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Planar Chiral Organoboranes with Thermoresponsive Emission and Circularly Polarized Luminescence: Integration of Pillar[5]arenes with Boron Chemistry

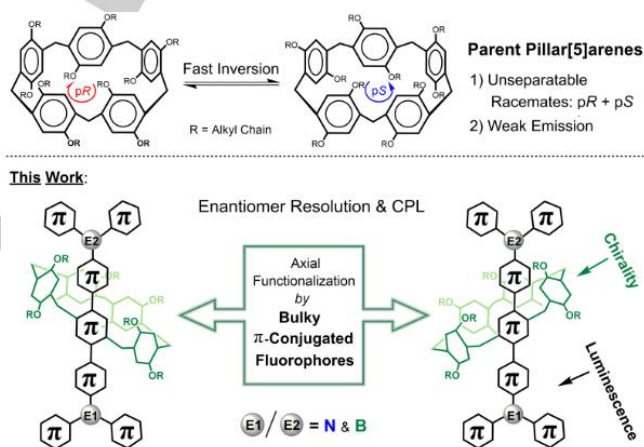
Jin-Fa Chen,^[a] Xiaodong Yin,^[a] Bowen Wang,^[a] Kai Zhang,^[a] Guoyun Meng,^[a] Songhe Zhang,^[a] Yafei Shi,^[a] Nan Wang,^[a] Suning Wang,^[b] and Pangkuan Chen*^[a]

Abstract: Enantiopure molecules based on macrocyclic architecture are unique for applications in enantioselective host-guest recognition, chiral sensing and asymmetric catalysis. Taking advantage of chiral transfer from the intrinsically planar chirality of pillar[5]arenes, we herein present an efficient and straightforward approach to achieve early examples of highly luminescent chiral systems (**P5NN** and **P5BN**). The optical resolution of their enantiomers has been carried out via preparative chiral HPLC, which was ascribed to the molecular functionalization of pillar[5]arenes with π -conjugated, sterically bulky triarylamine (Ar_3N) as an electron donor and triarylborane (Ar_3B) an acceptor. This crucial design enabled investigations of the chiroptical properties, including circular dichroism (CD) and circularly polarized luminescence (CPL) in the solid state. Furthermore, the intramolecular charge transfer (ICT) nature in **P5BN** afforded an interesting thermochromic shift of the emission over a wide range of temperature.

Chirality represents one of the most important phenomenon in nature due to a high relevance to biological mechanism, and a better understanding of this can also significantly advance wide applications in life, medicine and material science.^[1] As a recently burgeoning investigation of chiroptical materials, the circularly polarized luminescence (CPL) is of particular interest in many areas such as photonics, information technology, smart sensing and 3D (bio)imaging.^[2] The CPL technique is a measure of differential emission of the excited states in chiral systems upon the circularly polarized radiation, and it depends both on the remarkable chirality and fluorescent property of materials.^[3] Each requirement in principle can be fulfilled via supramolecular assembly (e.g. supramolecular chiral induction, chiral liquid crystals, and aggregation-induced emission),^[4-6] but sometimes these systems likely suffer from low efficiency and strong dependence on external stimuli. As a consequence, the design and construction of CPL-persistent, structurally well-defined organic dyes are essentially vital to the development of next-generation functional materials.

The common approach to achieve robust CPL-active materials is to covalently functionalize a chiral skeleton using highly

luminescent fluorophores. Several types of organic CPL materials have been reported over years, such as axially chiral binaphthyls, helicenes, and mechanically planar chiral cyclophanes.^[7-10] Pillar[n]arenes that show size-dependent cavity structures are recognized as a class of unique macrocycles with intrinsic planar chirality due to the specific orientation of phenyl rings.^[11] A variety of advances have been derived from considerable efforts in supramolecular chemistry and host-guest recognition of pillararene since its first discovery by Ogoshi in 2008.^[12-16] In contrast, the remarkable promise in chiral scaffolds remains rarely explored because of the dynamic rotation of phenyl subunits against methylene bridges ($-\text{CH}_2-$), leading to fast inversion of the enantiomers (*pS* and *pR*) (Scheme 1). To tackle this challenge, dramatically enhanced steric effects should be sought by replacement of the alkoxy groups on parent pillar[n]arenes with sufficiently bulky substituents.^[17]



Scheme 1. Proof-of-concept design of planar chirality via the integration of conjugated boron chemistry and macrocyclic pillar[5]arenes for circularly polarized luminescence (CPL).

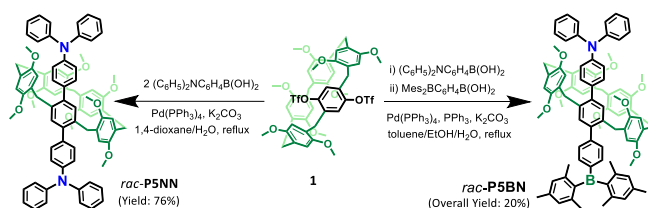
In view of the weakly emissive nature of non-substituted pillar[n]arenes, a judicious choice of appropriate fluorophores can greatly impact their CPL characters. To address this issue, some highly emissive π -conjugated substitutions would preferably be considered to incorporate electron donors and acceptors.^[18] As a typical electron-accepting functionality, triarylborane (Ar_3B) has been widely employed in luminescent materials and many other applications.^[10,19,20] Organoboranes are enabled to show unusual tunable emissions and fully reversible optical responses once they are electronically coupled with donors via π -conjugation.^[21]

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Even though a few examples were reported to show pillararene-based planar chirality,^[17] to the best of our knowledge, the analogues with CPL activity have not been experimentally navigated. As one of our continuous pursuits of macrocycles functionalized with boron chemistry,^[22] we herein propose a facile methodology to the first chiral luminescent molecules (**P5NN** and **P5BN**) based on the easily accessible chirality transfer from pillar[5]arenes. An axial functionalization of pillar[5]arene by π -conjugated bulky fluorophores (Ar_3B and Ar_3N) would allow the enantiomeric resolution of these systems. Meanwhile, this design strategy can also serve purposes for the temperature-dependent emission and CPL production.



Scheme 2. Structures and synthetic approach of *rac*-**P5NN** and *rac*-**P5BN**.

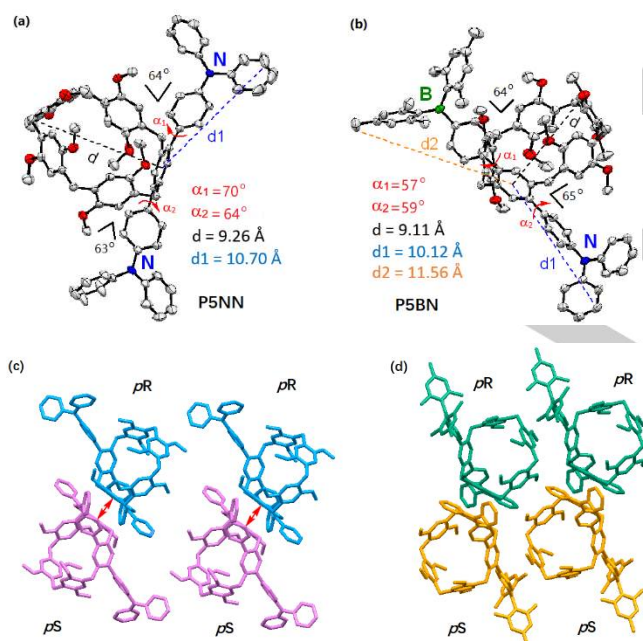


Figure 1. Crystal structures of (a) *rac*-**P5NN** and (b) *rac*-**P5BN** in elemental colors (C: grey, O: red. 50% thermal ellipsoids). Distances (Å) are measured for the cavity size of pillar[5]arenes and extension of bulky substitutions. (c) Molecular packing in *rac*-**P5NN** with π - π stacking ($d = 3.28$ Å) between enantiomers. (d) Stacks in *rac*-**P5BN** via C-H... π interactions. Enantiomers are highlighted in different colors. All the hydrogen atoms and solvent molecules are removed for clarity.

The pillar[5]arene-based bifunctional triflate **1** (-OTf) as the key intermediate was synthesized by a previously reported protocol.^[23] Synthetic details were shown in Scheme 2 and the Supporting

Information (SI). A Suzuki coupling reaction of **1** with triarylamine-containing boronic acid (2.0 equiv) gave **P5NN** in 76% yield. **P5BN** was obtained very similarly via two-step reactions with Ar_3N followed by the Ar_3B precursor under refluxed conditions in an overall yield of 20%. These molecules were fully characterized through ^1H , ^{13}C and ^{11}B NMR and HRMS spectroscopy after standard workup and analytical purification.

Single crystals of *rac*-**P5NN** and *rac*-**P5BN** were grown by slow evaporation from acetone, and their solid state structures were examined by X-ray diffraction analysis. On equatorial position, they clearly display well-defined cavities of the pillar[5]arenes, and they are axially extended through π -conjugation with N donor and B acceptor end-capped (Figure 1a and 1b). They show similar angles ($\sim 64^\circ$) of the π -extension against the pillar[5]arene plane defined by five $-\text{CH}_2$ groups. A more sufficient π -conjugation was observed in **P5BN**, as indicated by smaller dihedral angles (57° and 59°) than those of 70° and 64° for **P5NN** within the terphenyl units. Molecular size determination revealed that the distance from centroid of the functionalized phenyl ring to the Ar_3N periphery ($d_1 = 10.70$ Å) is greater than the cavity diameter of **P5NN** ($d = 9.26$ Å). The π -substituents in **P5BN** ($d_1 = 10.12$ Å, $d_2 = 11.56$ Å) were also much larger than its cavity size of $d = 9.11$ Å (Figure 1 and S11). Thus, these conjugated substitutions have been demonstrated to be bulky enough to circumvent possible racemization of both molecules. Equimolar enantiomers of *pR*-**P5NN** and *pS*-**P5NN** are contained in a unit cell with a face-to-face π - π stacking ($d = 3.28$ Å). C-H... π interactions lead to the supramolecular packing of *rac*-**P5BN**. Stacks in both cases adopt the same alignment of homo- and heterochiral molecular packing oriented in two directions (Figure 1c, 1d).

UV/Vis absorption and emission spectra were recorded for racemic **P5NN** and **P5BN** in THF, and the data of electronic structures are summarized in Table 1. They exhibit a strong absorption profile of π - π^* transition at ~ 305 nm. The absorption spectrum of **P5BN** also shows a shoulder peak red-shifted to 330 nm due to an intramolecular N/B charge transfer (ICT). The optical energy gaps (E_g) were estimated to be 3.49 and 3.41 eV for **P5NN** and **P5BN**, respectively, and are close to the computational results (Table S5). Both molecules show strong emissions in the solid state as well as in solution (**P5NN**: $\Phi_L = 0.61$, $\Phi_S = 0.19$, $\tau = 1.2$ ns; **P5BN**: $\Phi_L = 0.99$, $\Phi_S = 0.57$, $\tau = 6.4$ ns), which is particularly useful for potential applications in light-emitting devices (Figure 2a). These highly enhanced emissions are in sharp contrast to the parent pillar[5]arenes with much lower fluorescence quantum efficiency ($\Phi_f < 0.01$), a result of the introduction of Ar_3B and Ar_3N as key π -conjugated fluorophores. In addition, **P5BN** displayed a considerably broad emission spectrum ($\lambda_{em} = 493$ nm) and a larger Stokes shift of approximately $12,700$ cm^{-1} in comparison to that of $7,200$ cm^{-1} for **P5NN**.

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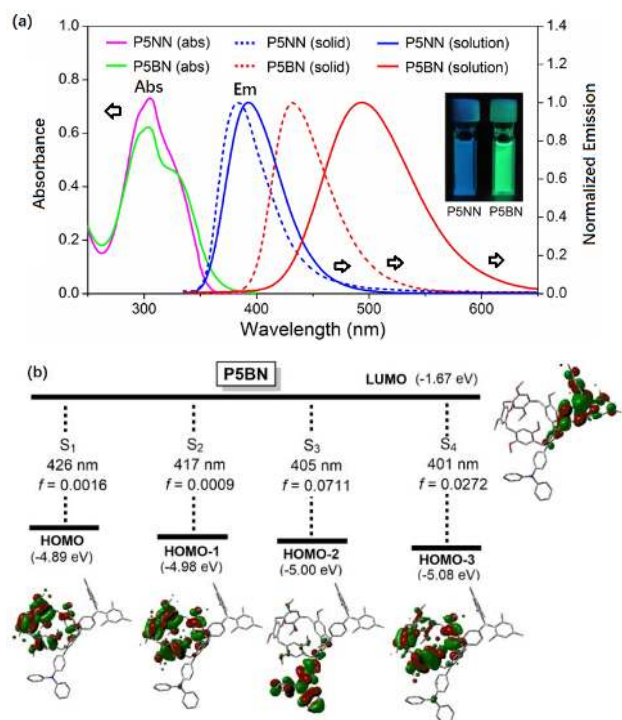


Figure 2. (a) UV-vis absorption and emission spectra of *rac*-**P5NN** ($\lambda_{\text{ex}} = 306$ nm) and *rac*-**P5BN** ($\lambda_{\text{ex}} = 303$ nm, THF, $c = 1.0 \times 10^{-5}$ M). Inset: photographs showing the emission colors of *rac*-**P5NN** and *rac*-**P5BN** in THF under 365 nm UV irradiation. (b) Key electronic transitions contributing to vertical excitations of *pS*-**P5BN** (TD-DFT, B3LYP/6-311G**) as an example with molecular orbital plots (iso=0.02, DFT-B3LYP/6-31G*).

Table 1. The photophysical and computational data of **P5NN** and **P5BN**.

	$\lambda_{\text{abs}}^{\text{[a]}}$ (nm)	$\lambda_{\text{em}}^{\text{[a]}}$ (nm)	$\Phi_{\text{L}}^{\text{[b]}}$ (%)	$\Phi_{\text{S}}^{\text{[c]}}$ (%)	$\tau_{\text{ave}}^{\text{[d]}}$ (ns)	$E_{\text{HOMO}}^{\text{[e]}}$ (eV)	$E_{\text{LUMO}}^{\text{[e]}}$ (eV)
P5NN	306	393	61	19	1.2	-4.88	-0.64
P5BN	303	493	99	57	6.4	-4.89	-1.67

[a] Recorded in THF (1.0×10^{-5} mol/L) at room temperature. [b] Fluorescence quantum yield (Φ_{L}) measured in THF. [c] Φ_{S} measured in solid state. [d] Average fluorescence lifetime in THF. [e] HOMO and LUMO energy levels obtained by DFT calculations (B3LYP, 6-31G*).

The electronic π -conjugated characteristics calculated for **P5NN** and **P5BN** using DFT (B3LYP/CAM-B3LYP, 6-31G*) and TD-DFT (B3LYP, 6-311G**) are presented in Figure 2b and the SI. According to TD-DFT studies, the absorption of **P5NN** is mainly attributed to the π - π^* transition to S_1 state (HOMO-1 \rightarrow LUMO, $f = 0.8991$) of the axially delocalized π system. On the other hand, **P5BN** indeed represents another distinct example of π -extended ambipolar species with a macrocyclic decoration. All of the lowest electronic transitions to S_1 , S_2 , S_3 and S_4 are derived from vertical excitations to the B-centered LUMO orbital either from the N-centered HOMO-2 or pillar[5]arene-localized HOMO,

HOMO-1 and HOMO-3 orbitals, featuring a typical charge transfer character of transition. Cyclic voltammetry (CV) of **P5BN** showed a reversible one-electron reduction band with half-wave potential at $E_{1/2} = -2.49$ V (vs Fc^+/Fc , in THF) as well as multi-step oxidation curves with the first half-wave potential at $+0.59$ V in CH_2Cl_2 (Figure S13), leading to an electrochemical HOMO-LUMO gap (3.08 eV) consistent well with the DFT calculation (3.22 eV). As expected, the first electrochemical oxidation of N donor occurred at a slightly lower potential of $+0.52$ V in **P5NN**.

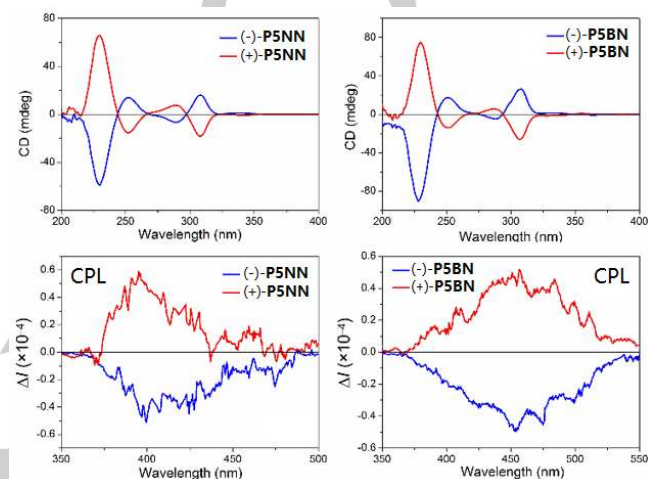


Figure 3. Top: CD spectra of enantiomers for **P5NN** and **P5BN** after optical resolution in THF ($c = 1.0 \times 10^{-5}$ M); Bottom: solid-state CPL spectra of enantiomers for **P5NN** ($\lambda_{\text{ex}} = 306$ nm) and **P5BN** ($\lambda_{\text{ex}} = 303$ nm) at r.t. Negative (-) and positive (+) signs correspond to the first and second peak in HPLC traces, respectively.

As indicated in the X-ray structures of *rac*-**P5NN** and *rac*-**P5BN**, we envisaged that the configuration of both enantiomers could be sufficiently maintained by bulky, rigid π -conjugated substituents. Motivated by this fact, we have performed optical resolution of the racemic mixtures for further investigation. The initial injection of *rac*-**P5NN** into a chiral HPLC with a Daicel Chiralpak IA-3 column (hexanes/isopropanol = 95 / 5, v/v) resulted in two separated peaks with 1:1 area (Table S4). The single peak position was reproduced in each collected fraction, indicative of a reasonably good isolation of *pR*-**P5NN** and *pS*-**P5NN** with an enantiomeric excess (>96% ee, Figure S17). In *rac*-**P5BN**, a similar procedure gave rise to a pair of sufficiently well-separated enantiomers (>98% ee) via preparative chiral HPLC with IG-3 column (Figure S18). Isolation of the enantiomers was confirmed by the mirror images in circular dichroism (CD) spectra with opposite Cotton effects in THF (Figure 3). The CD dissymmetry factors (g_{abs} , defined as $\Delta\epsilon/\epsilon$ at 306 nm) were calculated to be 6.68×10^{-6} and 1.32×10^{-5} for **P5NN** and **P5BN**, respectively. The first peak with shorter retention time in HPLC traces and the second one were assigned to be negative (-) and positive (+) sign, respectively (see the SI and Table S4). Each pair of enantiomers exhibited an almost mirror-symmetric CPL spectrum in the solid state, and the g_{lum} values were determined to be -2.02×10^{-4} for (-)-**P5NN** at 398 nm

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and -8.78×10^{-4} for (-)-**P5BN** at 455 nm. The CPL properties demonstrated in these solid-state materials would be valuable for future uses in chiral luminescence devices. In solution phase, enantiopure **P5BN** showed CPL activity only in hexane at room temperature (Figure S19b), and no CPL signal was observed for **P5NN** in common organic solvents. These observations are supposed to indicate that type of luminogens and solvent media also take an important role in the production of CPL emission.^[9d]

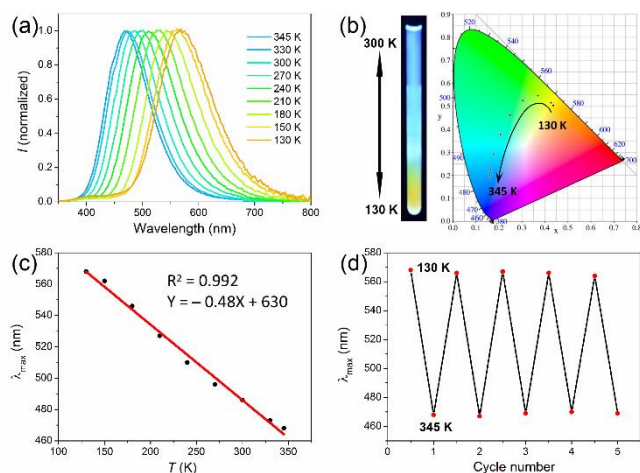


Figure 4. (a) Temperature-dependent emission spectra of *rac*-**P5BN** recorded in 2-methyltetrahydrofuran between 130 and 345 K ($c = 5.0 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 303$ nm); (b) Photograph shown in an NMR tube and CIE color coordinates; (c) Data fitting of the emission (λ_{max}) dependence on T for *rac*-**P5BN**, and (d) reversible emission modulation with cycling T changes for *rac*-**P5BN**.

To further explore the potential applications of **P5BN** as smart materials in response to external stimuli, we first monitored the photoluminescence at different temperatures. As shown in Figure 4, *rac*-**P5BN** experienced a bathochromic shift in the emission spectra as temperature decreased between 345 and 130 K, and a concomitant emission color change from blue to yellow occurred in the low melting point solvent 2-methyltetrahydro-furan. The emission wavelength was linearly enhanced with a high correlation coefficient of 0.992. Furthermore, a fully reversible emission response was corroborated by an excellent fatigue resistance without emission degradation upon its exposure to 5 cycles of temperature change over a broad range of ~ 215 K (Figure 4d). This thermochromic shift of the emission was likely induced by the temperature-dependent stabilization of ICT because the solvent properties show temperature dependence as well.^[10a, 24] Compared with similarly well-established fluorescent thermometers,^[10a,19g,21b] the emission responses of **P5BN** at low temperature of -90 °C are particularly distinct. Additionally, **P5BN** showed a gradual emission quenching in response to fluoride ion titration (Figure S15 and S16), similar to that frequently observed in other triarylboranes due to the loss of electron-deficiency of B caused by anion binding with F^- ion as a Lewis base. On account of multiple characteristics such as macrocyclic host, ambipolar donor-acceptor and tunable emission integrated in one molecule,

we anticipate that the enantiopure analogues of **P5BN** could be applied to chiral separation of guest species and CPL sensing of temperature, media and electron donors.

In summary, we have proposed a facile and highly efficient strategy to achieve well-defined planar chiral luminescent systems by taking advantage of pillararenes and boron chemistry. Incorporation of the sterically bulky, rigid and π -conjugated fluorophores (Ar_3B and Ar_3N) has enabled the optical resolution of *pR/pS* isomers. Other than the chiral transfer from pillar[5]arene, this approach also offered strong persistent luminescence in **P5NN** and **P5BN**. The chiroptical properties of CD and solid-state CPL emission were acquired, indicating a remarkable promise of this modular design. Meanwhile, **P5BN** showed a unique temperature dependence of the emission due to the ICT character in the macrocyclic scaffold. These key findings provide an early proof of principle for future applications in chiral luminescent sensing, chiral supramolecular assembly (e.g. host-guest recognition, 3D network gelation) and CPL-based electronic devices. Systematic investigations of robust materials with large g_{lum} value will be pursued in our laboratory based on sophisticated planar chiral organoboranes by structural tuning of other type of functionalities.

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Conflict of interest

The authors declare no conflict of interest

Keywords: pillar[5]arene • organoborane • circularly polarized luminescence • planar chirality • thermochromic emission

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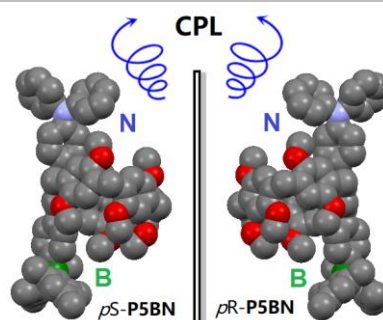
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Layout 1:

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Two examples of planar chiral systems were achieved by axial functionalization of pillar[5]arene with sufficiently bulky, rigid, π -conjugated and highly luminescent triarylborane and triarylamine moieties, leading to the enantiomeric resolution and circularly polarized luminescence (CPL) property. They represent the first chiral luminescent systems based on planar chiral pillar[5]arenes.



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Planar Chiral Organoboranes with Thermoresponsive Emission and Circularly Polarized Luminescence: Integration of Pillar[5]arenes with Boron Chemistry