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REVIEW ARTICLE

Creation of photofunctional materials through supramolecular complex formation and host–guest chemistry

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Abstract

Functional dyes can interconvert energies, such as light, heat, and electricity, and they have broad applications in various fields. This review highlights our endeavors in the creation of novel photofunctional materials in solution and solid states via molecular assemblies, linkage, and distortion and the integration of supramolecular complex formation and host–guest chemistry. One approach involves the synthesis of solid-state luminescent materials with the use of cocrystals comprising host molecules with dye backbones and guest molecules derived from aromatic compounds. Cocrystal formation is tuned via intermolecular interactions, such as hydrogen bonding, charge-transfer interactions, π-π stacking, and inclusion phenomena of the crystal engineering approach. This state leads to the emergence of properties such as fluorescence, room-temperature phosphorescence, and the potential for applications in optical sensors. In the second approach, functional dyes comprising multidentate ligands with various elements, which results in photofunctional properties in solution and solid states. This method delves into structural characteristics affected by the distortion and torsional angles of multinuclear complexes and their resulting photophysical properties. Multinuclear complexes encompass helical and axial chirality. Here, we discuss the isolation of enantiomers through optical resolution and their subsequent circular dichroism and circularly polarized luminescence characteristics. The position and nature of substituents considerably affected the ground and excited states of the complexes, which led to the formation of unique photofunctional materials. These methodologies offer insightful and effective avenues for the further improvement of the functionality and device applicability of functional dyes.

Keywords Multicomponent crystals · Chromism · Boron complexes · Helicates · Circularly polarized luminescence

Introduction

Pigments and dyes, which have been traditionally used for a century for coloring various materials, are integral to our lives. Meanwhile, functional dyes, which can interconvert energies, such as light, heat, and electricity, have opened up a myriad of advanced applications. Such applications include light wavelength conversion materials, organic solar cells, organic light-emitting diodes, organic lasers, catalysts, and bioimaging [1–7]. Recent advances in organic chemistry, coordination chemistry, and computational chemistry have considerably improved the accessibility and design of functional dyes with desirable properties [8]. However, despite the reliable behavior prediction offered by computational chemistry for isolated molecular structures, forecasting the functions of dyes in concentrated solutions or solid states remains challenging. The prediction of the crystal structure of organic molecules presents difficulty given their inherent flexibility [9]. Therefore, accumulation of knowledge regarding the structure–property relationships through experimental chemistry remains important. A comprehensive understanding of the mechanism underlying the effects of molecular structure, arrangement, and stacking modes on functionality, from molecular materials to metal

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complexes, is the key to advancing the field and unlocking the full potential of functional dyes.

This review describes the methodologies recently employed by our group for the development of novel functional dyes. One approach focuses on the creation of novel photofunctional materials through cocrystal generation. In dye development, various functions can be produced through the creation of new optical functions via the combination of different types of molecules [10]. In particular, our approach mainly focuses on the combination of host molecules containing dye skeletons with various guest molecules. These systems are participated by hydrogen bonding, charge-transfer (CT) interactions, π-π stacking, and inclusion phenomena, which play critical roles in cocrystal formation. This condition leads to the emergence of properties, such as fluorescence, room-temperature phosphorescence, and the potential for optical sensor applications. The strength of this system is that single-crystal X-ray diffraction (SCXRD) analysis allows detailed determination of the molecular arrangement and interactions of complex components, which enables the discussion of structure–property relationships. The second approach involves the synthesis of functional dyes based on the formation of multinuclear complexes composed of multidentate ligands with various elements. As a result, materials that exhibit photofunctional properties in solution and solid states can be developed. Through introduction of various substituents into these complexes and implementation of molecular distortions and torsional adjustments, this approach improves their unique optical absorption and emission properties. In addition, our research included dyes with helical and axial chiralities. In these cases, discusses the isolation of enantiomers via optical resolution and their circular dichroism (CD) and circularly polarized luminescence (CPL) properties in solution and in solid states. CPL-active materials have emerged as an important topic with potential applications in various fields, including chemical sensors, biological probes, and organic optoelectronics [11, 12]. These aspects add a new dimension of functionality to dyes. The design strategies are discussed in detail in the following sections.

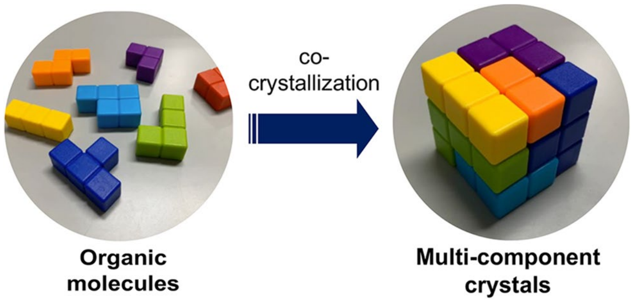


Fig. 1 Crystallization of multiple organic molecules to form multicomponent crystals as a challenging puzzle

Luminescent crystalline materials

Creation of photofunctional materials via cocrystal formation

This section describes a strategy for the preparation of functional dyes through the formation of cocrystals composed of multiple organic components. A common method involves two different organic molecules, each with a unique electronic state, to form a 1:1 cocrystal [10]. Over the years, cocrystals formed using various types of molecules have contributed to the development of organic conductors and superconductors. TTF-TCNQ is a well-known CT cocrystal first reported in 1973; it exhibits a high conductivity over a wide temperature range and has potential applications in metallic (super) conductivity [13]. The focus has been primarily on the combination of donor and acceptor molecules to induce charge separation, which results in crystal formation in segregated- or mixed-stack mode, with efficient electrical conduction pathways. In addition, studies have explored the creation of CT cocrystals with the use of relatively weak donors and acceptors. As a result, photoluminescent crystals that can emit light in the visible to near-infrared range emerged [14, 15]. Despite these advances, scholars still need to address specific challenges, such as irregular molecular orientation and increased energy barriers to crystallization due to weak interactions. Therefore, gaining insights into the precise structure and interactions of organic molecules is crucial for the optimal cocrystal formation, which requires continued research and the adoption of innovative approaches to realize desired photofunctional properties. Regardless, the formation of cocrystals composed of more than two components, i.e., three, four, five, or more components, remains a challenging task given that the components must be precisely combined in solid state, similar to a puzzle(Fig. 1).

Our research contributes to this field through the systematic investigation of the assembly of multiple molecular components for cocrystal formation. We focused on the inclusion phenomenon, in which organic compounds incorporate solvents or small molecules during crystallization [16]. Bulky substituents were introduced into organic compounds, which not only increased solubility but also prevented aggregation. This strategic approach facilitated the selective incorporation of the desired guest molecules and resulted in the formation of cocrystals with well-defined interactions and properties. As a result, scholars have discovered properties, such as fluorescence and room-temperature phosphorescence, and potential applications in optical sensors that respond to various external stimuli.

A 2015 report mentioned a three-component crystal system consisting of a naphthalenediimide derivative (NDI), tris(pentafluorophenyl)borane (TPFB), and aromatic guest molecules (Fig. 2) [17]. The interaction between the pyridyl groups of NDI and boron atoms of TPFB formed a boron–nitrogen (B–N) dative bond, which created nanospaces near the NDI, which resulted in the increased uptake of guest molecules through CT interactions and inclusion phenomena. The B–N bond is known to be a very attractive interaction in the assembly of supramolecular materials and polymers [18]. A typical preparation contained a mixture of NDI (50 mg, 1 equiv) and TPFB (125 mg, 2 equiv) in hot aromatic guest molecules (10 mL, excess as solvent). The mixture was cooled to room temperature to obtain multicomponent crystals (NDI•TPFB ⊃ guest) with an NDI: TPFB: guest ratio of 1:2:2. This study showed that regardless of guest molecules, the crystal structure showed the constant formation of a supramolecular host with a B–N bond that accommodated two guest molecules. The stacking of NDI and guest molecules occurred a distance of approximately 3.5 Å. Fluorescence microscopy revealed the multicolor luminescence emitted by these crystals, that is, from blue to orange under ultraviolet (UV) light, depending on the guest molecules. A long-wavelength shift in emission color occurred with the electron-donating nature of the guest molecule, with blue, cyan, green, and orange emissions for benzene, toluene, *m*-xylene, and 2-methylanisole, respectively. The emission color correlated with the ionization potential of guest molecules. It is important to note that the emissions occur with high photoluminescence (PL) quantum yields of 16.6% for NDI•TPFB ⊃ benzene, 20.2% for NDI•TPFB ⊃ toluene, and 26.3% for NDI•TPFB ⊃*m*-xylene in the crystalline state. The individual components (NDI, TPFB, and guest) showed no significant luminescence in the visible region, which suggests that these properties resulted from cocrystal formation. Extensive studies have been performed on the chemistry of naphthalenediimides in the fields of supramolecular materials, including ion channels, foldamers, catenanes, rotaxanes, metal–organic frameworks, fluorescent aggregates, crystals, and gelators [19–29]. This report presents the first systematic approach that demonstrates naphthalenediimide-based multicomponent crystals that yield multicolor emissions.

This study uncovered the unique capability to accommodate two or more types of guest molecules, which facilitated the synthesis of complex multicomponent crystals. This advancement enabled the intricate and effective tuning of photofunctional properties. A four-component crystal was successfully developed through the integration of two types of host molecules with two different guest molecules. The combination of cyan emission (from the interaction between NDI and 3-fluorotoluene) and orange emission (from the interaction between NDI and naphthalene) resulted in a white-light emission with effective energy transfer in solid state (Fig. 3) [30]. The peak emission wavelengths were identified at 466 nm and 556 nm when the composition ratio of 3-fluorotoluene to naphthalene was 96.7% and 3.3%, respectively. The PL quantum yield of the crystal was recorded at 19.5% when excited at 370 nm. Fluorescence microscopy confirmed the single crystal white-light emission, which indicates a mixed crystal structure rather than a segregated one. The substantial shift in emission color observed with the small addition of naphthalene implies the efficient energy transfer within the crystal.

In addition, our approach allows for the easy substitution of host molecules. A notable experiment used EBPDI, which is a large host framework (Fig. 4) [31]. An approach similar to our previous methods involved the use of a compound with a pyridyl group at the 3-position, and it served as the interaction site with TPFB for EBPDI. As a result, various three-component crystals (EBPDI•TPFB ⊃ guest) containing EBPDI, TPFB, and aromatic guest molecules,

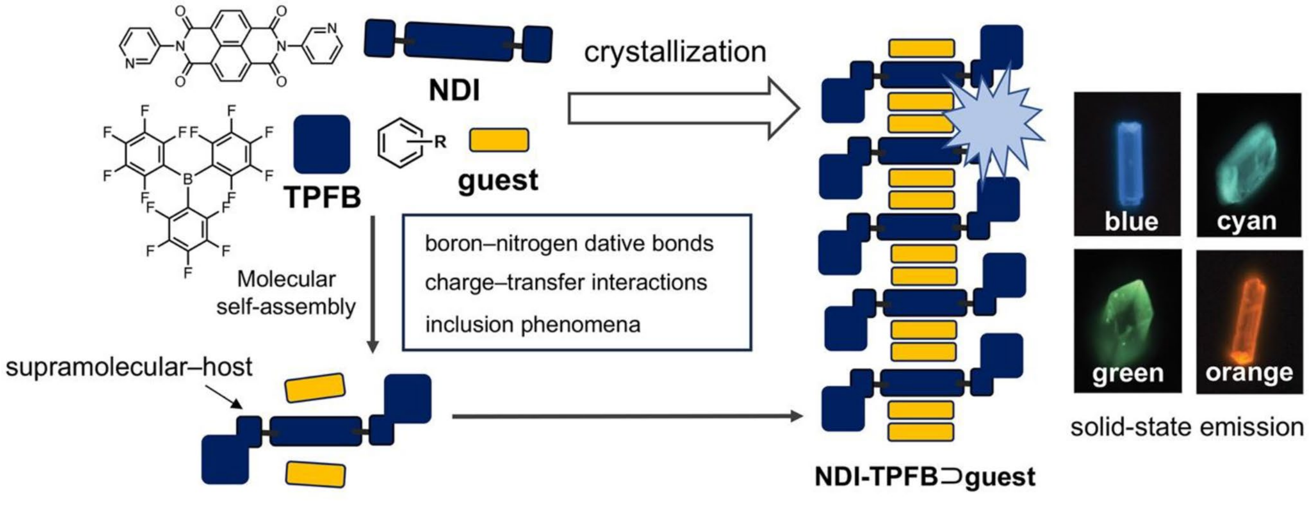
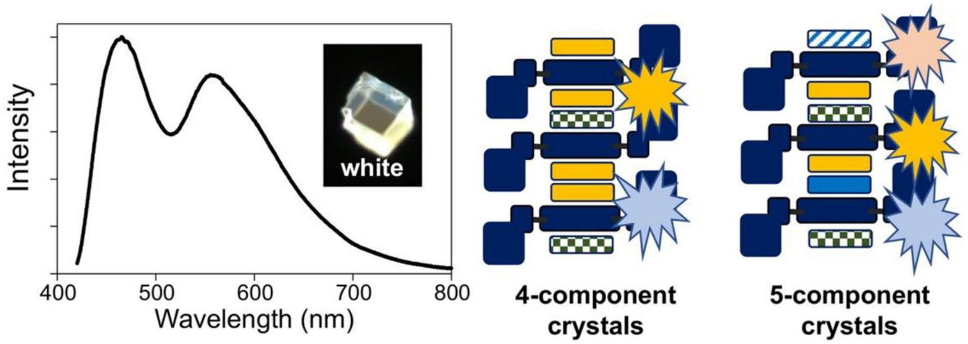


Fig. 2 Formation of three-component crystals and their optical functions

Fig. 3 Formation of multicomponent and white-light emitting crystals



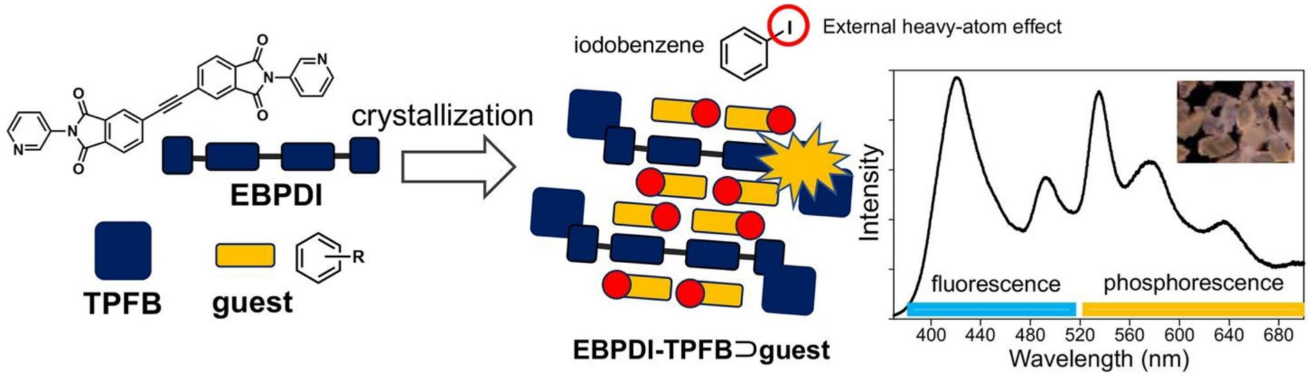


Fig. 4 Diagram illustrating the formation of three-component crystals and their optical functionalities

including hexafluorobenzene, toluene, anisole, and naphthalene derivatives, formed. According to SCXRD analysis, in all cases, EBPDI and TPFB formed a two-component supramolecular host with a B–N bond, which encapsulated multiple guest molecules. Vertical and horizontal insertion of the guest molecules into the nanospaces created by the supramolecular host was observed and they resulted in the formation of various molecular aggregation structures. The crystal with hexafluorobenzene as the guest molecule (EBPDI•TPFB ⊃ hexafluorobenzene) showed a monomer emission that due to the vertical stacking of hexafluorobenzene against the main backbone of EBPDI. The crystal exhibited a peak emission wavelength of 424 nm, and the PL quantum yield was 48.7%. Green fluorescence emission was observed with the introduction of strong donor guests, such as 3-methoxynaphthalene, which resulted in horizontally stacked 3-methoxynaphthalene against the main backbone of EBPDI. The crystal exhibited a peak emission wavelength of 499 nm, and the PL quantum yield was 16.0%. The use of iodobenzene as a guest molecule caused the dual emission of blue fluorescence and orange phosphorescence due to its microsecond-order emission lifetime. The peaks for fluorescence and phosphorescence were observed at 420 nm, 492 nm, and 640 nm, with respective lifetimes of 3.7 ns, 5.0 ns, and 499 µs. The external heavy atom effect induced by iodobenzene was assumed to efficiently facilitate intersystem crossing between the excited singlet and triplet states, which resulted in the phosphorescence of EBPDI. Notably, crushing the crystal changed the emission color, decreased the phosphorescent component, and increased the fluorescent component, which indicate mechanochromic properties. This finding suggests that the crystallinity and packing of host and guest molecules are critical to obtaining photofunctional properties.

A new host framework with the host molecule containing pyridyl and carboxylic acid groups in one molecule (TI) has been reported (Fig. 5) [32]. Alone, this molecule creates intermolecular hydrogen bonds between the pyridyl group and carboxylic acid to form a one-dimensional network (Fig. 5b). This formation results in a low-solubility solid, that is, it is insoluble in most solvents, including aromatic and halogenated solvents. We hypothesized that by promoting binding with TPFB, which strongly interacts with pyridine, intermolecular hydrogen bonding between the pyridyl group and the carboxylic acid can be switched to a B–N bond with TPFB (Fig. 5a). This approach will serve as a "wedge" in hydrogen bonds, which will increase solubility and enable the formation of three-component crystals via cocrystallization with supramolecular host and guest molecules.

To achieve such goal, we employed a solid-phase reaction method using a mixer mill. Specifically, we used liquid-assisted grinding (LAG), which involves the mixing of solid-state constituent molecules in a mortar or mixer mill.

The application of LAG the development of organic synthesis and multicomponent crystals has attracted considerable [33–36]. TI, TPFB, and an aromatic guest molecule were mixed in a stainless steel container, and a small amount of chloroform was added. The mixture was milled at 30 Hz to induce a solid-phase reaction, and the resulting solid powder was collected. The powder was dissolved in solvents, such as dichloroethane, and recrystallization formed the desired three-component crystals, which were confirmed by SCXRD analysis (Fig. 5c). The analysis revealed that the initially formed hydrogen bonds between pyridine and carboxylic acid were replaced by boron–nitrogen bonds between pyridine and TPFB, with the liberated carboxylic acid forming dimers and a large supramolecular host structure (TI•TPFB). Various aromatic molecules were incorporated as guest molecules, and multicolor solid-state luminescence based on the formation of CT complexes occurred.

Powder X-ray diffraction (PXRD) analysis of the post-milled solid powder revealed patterns consistent with those of the simulated single-crystal structure. This result strongly suggests molecular self-assembly during the solid-phase reaction, which resulted in the formation of three-component crystals. In situ PXRD measurements during milling at a synchrotron radiation facility revealed the assembly of multicomponent crystals. Through the control of appropriate molecular structures and intermolecular interactions, cocrystals with different molecular combinations and new photofunctional properties can be created.

The successful cocrystal formation led to synthesis of a host molecule composed of naphthalenediimides covalently modified with bulky substituents. As a result, a remarkable guest inclusion capability was observed in the host molecule (2BP-NDI) modified with naphthalenediimide via benzophenone. Compound 2BP-NDI efficiently incorporated toluene, 4-fluorotoluene, and *p*-xylene and formed cocrystals through cooperative intermolecular interactions, such as CT interactions and inclusion phenomena (Fig. 6) [37]. In addition, intense guest-dependent fluorescence emission by crystals (2BP-NDI ⊃ guest) transpired under UV-light excitation. 2BP-NDI ⊃ toluene, 2BP-NDI ⊃ 4-fluorotoluene, and 2BP-NDI ⊃ *p*-xylene exhibited emission peaks at 491, 490, and 527 nm, with PL quantum yields of 27.1%, 9.8%, and 18.9%, respectively. 2BP-NDI alone or the guest molecule alone did not show such emission in the visible region. Thus, its emission resulted from cocrystal formation. Furthermore, cocrystals of 2BP-NDI with halobenzene as a guest exhibited room-temperature phosphorescence [38]. In particular, 2BP-NDI ⊃ bromobenzene and 2BP-NDI ⊃ iodobenzene showed yellow and red emissions, with lifetimes on the order of microseconds. Such a result was due to the inclusion of guest molecules containing heavy atoms in the crystal lattice promoting intersystem crossing as a result of the external heavy atom effect. This condition led to the efficient formation of the excited triplet state of the benzophenone and/or naphthalenediimide moieties and generation of phosphorescent emission. Therefore, cyan fluorescence emission occurred with the use of crystals containing chlorobenzene (2BP-NDI ⊃ chlorobenzene), which had a small heavy atom effect. SCXRD analysis revealed that each NDI molecule formed a cocrystal structure with a

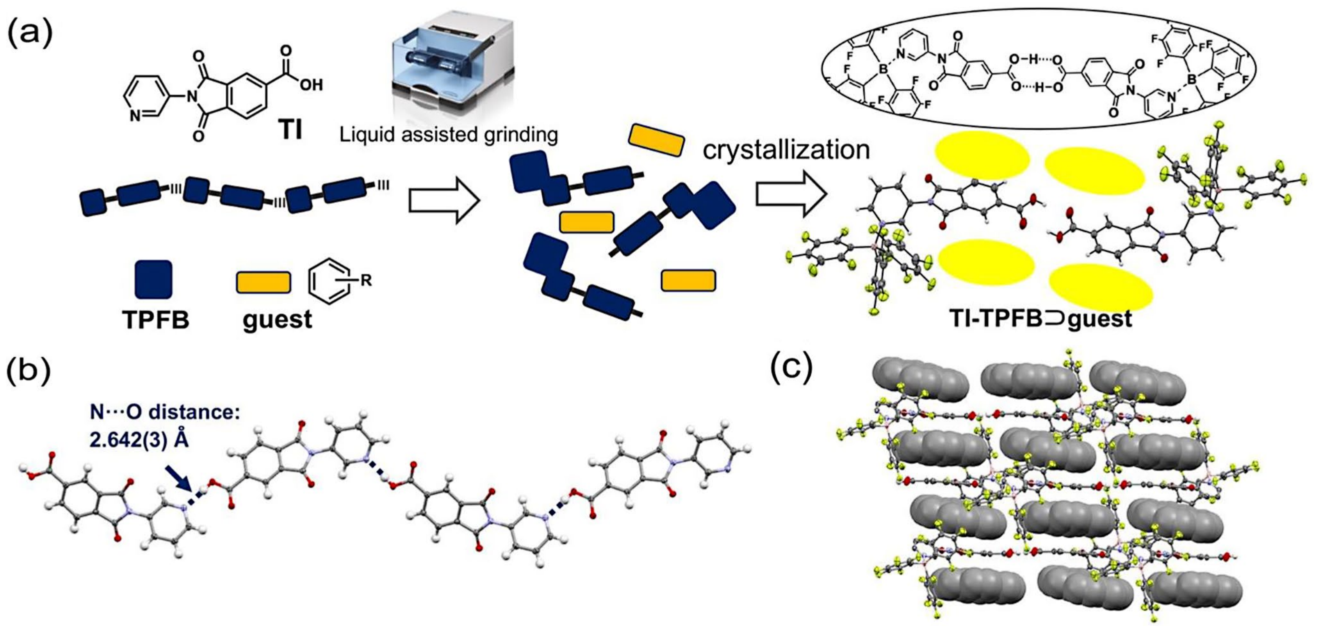


Fig. 5 (**a**) Schematic of the formation of three-component crystals using TI, TPFB, and guest molecules via LAG. Crystal structures of (**b**) TI and **c** TI•TPFB ⊃ pyrene. Reproduced with permission from ref 372. Copyright 2022 Wiley-VCH

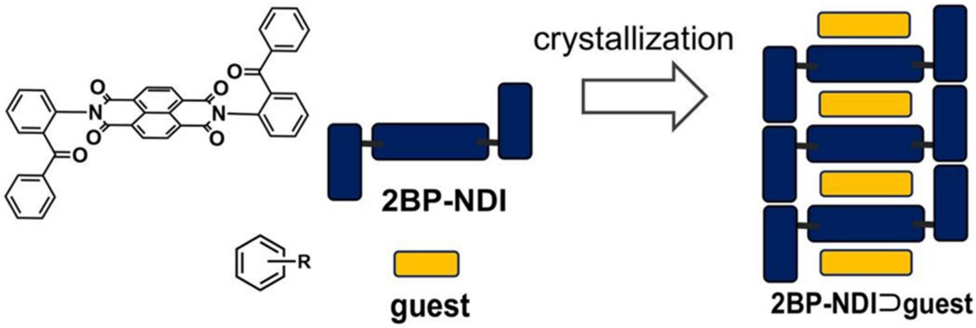


Fig. 6 Schematic of the formation of two-component crystals by 2BP-NDI and guest molecules

single aromatic molecule. Notably, compound 2BP-NDI did not form a cocrystal with benzene and exhibited a poor guest incorporation capability. This phenomenon may be due to the smaller size of the benzophenone, which was introduced as a bulky substituent in 2BP-NDI, compared with the previously described NDI•TPFB supramolecular host. Thus, this host molecule exhibits selectivity with respect to the electronic states and sizes of guests and uniquely forms cocrystals with specific guest molecules.

Development of optical sensor materials using cocrystals

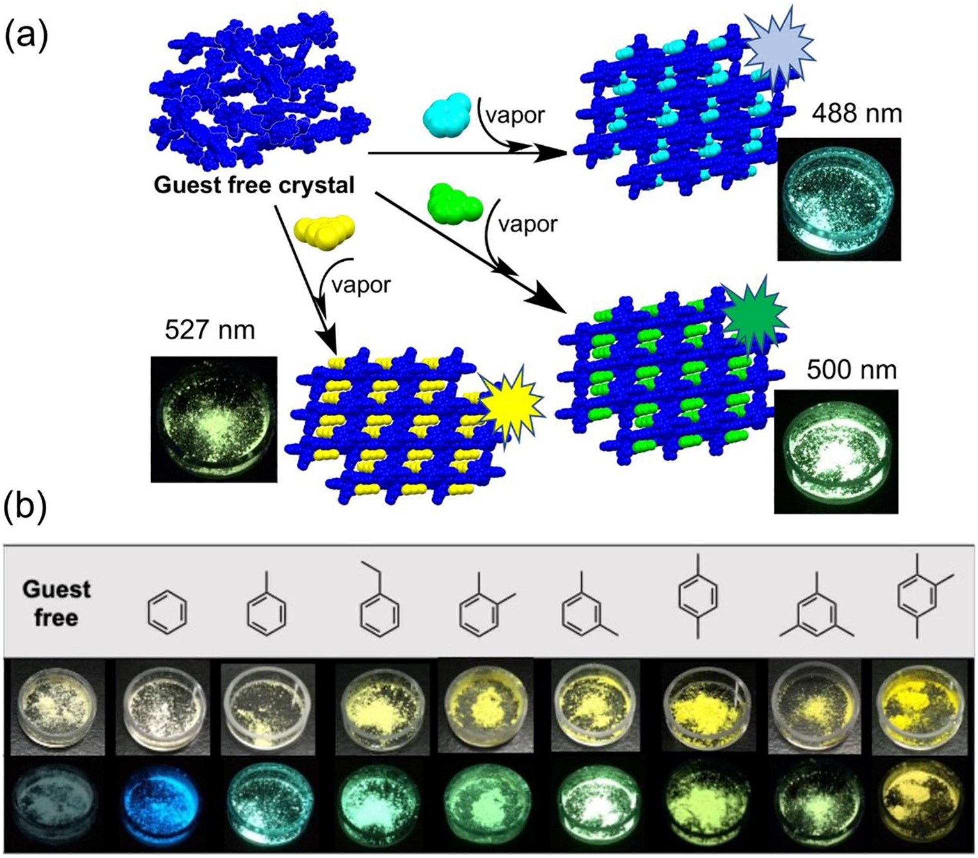
The following section presents the research on functionalities that respond to external stimuli, such as light, heat, vapor, electricity, and pressure, in the form of alterations in apparent or luminescent color. These alterations include phenomena, such as photochromism, thermochromism, vapochromism, electrochromism, mechanochromism, and piezochromism. “Soft crystals,” which have attracted considerable attention, refer to crystalline materials that change their optical functional properties in response to external stimuli [39]. Strategic design and application of these dyes will facilitate their application in optical sensor materials. This work will exclude the discussion on stimuli-responsive dyes with macrocyclic structures, such as calixarenes and pillararenes, because a number of reviews have shown the external stimuli responsiveness of these molecules, particularly vapochromism, due to their intrinsic cavities and host–guest chemistry [40–49].

This review explored the field of functional dyes and extended its focus from traditional macrocyclic molecules to compounds that form inclusion crystals (cocrystals) and their response to external stimuli. The underlying hypothesis indicates that compounds prone to exhibit inclusion phenomena are likely to exhibit vapochromic properties because of their capability to recognize guest molecules at the solid–air interface. These compounds should be able to recognize and adsorb guest molecules through the solid–air interface, which will result in observable changes in appearance and emission color (vapochromism). A key element of this research is the utilization of solid powders derived from inclusion crystals from which guest molecules had been removed via processes, such as heating and/or vacuum application. This approach not only expands the range of materials with potential vapochromic applications but also provide further insights into molecular interactions at the solid–air interface.

We focused on the development of selective sensors for benzene, toluene, ethylbenzene, and three xylene isomers (BTEX), which are aromatic hydrocarbons that are beneficial and harmful to humans [50]. The detection of BTEX is crucial for the assessment of groundwater and soil pollution. Thus, the development of high-selectivity methods for the detection of these volatile organic compounds is crucial for environmental monitoring and health protection. The development of chemical sensors that visually detect gaseous substances through changes in absorption or luminescence is especially appealing because it avoids the need for specialized equipment or skills, such as gas chromatography or nuclear magnetic resonance (NMR).

The NDI•TPFB ⊃ benzene crystal introduced in Sects. 2 – 1 released its benzene guest above a certain temperature during thermogravimetric analysis. Benzene guest molecules were removed from the NDI•TPFB ⊃ benzene crystal through preparation of guest-free crystals (NDI•TPFB complex) via by treatment at 150 °C for 4 h under vacuum [51]. The guest-free crystals transformed into nearly nonluminescent powders with a PL quantum yield of less than 0.5%. The study exposed the finely ground powder, which prepared using an agate mortar and pestle, to various aromatic molecular vapors. Consequently, the crystals adsorbed vapors, such as benzene, toluene, ethyl benzene, and xylene, at the solid–air interface, which caused their color to change from pale ochre or yellow to strong blue, aqua, and yellow–green luminescence under UV light (Fig. 7). Importantly, increases in the emission intensity of 76-, 46-, 37-, 17-, 14, 11-fold light-up signals were obtained with toluene, benzene, *m*-xylene, ethylbenzene, *p*-xylene, *o*-xylene, as guest molecules, respectively. The coloration and luminescence change upon vapor exposure is a classic example of vapochromism, in which changes in the

Fig. 7 Development of a fluorogenic sensor for aromatic molecules based on the vaporochromic properties of host molecules. Reproduced with permission from ref 51. Copyright 2017 Wiley-VCH



material's optical properties occur as a response to vapor phase molecules. These changes are due to the formation of CT complexes between aromatic guest molecules and NDI. Furthermore, exposure to guest molecule vapors caused the reappearance of crystallinity in the PXRD analysis patterns, which aligns with the simulated patterns observed from SCXRD analysis. This transformation from an almost non-luminescent state to a luminescent one during guest vapor adsorption indicates its function as a turn-on sensor material. This system also demonstrated a lack of response to common organic solvents, such as methanol, chloroform, and hexane.

To further extend this concept, we investigated the vapochromism properties of 2BP-NDI [37]. The vapochromism of 2BP-NDI powder was verified by its adsorption of vapors, such as toluene and *p*-xylene, which caused changes in absorption and luminescence color. Detection limits in the parts-per-million (ppm) range are accomplished. However, the compound showed minimal response to benzene, which indicates selectivity. These features suggest that the creation of a mini sensor array can allow for detailed compound differentiation (Fig. 8) [52]. Excellent vapochromism was also observed when this type of host molecule was used in films cast from chloroform solutions [53–55].

Piezochromism, which is another application of stimulus-responsive materials, involves materials that change color (apparent coloration or emission) in response to external high pressure. Early stages of research reported high-pressure effects on the electrostatic structure of organic crystals, such as anthracene, chrysene, and pyrene [56, 57]. Studies have also revealed the use of single crystals consisting of dyes with complex structures to produce piezochromic properties [58–61]. The aforementioned two- and three-component crystals exhibit interesting solid-state luminescence due to CT interactions between electron-deficient host molecules and electron-rich guest molecules within their crystal structures. These structural features have potential use in the creation of pressure sensors with luminescence properties that change in response to external stimuli. To realize this idea, we packed a two-component crystal (2BP-NDI $\supset$ 4-fluorotoluene) into the sample space of a diamond anvil cell and sealed it with kerosene as a pressure medium [62]. Diamond anvil cells are widely used to apply ultrahigh pressures in the giga pascal (GPa) range. The emission of the two-component crystal of 2BP-NDI $\supset$ 4-fluorotoluene, which exhibited a cyan emission peak at 480 nm under ambient pressure (1 atm), gradually changed color from cyan to green to yellow to red under external pressure in the GPa range (Fig. 9). This reversible response

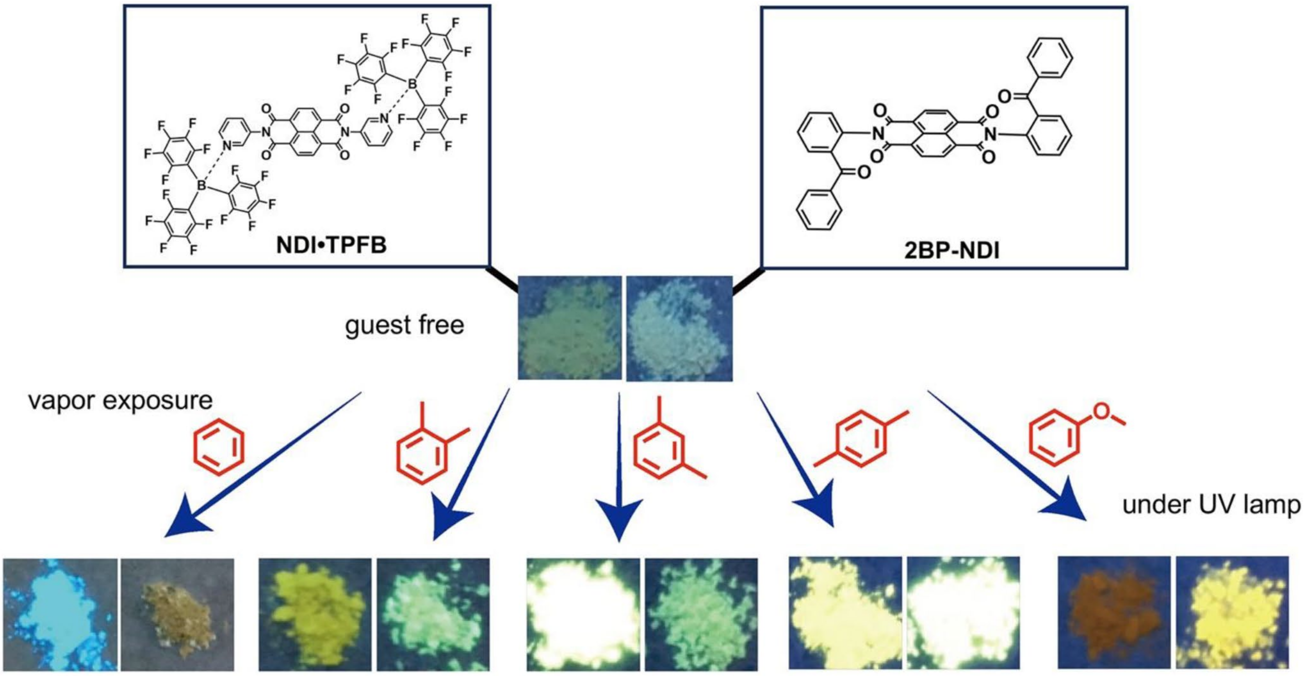


Fig. 8 Development of a fluorogenic sensor for aromatic molecules based on the vaporochromic properties of host molecules. Reproduced with permission from ref. 52. Copyright 2019 Royal Society of Chemistry

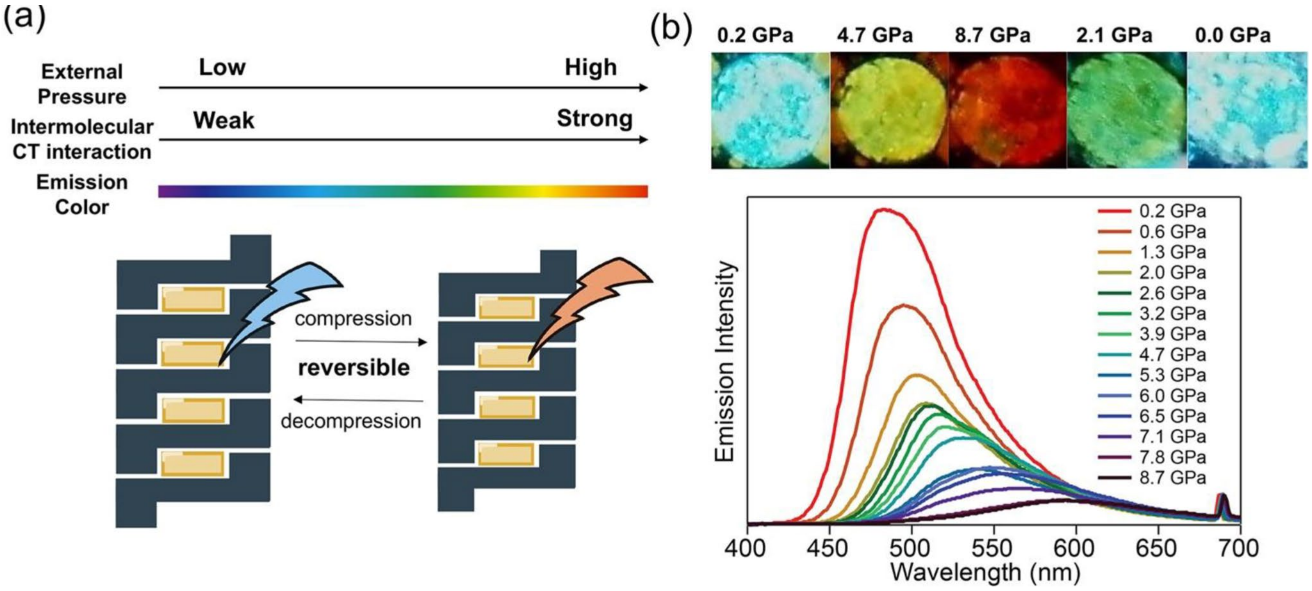


Fig. 9 (**a**) Schematic showing piezoceramic properties using cocrystals and (**b**) PL spectra of 2BP-NDI ⊃ 4-fluorotoluene crystal recorded in compression. Reproduced with permission from ref. 62. Copyright 2019 Wiley-VCH

suggests that the shift in emission color was not due to the destruction of molecular aggregation structure (shift to a random structure) but rather the compression and restoration of the molecular aggregation structure in response to external pressure. As shown by SCXRD analysis, compression of the intermolecular distance between the naphthalenediimide moiety of 2BP-NDI and 4-fluorotoluene from 3.52 Å to 3.31 Å occurred under 1 atm and high pressure (3.2 GPa). The forced proximity of molecules due to external pressure suggests an electronic perturbation in intermolecular interactions (CT interactions), which resulted in a long wavelength shift in luminescence characteristics. This color change in luminescence was absent during mechanical grinding involving the use of an agate mortar. This example demonstrates the characteristic piezofluorochromism of functional dyes used as pressure sensors.

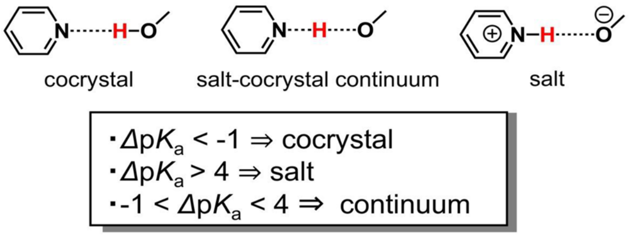


Fig. 10 Schematic of a cocrystal (O–H⋯Npyr), a salt (O−⋯H–Npyr+), and a salt–cocrystal continuum (O⋯H⋯Npyr) (where the H-atom position is shared between two heavy atoms) in a typical O⋯H⋯N interaction

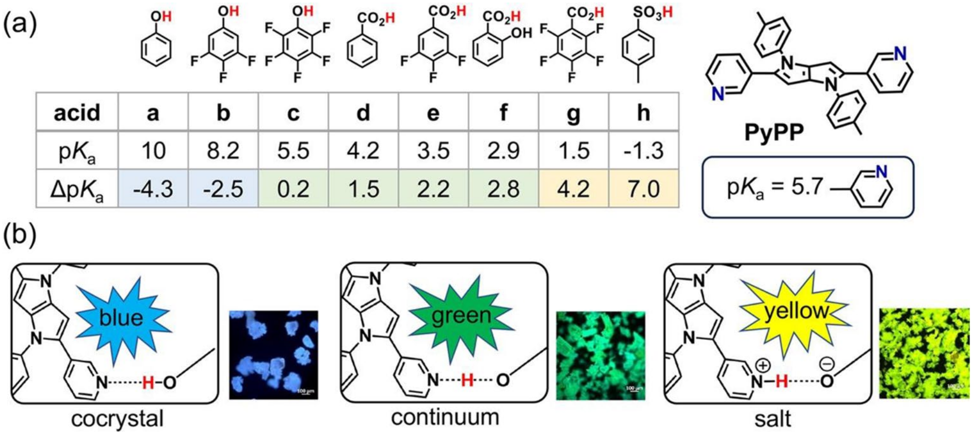
Creation of photofunctional materials using a salt–cocrystal continuum

This section discusses the creation of photofunctional materials derived from complexes of acids and bases, which are broadly divided into two categories: cocrystals formed by hydrogen bonding and salts composed of cations and anions. Salts are usually distinguished from cocrystals as ionic crystals. However, this discussion focuses on a phase in between, that is, the salt–cocrystal continuum, which is generally accepted in the field of crystal engineering. We believe that the salt–cocrystal continuum represents a new category in the creation of photofunctional materials, which we aim to explore.

In crystal engineering, interest lies at the boundary between salts and cocrystals, particularly in the proton locations within the salt–cocrystal continuum. This continuum encompasses three states: ionic "salts" involving proton transfer, neutral "cocrystals" without proton transfer, and "salt–cocrystal continuum" with partial proton transfer (Fig. 10) [63]. The pK_a difference between bases and acids ($\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid})$), known as the "p$K_a$ rule" govern these states; pK_a rule is a critical concept in crystal engineering and pharmaceutical development [64]. Empirically, $\Delta pK_a > 4$ indicates "salt," and $\Delta pK_a < -1$ suggests a "cocrystal." The range of $-1 < \Delta pK_a < 4$ can yield salts, cocrystals, or salt–cocrystal continua, influenced by molecular aggregation and external factors, which makes the prediction challenging. However, the use of these states as metastable phases can lead to changes in the coloration or luminescence of cocrystals upon exposure to external stimuli. Jones et al. reported thermochromism, which indicated a change from red to colorless upon heating, in acid–base complexes of haloanilines and benzoic acid derivatives [65]. This phenomenon occurred presumably due to proton transfer from the cocrystal to a more stable salt form with the increase in temperature.

Here, we present photofunctional materials using cocrystals of pyridine-modified pyrrolopyrrole derivatives (PyPP) and various organic acids, such as phenols (**a**–**c**), carboxylic acids (**d**–**g**), and sulfonic acid (**h**) derivatives (Fig. 11). Pyrrolopyrrole derivatives are electron-rich aromatic complex rings, and they function as dyes through intramolecular CT (ICT) [66, 67]. Either weak intermolecular interactions through hydrogen bonding between pyridine and organic acids or salt formation through complete protonation of pyridine will result in considerable modulation of optical properties [68, 69]. In particular, complexes with various pK_a organic acids and tunable photofunctional properties based on the three states of proton transfer were prepared, with a focus on the pK_a difference between bases and acids. As a result, acid–base complexes prepared with $\Delta pK_a < -1$ showed blue luminescence as cocrystals (PyPP•**a** and PyPP•**b**); those with $-1 < \Delta pK_a < 4$ formed green luminescent salt–cocrystal continua (PyPP•**a** and PyPP•**c**, PyPP•**d** and PyPP•**e**, and PyPP•**f**); complexes with $\Delta pK_a > 4$ suggest the formation of yellow luminescent salts (PyPP•**g** and PyPP•**h**). The modulated solid-state luminescence was possibly due to the various degrees of protonation of pyridyl groups in PyPP, which affected the ICT properties.

PyPP•**f**, a two-component crystal consisting of PyPP and salicylic acid, exhibited green emission. By contrast, PyPP•**f**$\supset CH_2Cl_2$, which includes CH_2Cl_2 as a solvate in its three-component structure along with PyPP and salicylic



acid	a	b	c	d	e	f	g	h
pK_a	10	8.2	5.5	4.2	3.5	2.9	1.5	-1.3
ΔpK_a	-4.3	-2.5	0.2	1.5	2.2	2.8	4.2	7.0

Fig. 11 (**a**) Structures and pK_a values of various acids and PyPP. pK_a value of the pyridyl moiety of PyPP was assumed to be 5.7, which was obtained from the pK_a of 3-methylpyridine. (**b**) Suggested mechanism for photofunction modulation via the increase in ICT strength. Change in the protonation degree in accordance with the ΔpKa rule (salts for $\Delta pK_a > 4$, salt–cocrystal continuum for $-1 < \Delta pK_a < 4$, and cocrystal for $\Delta pK_a < 0$)

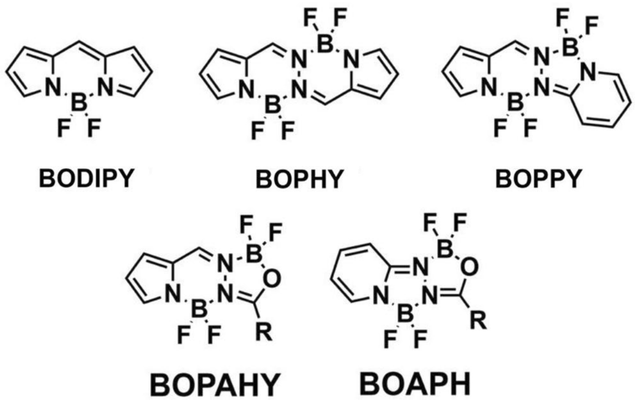


Fig. 12 Representative luminescent boron complexes

acid, displayed yellow emission. Although both compounds had $-1 < \Delta pK_a < 4$, they emission colors varied. This difference suggests that the incorporation of CH_2Cl_2 as a solvent molecule altered the surrounding environment of pyridine and acids, which led to variations in the protonation degree. Moreover, heating the PyPP•**f**⊃CH_2Cl_2 crystals for CH_2Cl_2 release caused the luminescence to change into the same green color as PyPP•**f**. In addition, crystal exposure to the vapor of CH_2Cl_2 induced vapochromism, in which the luminescence shifted back to the yellow color similar to that of PyPP•**f**⊃CH_2Cl_2. This finding proves that emission color can change in response to external stimuli, and we believe that the corresponding process involves proton transfer between acids and bases associated with vapor adsorption and desorption. This finding showcases a new design paradigm for functional materials that respond to external stimuli through subtle differences in hydrogen bonding. Studied have also investigated vapochoromic behavior using acid–base complexes that respond to changes in proton position. The position of hydrogen was detected via neutron diffraction to determine the relationship between protonation degree and optical properties. SCXRD analysis and Hirshfeld atom refinement revealed the short N•••H distances resulting from the presence or absence of CH_2Cl_2, which indicates the strong protonation of the pyridyl group. However, the present findings are only those of a ground-state structural evaluation. To discuss luminescence color change in more detail, scientists should consider the evaluation method for determining the proton position in excited state. Further progress in this research is expected in the future.

Multinuclear main group metal complexes

Multinuclear boron complexes

Boron-containing luminescent complexes, such as BODIPY, are molecular platforms with a strong luminescence for various applications [70–73]. Numerous derivatives of BODIPY have been synthesized and are now commercially available, which result in their applications in wavelength conversion materials, organic lasers, luminescent devices, CPL materials, viscosity sensors, and bioimaging. Mononuclear and multinuclear novel boron complexes, such as BOPHY [74–76], BOPPY [77], BOPAHY [78], BOAPH [79], and others [80, 81], have been vigorously explored (Fig. 12). Different from BODIPY, which possesses a symmetric skeleton, these compounds often contain unsymmetric skeletons, which lead to intramolecular donor–acceptor-based ICT transitions that combine large Stokes shifts with a strong luminescence. However, compared with the prolific research on BODIPY derivatives, studies rarely focused on other mononuclear and multinuclear boron complex derivatives. In particular, the creation of CPL-active boron-containing chiral systems is hindered by the planar and achiral structures of most boron complexes. Popular methods for the preparation of chiroptical boron-containing chromophores are mainly based on BODIPY skeletons that incorporate chiral perturbation [82], such as chiral substituents with boron difluoride (BF_2) configurations [83, 84], boron-bridged orthogonal combination fluorophore and chiral elements [85–87], or those with boron as a chiral center attributed to tetra-coordination-induced asymmetry [88, 89]. Thus far, scholars still struggle with the development of diverse chiral boron complexes based on other boron complexes except BODIPY. We believe that the research on other mononuclear and multinuclear boron complex derivatives via molecular engineering has the potential to surpass existing studies on BODIPY derivatives. Currently, the focus centers on the creation of new photofunctional properties through dimerization of these new mononuclear and multinuclear boron complexes.

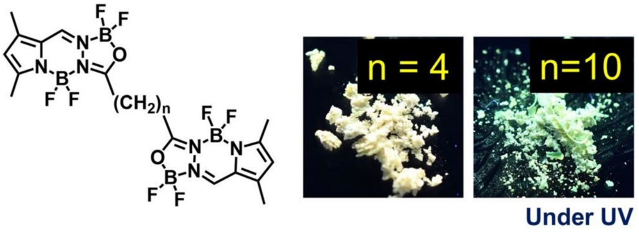


Fig. 13 Structure of BOPAHY linked by flexible alkyl chains and solid-state luminescence properties at different chain lengths ($n = 4$, 10)

A study reported the synthesis of a BOPAHY dimer linked by flexible alkyl chains (Fig. 13) [90]. This synthesis occurred in straightforward manner and involved the creation of a Schiff base by mixing 2,5-dimethylformylpyrrole and adipic acid dihydrazide (or dodecanedioic dihydrazide), followed by the addition of triethylamine and BF_3•OEt. The resulting BOPAHY dimers, especially those with four and ten alkyl chain lengths, exhibited absorption and blue emission characteristics in solutions similar to those of unlinked boron complexes (BOPAHY). However, in the solid state, dimer with an alkyl chain length of four exhibited white-light emission with a PL quantum yield of 16.0%. In contrast, the dimer with an alkyl chain length of ten exhibited green emission with a PL quantum yield of 8.6%. These findings imply the possibility of tuning the photofunctional properties of complexes through changes in the aggregation state induced by flexible alkyl chain modification.

The exploration extended to the synthesis of a directly linked dimer of BOPPY with 2,2′-bipyrroles as a precursor, which is a building block for pyrrolic macrocycles [91–98]. The directly linked dimers of BOPPY were synthesized using 2,2′-diformylbipyrrole (**1**–**3**) to form a Schiff base with hydrazinopyridine or hydrazinoquinoline (**i**–**l**), followed by the addition of a base and $BF_3 \bullet OEt_2$ (Fig. 14) [99]. The targeted tetra-BF_2 complexes (**1i**–**1 L**, **2i**–**2 L**, and **3i**–**3 L**) were identified via NMR, high-resolution mass spectrometry, and SCXRD analysis.

Tetra-BF_2 complexes in solution exhibited PL spectra having intense green to orange emissions with PL quantum yields of up to 100% (Fig. 14). With a focus on substituent modifications, complexes with *n*-propyl groups at the R^1 position (**3i**–**3 L**) showed a longer wavelength shift in absorption and emission compared with their unsubstituted counterparts (**1i**–**1l**), which suggests conjugation extension due to the presence of *n*-propyl groups. Conversely, a short-wavelength shift in emission occurred with the introduction of four ethyl groups at the R^1 and R^2 positions (**2i**–**2l**), presumably due to the increased bending angle around the bipyrrole single bond caused by steric hindrance. Complex (**2i**–**2l**) had a structure that was considerably bent by approximately 70°. Notably, the crystal structure included racemic mixtures of (*R*)- and (*S*)- enantiomers. Therefore, the optical resolution of complex (**2i**–**2l**) was achieved via the combination of chiral column chromatography with recycling chromatography. Each enantiomer exhibited mirror-image CD and CPL properties in various organic solvents and solid states. The obtained luminescence dissymmetry factor (g_{lum}) was in the order of 10^{-3}. Tunable CPLs with high g_{lum} were achieved by designing new tetra-BF_2 complexes modified by terthiophene at appropriate positions via the Suzuki–Miyaura coupling reaction. Complex 4 exhibited a yellow PL and CPL with a high g_{lum} up to the order of 10^{-2}, in which terthiophene was modified at the *para*-position relative to the pyridine moiety of the non-substituted tetra-BF_2 complex (Fig. 15) [100]. This finding was attributed to the extension of the π-conjugation and improvement of ICT interactions via terthiophene modification. The highly luminescent multicolor CPL achieved via docking of an emissive boron chromophore will pave the way for broad applications of CPL technology.

The applications of tetra-BF_2 complexes are further expanding. Tetra-BF_2 complexes are being considered as functional materials for the generation of

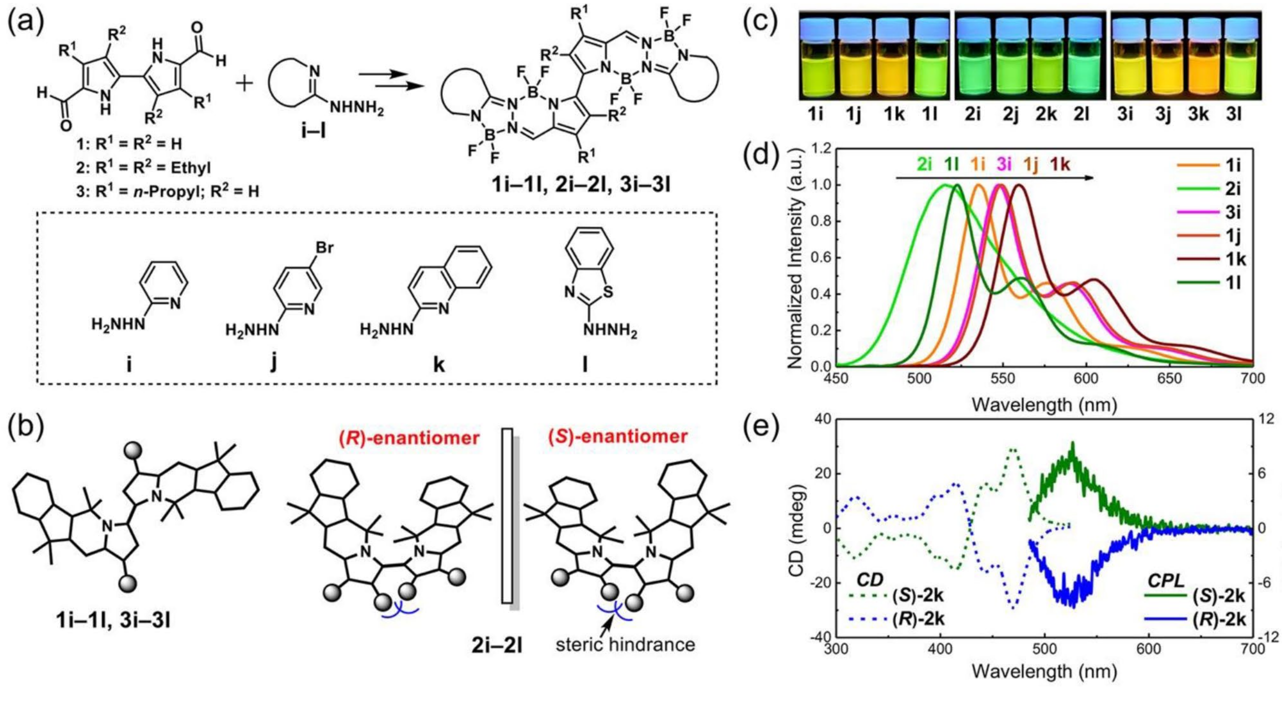


Fig. 14 (**a**) Synthesis of tetra-BF_2 complexes, (**b**) bent conformation of tetra-BF_2 complexes depending on substituent position, (**c**) emission color of tetra-BF_2 complexes in dichloromethane under UV light irradiation, (**d**) emission spectra of tetra-BF_2 complexes, and (**e**) CD and CPL spectra of complex **2k** in dichloromethane

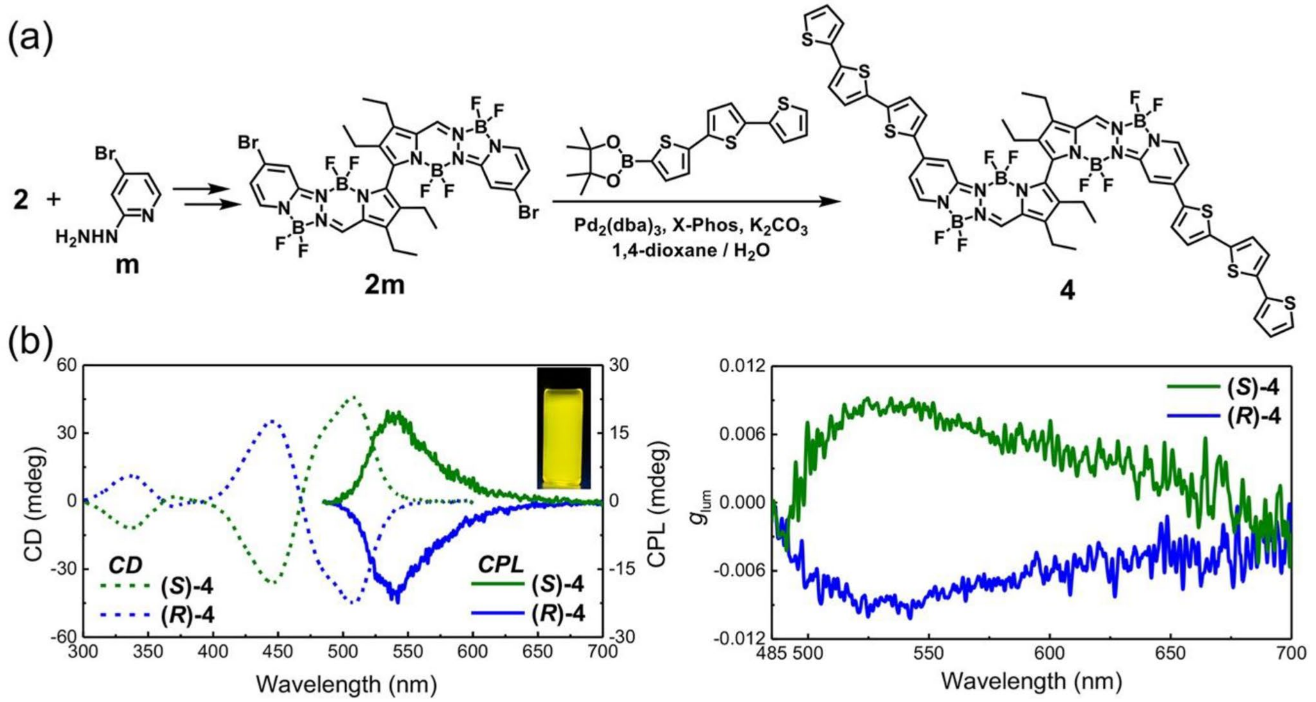


Fig. 15 (**a**) Synthesis of terthiophene-modified tetra-BF$_2$ complex (**4**) via the Suzuki–Miyaura coupling reaction. (**b**) CD, CPL, and g_{lum} spectra of complex 4 in toluene

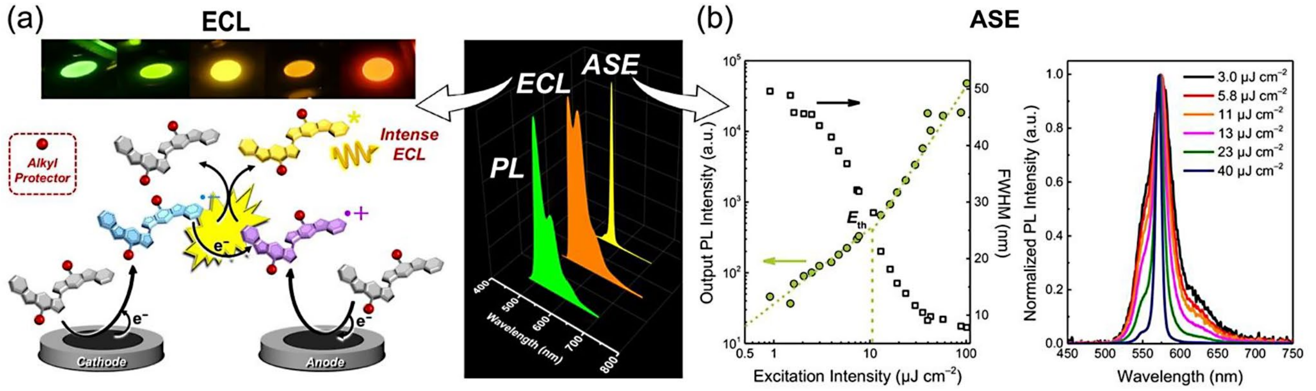


Fig. 16 (**a**) Multicolor ECLs of tetra-BF$_2$ complexes generated via ion annihilation. (**b**) ASE threshold (E_{th}) determined using the output PL intensity and full width half maximum from the edge of a tetra-BF$_2$ complex-doped CBP film prepared by spin coating as a function of the excitation energy and PL spectra for different excitation energies below and above the ASE threshold. Reproduced with permission from ref. 101. Copyright 2024 Wiley-VCH

electrochemiluminescence (ECL) and amplified spontaneous emission (ASE) properties (Fig. 16) [101]. Appropriate substituent modification can be used to stabilize radical anions and cations for efficient ion annihilation to generate ECLs. Tetra-BF$_2$ complexes with various alkyl substituents at different positions exhibit ion-annihilation ECLs in the green to orange region. The lasing properties of these tetra-BF$_2$ complexes in a solid-state blend film using 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl (CBP) host exhibited low ASE thresholds of ≈6–10 μJ cm^{-2} for green to yellow emission. The excellent ASE properties indicate the potential of these tetra-BF$_2$ complexes for organic laser development.

The synthesis study of tetra-BF$_2$ complexes yielded tri-BF$_2$ complexes, in which three of the four coordination sites were occupied by BF$_2$, as by-products [102]. These tri-BF$_2$ complexes were isolated via column chromatography, and their structure and photophysical properties were evaluated. The tri-BF$_2$ complexes exhibited red to near-infrared PL behavior in solution and solid states. This result was due to the increased ICT caused by the unsymmetrization of

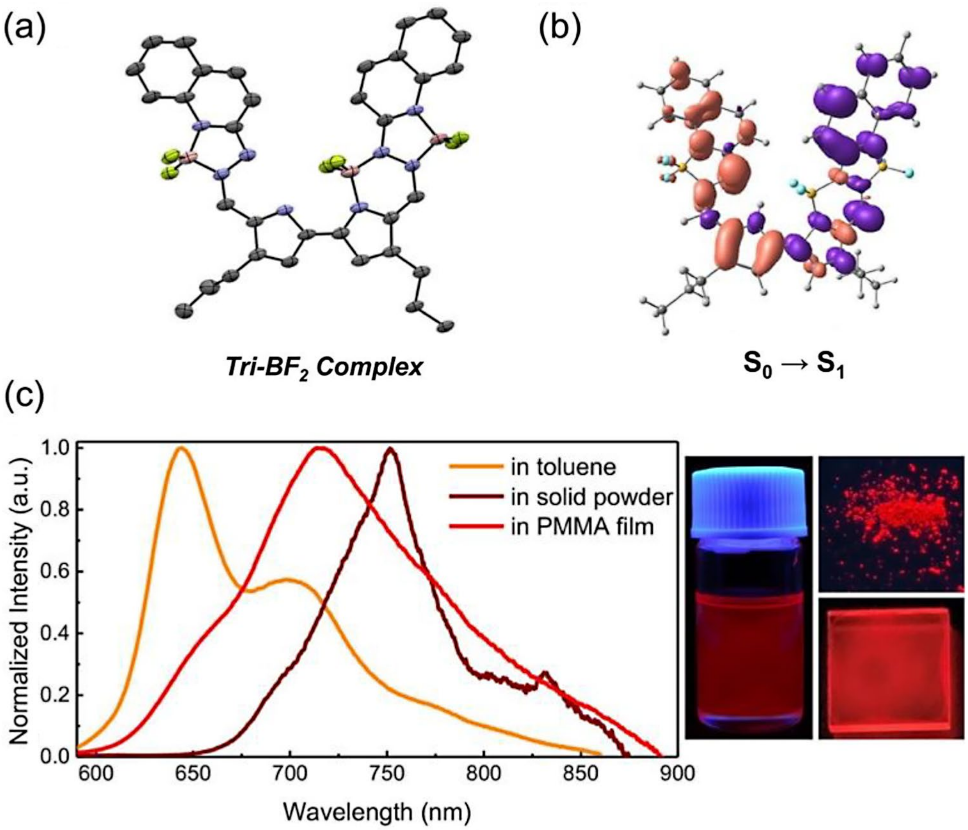


Fig. 17 (**a**) Crystal structure of the tri-BF$_2$ complex. (**b**) Time-dependent density-functional theory (TD-DFT)-calculated $S_0 \rightarrow S_1$ transition. The electron density shifted from pink to purple areas, which indicates ICT interaction. (**c**) Emission spectra and photographs under UV light irradiation of the tri-BF$_2$ complex in toluene, solid powder, and poly(methyl methacrylate) film

the complex. Thus, variations in coordination modes lead to modulation of optical properties.

Dinuclear triple stranded helicates based on aluminum, gallium, and indium complexes

A previous section highlighted the active research on boron complexes, such as BODIPY, in the investigation of functional dyes involving main group complexes. Studies [103–105] have been showing the rapidly growing interest in the research on luminescent main group complexes containing elements other than boron. Prompted by this trend, scholars have pursued the synthesis of luminescent complexes using Group 13 elements, namely, aluminum, gallium and, indium, which are in the same group as boron. Complexes composed of aluminum (III) ions show promise because of the abundance and low cost of the element, with several complexes having been documented (Fig. 18). Alq3, a well-known aluminum complex (Al-1), attracted attention following its application in organic electroluminescent diodes, as reported by Tang and VanSlyke in 1987 [106]. Since its initial reporting, investigations focused on the modulation of luminescence properties of Alq3 with the use of various substituents [107–109]. Numerous aluminum complexes with luminescent properties have since been identified, and studies have vigorously focused on the mechanism of these substituents in the modulation of luminescence [110, 111]. Nabeshima reported that aluminum complexes of N_2O_2-type dipyrrin (Al-2) exhibited a red emission ($\lambda_{em} = 647$ nm) with a high PL quantum yield (72%) [112, 113]. Tanaka reported an aluminum hydride complex supported by a β-diketoiminate ligand (Al-5); this complex exhibited crystallization-induced emission properties at room temperature and long-lifetime phosphorescence at 80 K [114]. In addition, a fluorescent dinuclear aluminum complex (Al-6) with PL quantum yields of up to 100% has been reported [115]. However, aluminum ions are inherently labile in coordination chemistry because of their high reactivity. Thus, the synthesis and improvement of the stability of aluminum-based luminescent complexes present a challenge.

In 2021, aluminum-based dinuclear triple-stranded helicates consisting of a multidentate ligand with a Schiff-base skeleton and an aluminum(III) ion were reported (Fig. 19) [116]. The resulting complexes comprised the same Schiff-base ligands as BOPHY, which were introduced earlier, and synthesis involved the replacement of the boron source (BF_3• OEt_2) with an aluminum source ($AlCl_3$) during complex formation. Regardless of the ligand with various substituent positions (**L5**–**L7**), helical complexes ALPHY (**5**–**7**) were formed, with three ligands coordinating in a six-coordinate manner around two aluminum ions. SCXRD analysis revealed the neutrality of the complex, without any

Fig. 18 Representative luminescent aluminum complexes

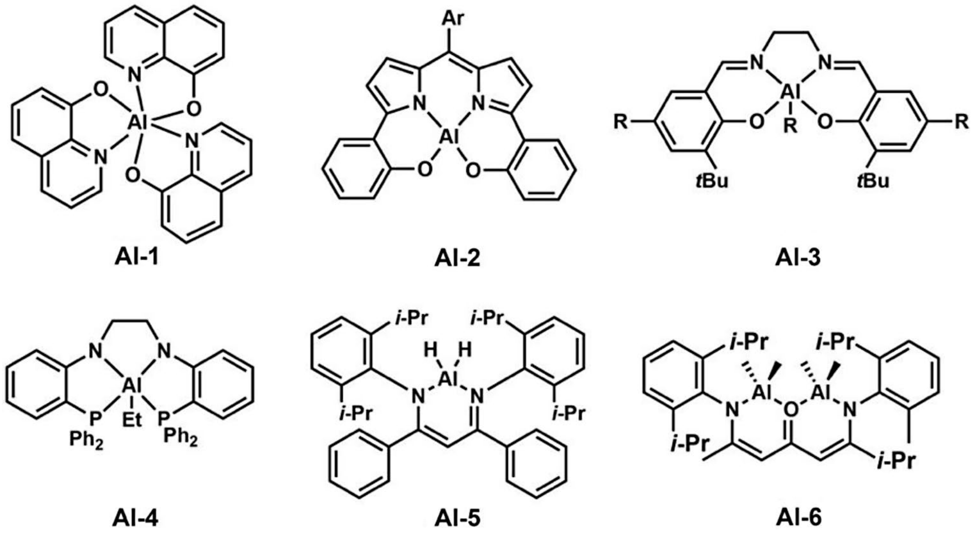
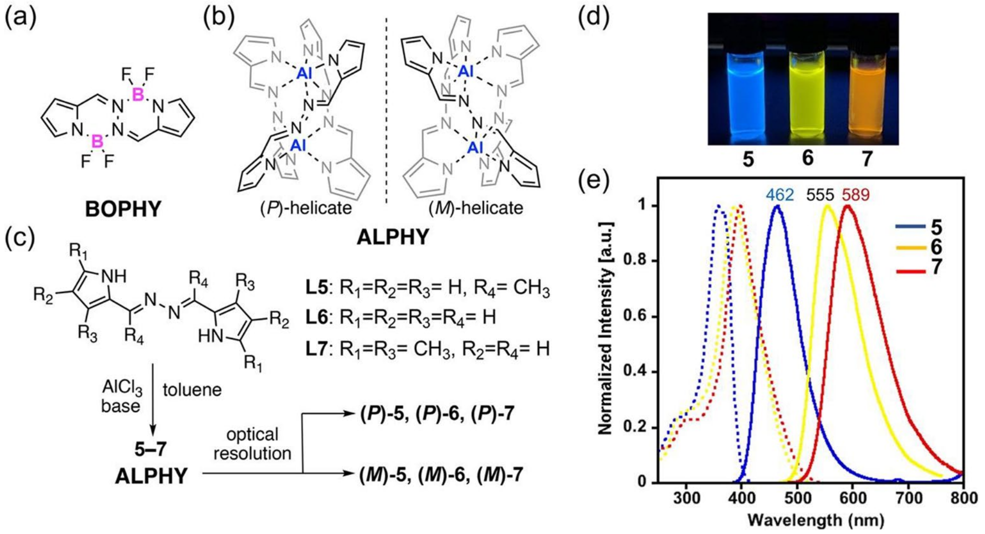


Fig. 19 Representative chemical structures of (**a**) BOPHY and (**b**) ALPHY. (**c**) Synthesis of ALPHY. (**d**) Photographs of ALPHYs in toluene under UV light irradiation. (**e**) Absorption and emission spectra of ALPHYs in toluene. Reproduced with permission from ref. [116]. Copyright 2021 Wiley-VCH



counter ions present, and confirmed the presence of (*P*)- and (*M*)-helical structures in the crystal lattice. Notably, the resulting complexes exhibited intense blue (**5**), yellow (**6**), and orange (**7**) emission under UV light irradiation and a large Stokes shift of approximately 7000 cm^{-1}, which indicates a minimal overlap between absorption and emission. This property is attributed to the excited-state conformational relaxation of the complex. In toluene, the PL quantum yields were 79% for **5**, 20% for **6**, and 54% for **7** [117].

Stable (*P*)- and (*M*)-enantiomers were isolated via optical resolution through chiral column chromatography. The CD spectra of the isolated compounds were mirror images of those for the corresponding isomers, which implies the success of optical resolution (Fig. 20). The absolute configuration assignments of enantiomers were validated through spectral simulations obtained from electronic transition energies and rotational strength in TD-DFT calculations. In solutions and solid states, multicolor CPL spectra were recorded, and the maxima of the CPL spectra matched those of the PL spectra. Finally, we produced a white CPL by properly mixing blue and yellow luminescent helicates. This concept applies not only to aluminum complexes but also to gallium and indium complexes [118]. Although these complexes are not highly luminescent, they can be optically resolved and isolated as stable enantiomers.

Conclusion

This review introduced the development of functional dyes using organic molecules and multinuclear complexes. In addition, this work incorporates the essence of supramolecular and host–guest chemistry, with a focus on the author's research. The initial research stage centered on the synthesis of host molecules based on arylene diimide with pyridyl moieties and their complexation with tris(pentafluorophenyl)

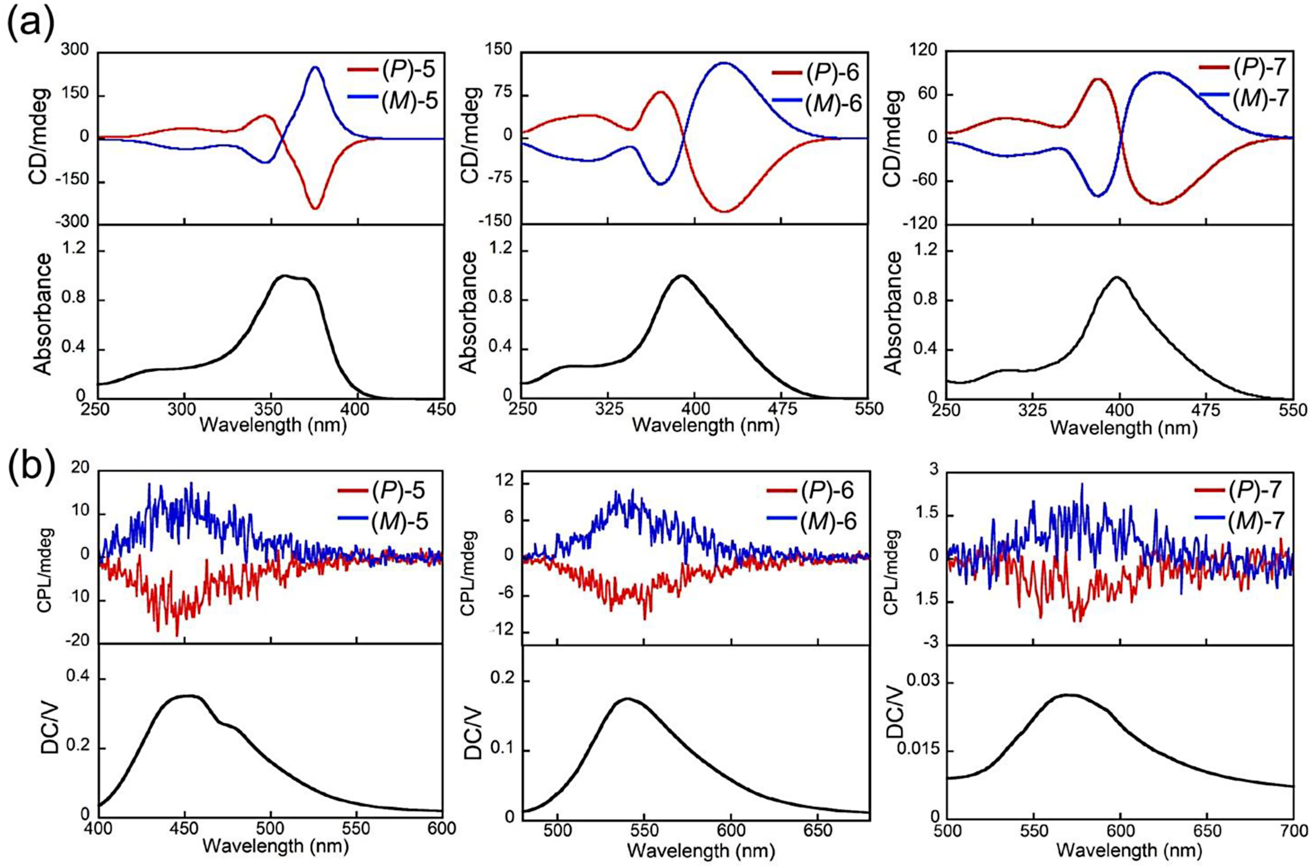


Fig. 20 (**a**) CD and absorption spectra of (*P*)-**5**, (*M*)-**5**, (*P*)-**6**, (*M*)-**6**, (*P*)-**7**, and (*M*)-**7** in CH_2Cl_2 solution. (**b**) CPL and DC (= nonpolarized fluorescence) spectra of (*P*)-**5**, (*M*)-**5**, (*P*)-**6**, (*M*)-**6**, (*P*)-**7**, and (*M*)-**7** in CH_2Cl_2 solution

borane via boron–nitrogen dative bonds, which demonstrated the successful tuning of optical properties through cocrystallization with various aromatic guest molecules. Two- to five-component cocrystals developed systems that can be used to tune emission color, lifetime, and PL quantum yields were prepared, and they provided insights into emission mechanisms, such as fluorescence and room-temperature phosphorescence. Precise evaluation of these molecular systems was achieved via SCXRD analysis, and the result revealed the correlation between structure–property relationships. In addition, recent efforts toward mechanochemical cocrystallization and the application of emerging topics, such as vapochromism and piezochromism to sensor materials, have been presented. Furthermore, we reported the creation of cocrystals that change their luminescence properties through alteration of the CT interaction of dyes depending on the proton position and focused on salt cocrystal continuum as an intermediate state between cocrystals and salt. The latter part of this review highlighted the synthesis of boron and aluminum complexes via one-pot reactions and introduced their tuning of optical properties. We explored the application of boron complexes based on axial chirality and aluminum complexes based on helical chirality as circularly polarized luminescent materials. In addition, the potential applications of boron complexes in electrochemiluminescence and amplified spontaneous emission based on their stability and emission properties have been discussed.

This review demonstrated that in the field of chemical space, noble functionalities can be created through the combination of multiple components, similar to a puzzle, which suggests the possible expansion of material design through the use of supramolecular and host–guest chemistry. In fact, it is becoming possible to create six-component solids [119], organic solids that are close to solid solutions, and this is considered realistic as a new material design. The use of unexplored elements can be used to stabilize materials that were thought to be unstable, depending on how they are combined. Imagining the steric structure and pursuing new molecular design is particularly important. In the development of photofunctional materials, although chirality has been mentioned in this study, the discussion of structural changes not only in the ground state but also in the excited states, and studies combining ultrafast spectroscopic techniques and computational chemistry will become increasingly important [120, 121]. These achievements not only open up new possibilities in chemical design but also pave the way for the research and development in various fields, including materials science, nanotechnology, and biotechnology. The research results are directly linked to the development of new technologies and materials that will enrich our lives along with scientific progress and offer highly promising future developments.

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Author contributions T. O. wrote the manuscript and prepared all the figures.

Data availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

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