



Isomerization and rearrangement of boriranes: from chemical rarities to functional materials

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ABSTRACT Stimuli responsive materials have recently been the subject of tremendous research efforts owing to their numerous potential applications. Although there currently exist many different types of “smart” materials, those based on photoresponsive transformations are especially attractive. In this review, we focus on a relatively new class of photochromic molecules based on the photochemistry of chelate organoborates, which form intensely colored, base-stabilized boriranes. Recent efforts to exploit the reactivity of these systems are summarized, and future prospects in materials science discussed.

Keywords: Smart materials, photochemistry, boriranes

INTRODUCTION

Molecular systems whose physical or chemical properties can be controlled by external stimuli represent an emerging class of functional materials with wide-spread applications in a number of topical fields [1–5]. Of the many so-called “smart” materials that respond to a variety of triggers, including electric field [6], pressure [7,8], temperature [9–12], pH [13,14], etc., photoresponsive systems offer several unique opportunities due to their quick response and remote delivery of the external stimuli [15,16]. These types of systems are often based on photochromism, which is defined as the reversible transformation of a chemical species between two distinct states with different optoelectronic properties (Fig. 1), wherein at least one of the transformations is governed by light. In general, the mechanism of photochromic systems usually relies on either: 1) *cis-trans* isomerization of C=C or N=N π -bonds [17,18], or 2) the making and breaking of chemical bonds [19]. While the simplicity of the former does lend itself to certain applications [20], we will focus on the latter due to its relevance in the photochemical formation of azaboratabisnorcaradienes (hereafter referred

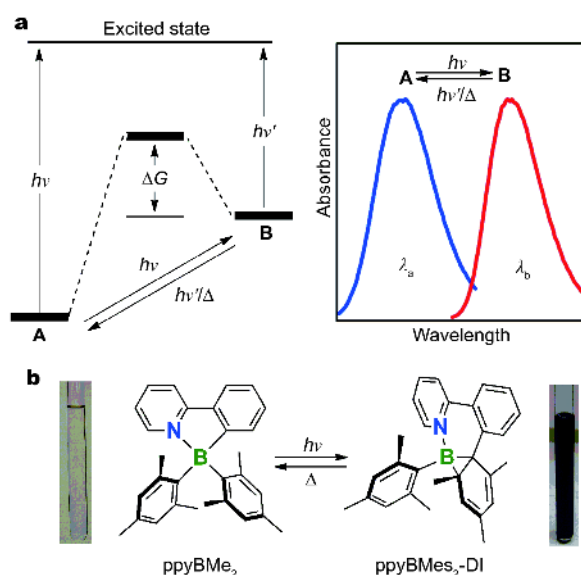


Figure 1 (a) General schematic showing the photochromic switching of A→B; (b) photoresponsive boron system ppyBMe₂ and its “dark” isomer (DI).

to as “dark isomers”, see ppyBMe₂-DI in Fig. 1). Many of the well-known photochromic systems that rely on this strategy tend to follow electrocyclic ring closing/opening reactions, with spiropyrans [21], fulgides [22], and diarylethenes [23] being some of the more prominent. Di-thienylethenes (DTEs) in particular are used in applications such as self-tinting ophthalmic lenses and memory devices [24].

Our interest in photochromic materials began with the serendipitous discovery that four-coordinated N,C-chelate organoboron compounds (ppyBMe₂; ppy = 2-phenylpyridine, see Fig. 1) undergo thermally reversible C–C bond formation/rearrangement around the boron core to afford a base-stabilized borirane [25].

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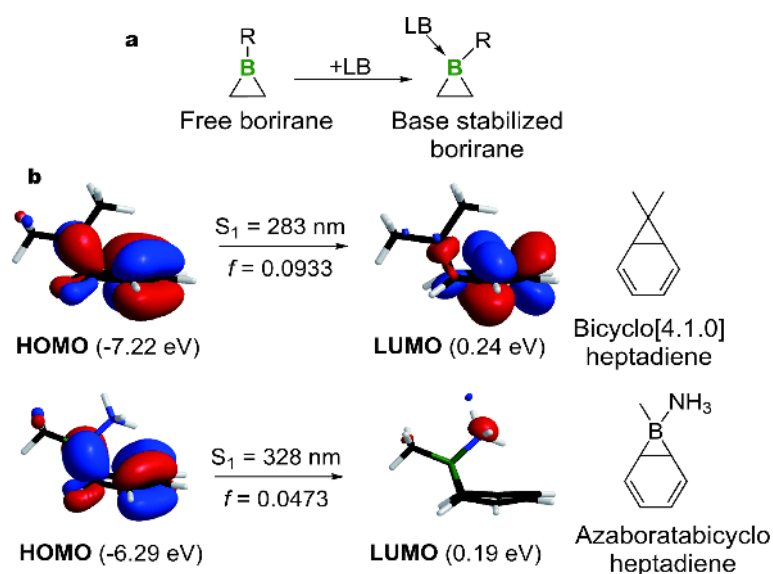


Figure 2 Free vs. base-stabilized boriranes (a) and calculated TD-DFT data of B–N isomerism in simple bicyclo[4.1.0]heptadienes (b; B3LYP/6-31G*).

These “dark” isomers are intensely colored and often absorb strongly in the visible region of the spectrum. Furthermore, appropriate substitution can lead to additional photo- and/or thermal reactivities of the boron chromophore, yielding a variety of new isomers with interesting photophysical properties. This mini-review will provide a brief introduction to base-stabilized boriranes, with particular emphasis on what makes them special among photochromic systems, as well as describe recent attempts to demonstrate their potential as a new class of “smart” materials.

BORIRANES

Analogous to cyclopropanes, boriranes are molecules bearing a three-membered ring containing one boron and two carbon atoms (Fig. 2). In addition to having significant ring strain, they are also π -acidic due to the incorporation of an electron deficient B atom, which makes them highly reactive in comparison to other analogues of cyclopropanes (e.g., aziridines, epoxides, silacyclopropanes, etc.) [26–28]. In fact, free boriranes remain extremely rare [29,30]. One method of stabilizing such systems is the use of Lewis bases (LBs) which can coordinate to Lewis acidic boron, thereby suppressing some of its reactivity. This strategy has been effectively utilized by researchers [31–35] in the isolation and characterization of several different base-stabilized boriranes. Aside from stabilization, the bonding arrangement in these systems also gives rise to their intense colors as shown in Fig. 2.

From time-dependent density functional theory calculations, the all carbon analogues display the highest occupied molecular orbital (HOMO) (π -cyclohexadiene + σ -C–C bonds) to the lowest unoccupied molecular orbital (LUMO) (π^* -cyclohexadiene) as the main transition for S_1 at 283 nm. While the N–B isostere does have a similar HOMO orbital composition, its LUMO consists of the σ^* orbital of the N atom, meaning that the S_1 transition (328 nm) is of primarily charge-transfer (CT) character and bathochromically shifted by ~ 35 nm due to HOMO destabilization of ~ 1 eV. In the dark isomer of ppyBMes₂, the S_1 transition is an intense CT from the azaboratabicycloheptadiene core to the ppy backbone ($\pi \rightarrow \pi^*$). It is these unique electronic features, combined with the reversible nature of their phototransformations, that give ppyBMes₂ and derivatives their potential as photochromic materials.

FOUR-STATE COLOR SWITCHING

Despite the fact that photochromic switching at a boron core remains rare [36–39], there do exist several examples of photochromic systems which incorporate organoboron subunits to act as modulators of various chemical properties [40–42]. In particular, –BMes₂ substitution has proven to be an effective strategy for controlling the color and state-switching of DTEs *via* the introduction/removal of fluoride ions (F[−]), which bind strongly to three-coordinated boron atoms and disrupt the π -conjugation of the molecule [43–45]. This approach has also been successfully implemented in the development of diboron-

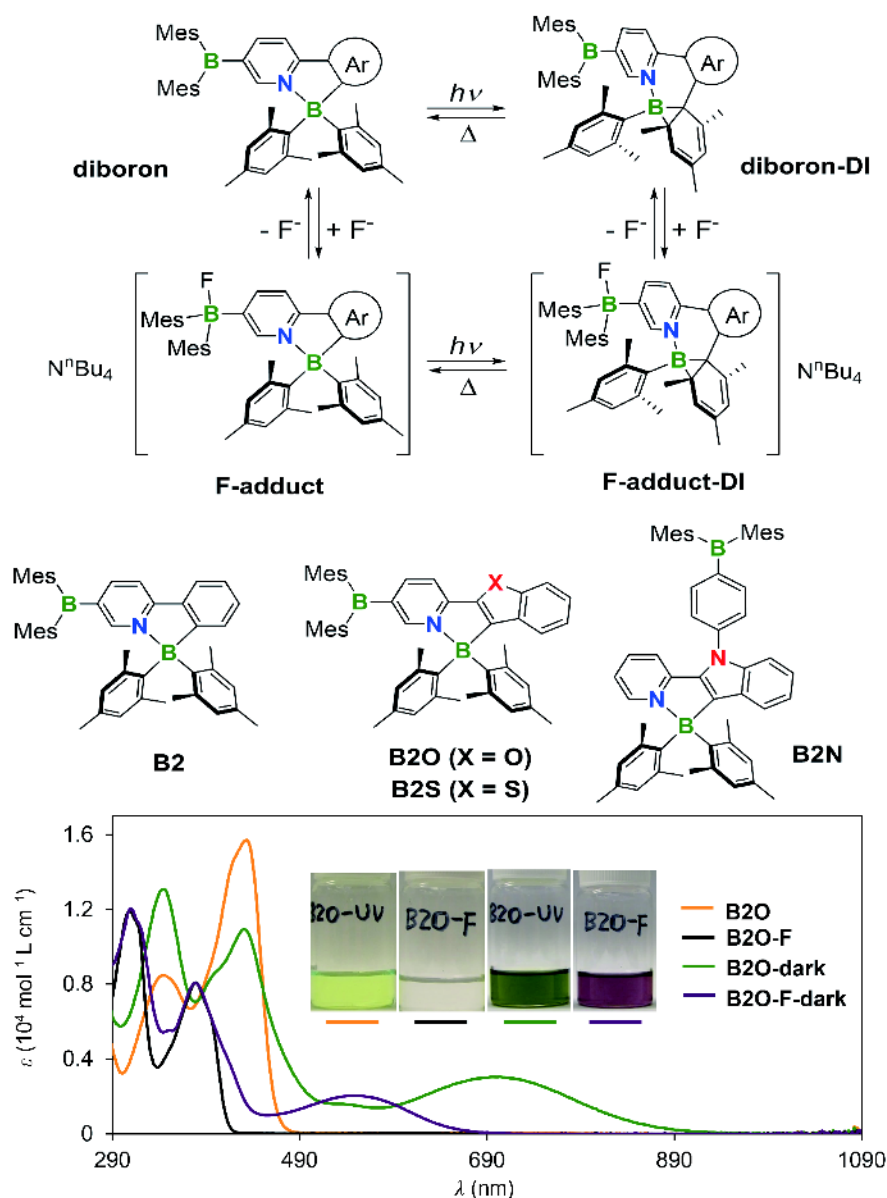


Figure 3 Top: four-state color switching and structures of selected diboron compounds. Bottom: UV/vis spectra and colors of the various isomers of B2O.

based photoswitches [46] capable of changing between four different states (Fig. 3). The $-\text{BMes}_2$ unit was attached at both proximal (**B2**, **B2O**, **B2S**) and distal (**B2N**) locations on the π -conjugated ligand to probe the impact of acceptor position on the color switching of the photochromic boron compounds. Placing the $-\text{BMes}_2$ further away from the π -conjugated backbone resulted in no obvious photophysical change upon the addition of F^- to **B2N** ($\lambda_{\text{fl.}} = 495$ vs. 480 nm) or **B2N-dark** ($\lambda_{\text{abs.}} = 614$ vs. 604 nm) due to its minimal participation in the π -con-

jugation of the molecules backbone. Conversely, F^- dramatically affects both the emission and visible color of **B2**, **B2O**, **B2S**, and their dark isomers (Fig. 3), as the empty p_z orbital of boron participates directly in the conjugated backbone. This is understood as a consequence of destabilizing their LUMO levels upon F-adduct formation, which hypsochromically shifts the λ_{max} of **B2O** vs. **B2O-F** and **B2O-dark** vs. **B2O-dark-F** by ~ 56 and 156 nm respectively, giving each state a unique color. Both the neutral and F-bound molecules undergo thermally re-

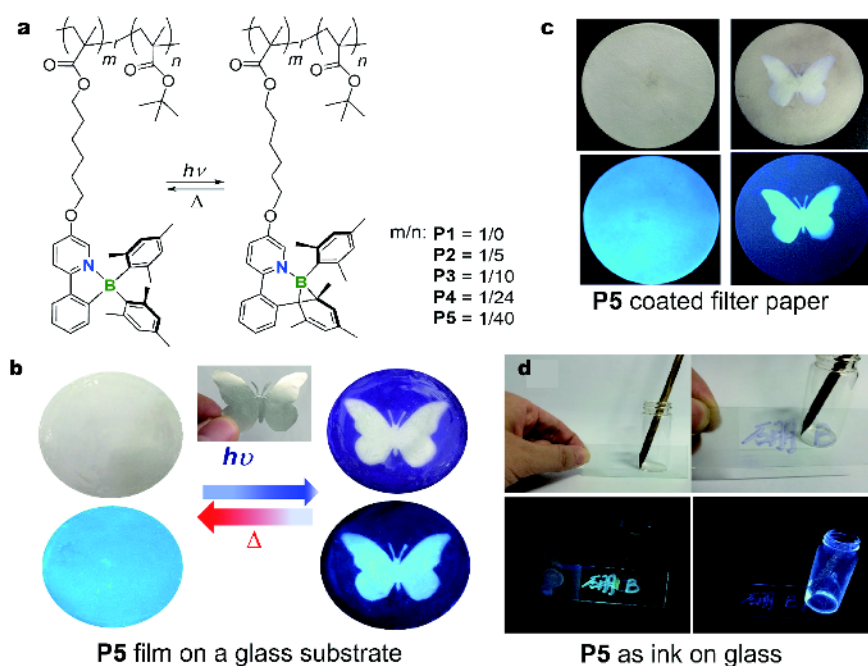


Figure 4 (a) Photochromic polymers/random copolymers based on the ppyBMes₂ unit. (b–d) Photographs showing the pattern created by photochromic switching of the P5 polymer film on a glass substrate (b), on a filter paper (c), and the writing with a Chinese brush and P5 polymer as the ink on glass (d), (top: illuminated by ambient light; bottom: by UV light). Images in (b) and (d) are reprinted with permission from Ref. [54]. Copyright 2017, the American Chemical Society.

versible switching with UV light irradiation with comparable efficiencies. Furthermore, the stability of the dark isomers towards water allows four-state switching to be achieved as shown in Fig. 3, where the fluoride ions can be readily extracted with a simple aqueous workup. The forward and reverse transformations of the diboron molecules and their F-adducts persist even when doped into a polystyrene matrix, suggesting that four-state switching of these photochromic systems is possible in the solid state with the appropriate choice of a water permeable polymer.

PHOTOCHROMIC ORGANOBORON COPOLYMERS

In general, polymeric materials are preferred over small molecules in practical applications due to their flexible, lightweight nature which makes them easier to process, compared to small molecules. Although polymers incorporating either traditional photochromic systems (e.g., spiropyrans and DTEs; [47,48]) or organoboron functionalities [49–53] have been widely explored, photochromic polymers with a switchable boron core remained unknown until recently [54]. These polymers (Fig. 4) were designed to minimize π -conjugation of the ppy backbone in order to maintain the high photoisomeria-

tion quantum yield (Φ_{PI}) of the boron chromophore.

Random co-polymers with varying -ppyBMes₂ (100 → 2.5%; P1–P5) content were prepared by atom transfer radical polymerization (ATRP) using mixtures of methacrylate derived photochromic units (BHMA) and *t*-butyl methacrylate. Much like BHMA and ppyBMes₂, the polymers absorb in the near-UV region of the spectrum (λ_{abs} =358 nm), display intense blue luminescence (λ_{em} ~476 nm, Φ_{PI} ~43%), and undergo photoisomerization at the boron core to give deep blue (λ_{abs} ~580 nm) color in solutions and as thin films, with the efficiency of the switching depending on the spacing of the photochromic units. The Φ_{PI} vs. the number of the ppyBMes₂ moieties follows a reciprocal relationship, with decreasing chromophore content from P1 to P5 yielding higher isomerization efficiencies. This observation is explained according to a Förster resonance energy transfer (FRET) mechanism, where the excited states of the unreacted ppyBMes₂ units are quenched *via* inter- and intrachain energy transfer to the dark isomers within the polymer [55]. Due to the comparable color purity but higher Φ_{PI} for polymers with less boron content, P5 was chosen for optical device applications. Patterned images can be generated on either transparent glass Petri dishes or P5-coated non-fluorescent filter papers by spin-casting

or soaking with toluene solutions of **P5** respectively and irradiating the substrates after applying an appropriate mask (Fig. 4b and c). Images generated in this way are fully erasable upon heating, and the write-erase cycles can be repeated at least five times without any significant loss of color purity. Polymer solutions can also be used as switchable ink when applied to substrates through a pen or Chinese brush (Fig. 4d). These blue patterned images are persistent for days at ambient conditions, which is in stark contrast to the dark isomer of the parent ppyBMes₂, which decomposes in a few hours under the same conditions. Incorporation of these photochromic molecules into a polymer therefore increases their applicability by protecting the boron core while it undergoes photochemical switching.

BORIRANES AS REACTIVE INTERMEDIATES TOWARDS LUMINESCENT MATERIALS

Aside from the direct use of base-stabilized boriranes in materials science, these high energy species can also be used as reactive intermediates in the facile preparation of functional materials such as singly annulated borepins [56] and chiral *N,B,X*-heterocycles (*X* = S or O) [57]. Borepins are charge neutral, boron-containing analogues of the tropylium cation, where the boron atom is typically protected by bulky substituents [58]. Due to integration of the boron's empty p_z orbital into the π-system of the molecule, these molecules often display substantially different photophysical/chemical properties compared to their carbon congeners such as intense blue to green luminescence ($\lambda_{em} = 400\text{--}491\text{ nm}$, $\Phi_{Fl.} \sim 50\text{--}70\%$) and tunable redox properties [59]. On the other hand, heterocyclic scaffolds that contain N, B, and either S or O, are virtually unknown, with the closest relatives being aza- [60], thia- [61], and oxaborinines [62]. This type of isosterism in aromatic systems has garnered increasing attention due to the potential use of these B,N- or B,X-embedded aromatics in optoelectronic materials and medicinal science [63].

Converting boriranes into novel molecular motifs relies on designing organoboron compounds with appropriate chelating ligands or substituents on boron. Beginning with choice of ligand, it was recently established that *peri*-substituted naphthalenes with 2-pyridine and *-*BMes₂ groups (**pynaphB**) are capable of undergoing a photochemical reaction involving C=C bond breaking in the arene ring with concomitant boron insertion and mesityl migration (Fig. 5a).

The product of this reaction was the base-stabilized

benzoborepin (**BBP**), which represents some of the only examples of singly annulated borepins. The **BBP** derivatives are all blue fluorescent with $\lambda_{em} = 411\text{--}472\text{ nm}$ and $\Phi_{Fl.} \sim 10\%$, while these values are quite low for luminescent materials. Achieving high $\Phi_{Fl.}$ and tunable emission colors should be possible with further modification of either the ligand or substituents, which is currently ongoing in our laboratory. The excited-state process that converts **pynaphB** to **BBP** involves several steps that culminate in the formation of a borirane (**pynaphB-a**), which is highly unstable and ring-opens to give the annulated borepin.

With respect to the aryl groups on boron, new photochemical C–X bond activation and boron insertion reactions have been discovered for chiral chelate organoboron compounds bearing heteroaromatic substituents (Fig. 5b). This reactivity takes advantage of the fact that regioselective borirane formation occurs on the less bulky substituent in these types of systems, and that H-boriranes are highly reactive [64]. Following photoexcitation, a C–C coupled biradical intermediate is expected, which either collapses to the H-borirane or undergoes C–X ring-opening to give unprecedented *N,B,X*-heterocycles. The H-borirane “side products” formed during this reaction are capable of converting into *N,B,X*-heterocycles *via* a second excited-state pathway which regenerates the biradical intermediate. The resulting *N,B,X*-heterocycles are weakly emissive in solution, but noticeably luminescent in the solid state due to restricted rotation of the mesityls (**ImBS**, **NHCBS**, and **pyBSPH** in Fig. 5b). In particular, **pyBSPH** exhibits orange-red emission with a $\Phi_{Fl.} \sim 10\%$, which is quite high for solid-state luminescence at these wavelengths considering the energy gap law [65]. Depending on the position of the N, B, and S atoms within the molecule, tunable emission from blue-green to orange-red is readily achieved. Therefore, the luminescent properties of *N,B,X*-heterocycles can be easily manipulated to make them better suited for materials applications.

CONCLUSIONS

In summary, the photochemistry of chelate organoborates is incredibly rich and diverse, offering various opportunities for innovation and discovery. As a product/an intermediate in the photoreaction, the borirane species plays a key role in the versatile applications and bond activation chemistry mediated by boron. The recently discovered four-state switchable systems, photochromic polymers, and novel luminescent materials based on boriranes show great promise for future applications in

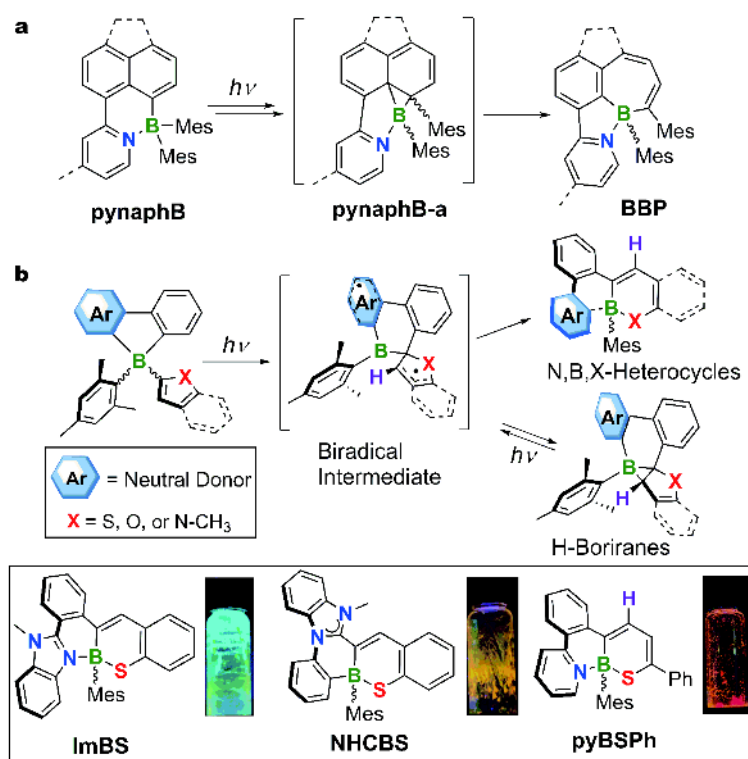


Figure 5 (a) Photoreactivity of *peri*-substituted naphthalenes (pynaphB), (b) heterocycle substituted chelate organoborates with borirane intermediates and the structures of ImBS, NHCBS, and pyBSPH as well as images showing their solid-state luminescence.

memory and optoelectronic devices, as well as write-erase technologies. Although still in its infancy, we anticipate a bright future for borirane-based photochromic/photo-responsive materials, with future developments focusing on the optimization of their photophysical/photochemical properties, as well as establishing new potential applications *via* unexplored reactivities.

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Author contributions Mellerup SK wrote the manuscript with input from Wang S and both authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.



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Boriranes异构和重排: 罕见的有机硼化合物及其在功能性材料中的应用

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摘要 刺激响应材料因其广泛应用而备受关注. 科学家们已开发了多种智能材料, 其中基于有机硼的新型光响应材料尤为引人注目. 本文侧重评论近期发现的基于含整合基团的光响应有机硼分子. 这类分子可发生高效率的光致变色, 生成罕见的、深颜色的Boriranes. 近期研究结果显示这类分子不仅具有独特的光化学性能, 还在材料化学里有多种应用. 此外, 本文介绍了近期对这类分子的研究和进展并展望了其应用前景.