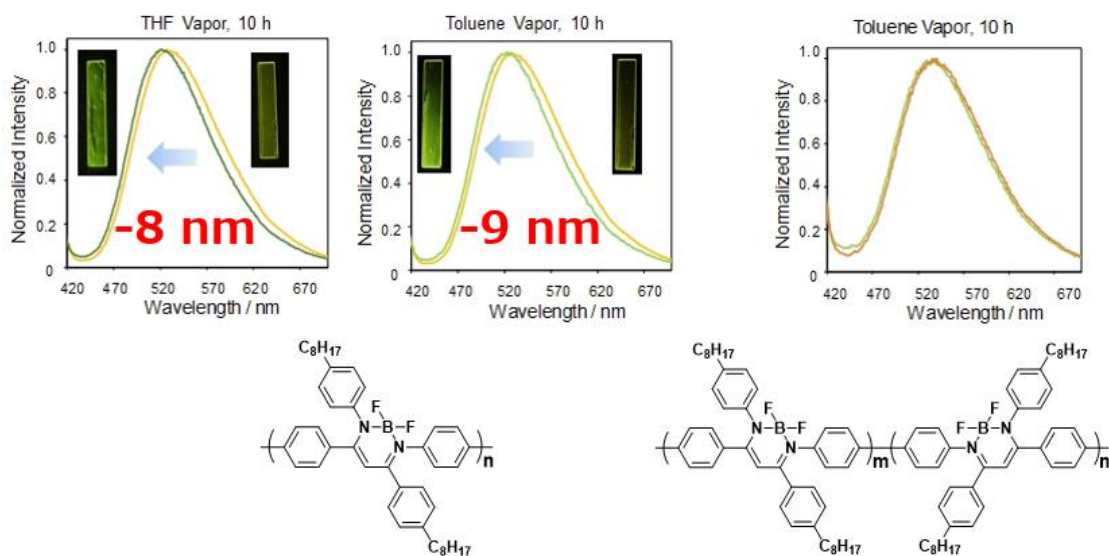


Figure 12. Vapochromic luminescent properties of the films consisting of the regioregular boron diiminate homopolymer with THF and toluene. Reprinted with permission from ref 36. Copyright 2022 Wiley-VCH Verlag GmbH & Co. KGaA.

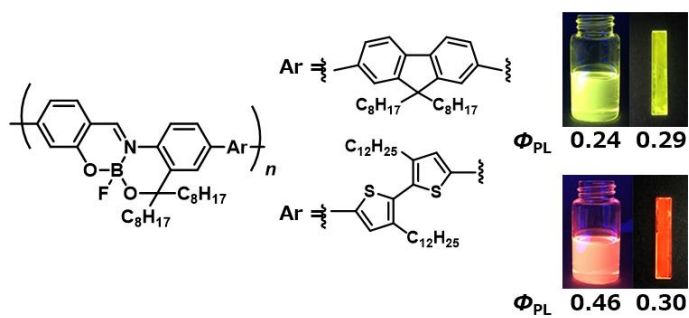


Figure 13. Solution and solid-state luminescent properties of the azomethine polymers.

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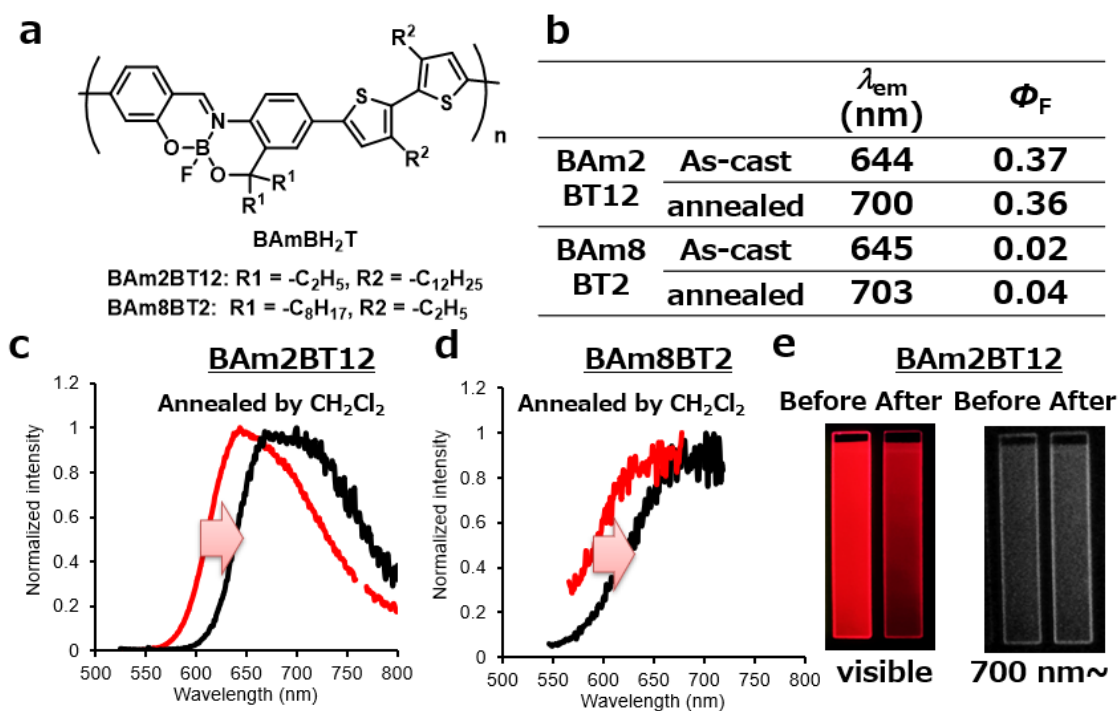


Figure 14. (a) Chemical structures and (b) luminescent properties of the azomethine polymers. Photoluminescence spectra of (c) Bam2BT12 and (d) Bam8BT2 and (e) pictures of BAmSBT12 and (e) appearances of Bam2BT12 before and after solvent annealing with dichloromethane. Reproduced from Ref. 47 with permission from The Royal Society of Chemistry.

GRAPHICAL ABSTRACT

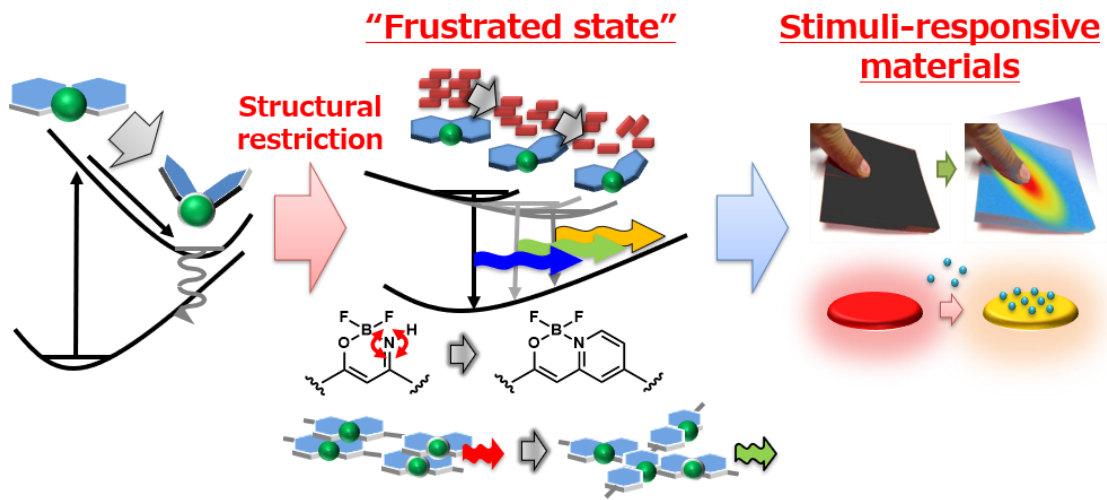


FIGURE LEGENDS

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