RESEARCH HIGHLIGHTS

Multi-layer 3D chirality: its enantioselective synthesis and aggregation-induced emission

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Chirality has been extensively studied in interdisciplinary fields for almost two centuries since its ubiquity was discovered by Louis Pasteur in 1848, when he successfully separated a pair of enantiomers. Indeed, chirality is present at all levels in nature—in the form of subatomic particles, macromolecules such as proteins and DNA, microscopic living organisms such as helical bacteria and even in the form of macroscopic objects such as sea shells and spiral galaxies. It is undeniable that the concept of chirality and the field of stereochemistry, which studies the three-dimensional (3D) structure and relationships of molecules, has had a monumental impact on chemical, biomedical and material sciences [1]. Not surprisingly, the design and synthesis of an ever-increasing number of small-molecule pharmaceuticals as well as optical materials heavily depend on our deep understanding and exploitation of molecular chirality. In chemistry, chirality is divided into point/central, spiro, axial, helical/planar as well as the multi-layer versions of helical/planar chirality [2]. With the exception of multilayer chirality all the other types exist widely in nature.

Professor Guigen Li's teams at Nanjing University and Texas Tech University have recently discovered and characterized the first examples of multi-layer 3D chirality where the layers are not bridged together; this is a novel form of chirality which is different from traditional planar and helical chirality (i.e. a highly compacted chiral fold held together primarily by π-stacking interactions), and the enantioselective synthesis

of this framework has been achieved [3]. This new chiral framework, a multi-layer organic framework (M-LOF), has unique C_2- and/or pseudo C_2-symmetry and features three layers that are arranged in a nearly parallel fashion: a top, a middle and a bottom aromatic ring. Interestingly, this multi-layer type framework displays elements of both planar and axial chirality (i.e. rotational stereoisomerism)—in the compounds that exhibit multi-layer 3D chirality the top and the bottom

layers have restricted rotation relative to each other. This means, in essence, that if either the top or the bottom layer is removed, multi-layer 3D chirality would no longer exist due to free rotation.

Professor Li's group isolated the first multi-layer 3D chiral molecule during their ongoing project on GAP (Group-Assisted-Purification) chemistry that takes advantage of certain functional groups that allow the greener and more atom economical synthesis of chiral
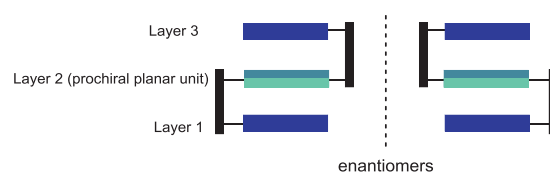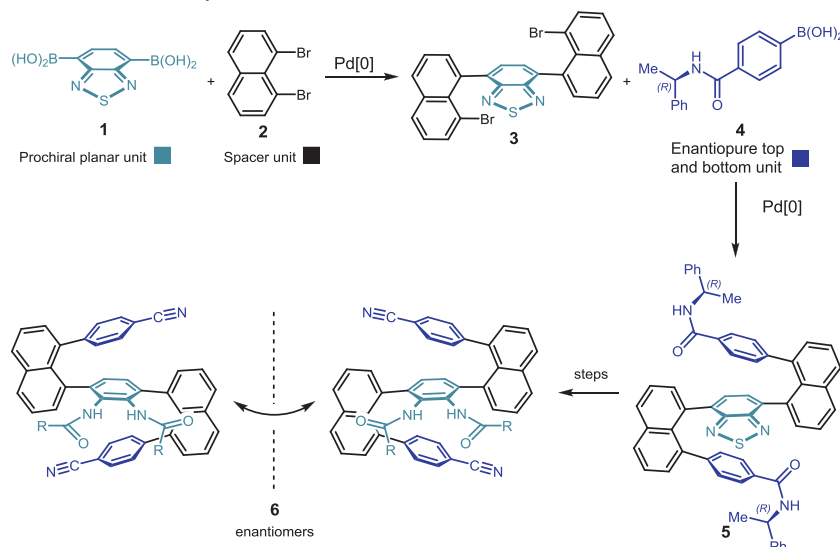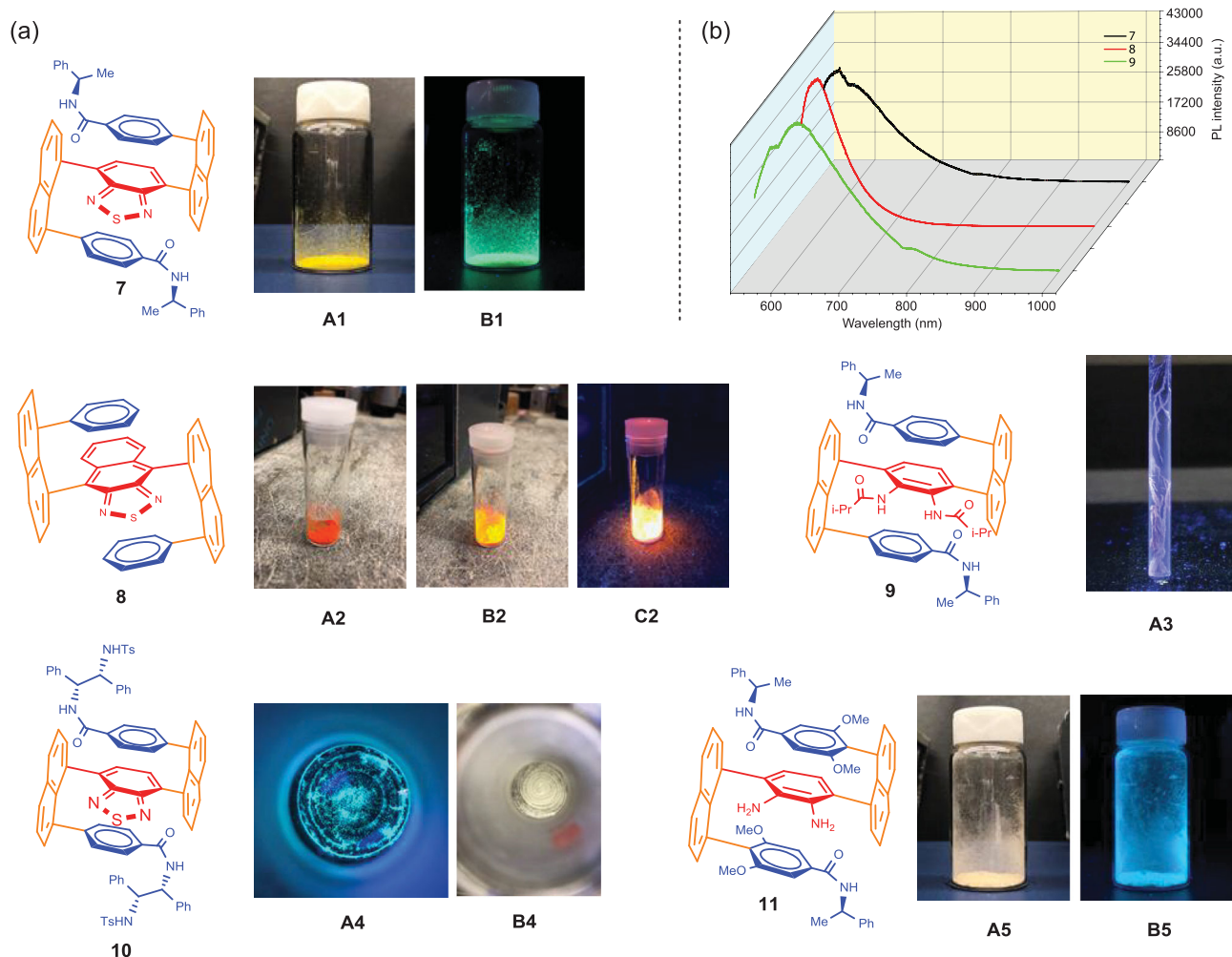

Scheme 1. Asymmetric synthesis of compounds exhibiting multi-layer 3D chirality.

Figure 1. (a) Luminescence of samples under UV light (365 nm): **A1** and **A5** without UV irradiation, **B1** and **B5** with UV irradiation; fluorescence images of **8** under different physical conditions (**A2**, appearance under natural light; **B2**, UV irradiation in natural background; **C2**, UV irradiation in dark background); spiro textile-type of macro-chirality of **9** formed inside (**A3**) NMR tube under UV irradiation; macro-chirality phenomenon of **10**: (**A4**) image under UV light (365 nm), (**B4**) image under natural light after rotavapor evaporation. (b) Photoluminescence (PL) spectra of **7**, **8** and **9** as solid test samples; excitation wavelength (λ_{ex}): 532 nm.

building blocks by avoiding the formation of non-crystalline intermediates [4]. The synthesis of compounds that exhibit C–N bond-based multi-layer 3D chirality of *pseudo* C_2-symmetry was achieved via employing a double Buchwald-Hartwig cross-coupling, while compounds that exhibit the C–C bond-based multi-layer 3D chirality of C_2-symmetry were obtained via a double Suzuki-Miyaura coupling and several additional steps. Enantiomers of the former were obtained via preparative chiral HPLC, and those of the latter through asymmetric synthesis (Scheme 1).

The synthetic sequence en route to compounds that exhibit C–C bond-based multi-layer 3D chirality utilized benzo[c][1,2,5]thiadiazole-4,7-diyldiboronic acid (**1**) as a key building block. This compound was used as the central bifunctional coupling partner (i.e. which ultimately serves as the bridging middle aromatic ring of the final multi-layer structure) in the subsequent double Suzuki-Miyaura cross-coupling to furnish compound **3**. The chirality was controlled by using two identical chiral amide scaffolds, derived from (*R*)-methylbenzylamine (**4**), which were attached to the naphthalene rings via two Suzuki-Miyaura cross-coupling reactions. Finally, the thiadiazole rings of multi-layer 3D enantiomers were opened

to give the corresponding diamino products (**6**) that were isolated in the N-protected form. Scheme 1 shows the structure of a pair of enantiomers side-by-side. Macro-chirality of some chiral 3D molecules can be directly observed with the naked eye without the need for instrumentation (Fig. 1(a)A3 and A4). Many of the 3D products showed strong fluorescence sensitivity even in their solid forms under UV light at 365 nm (Fig. 1(a)) and displayed aggregation-induced emission (AIE) [5] properties (Fig. 1(b)). Furthermore, the enantiomers of several multi-layer 3D chiral compounds showed unusually high optical rotational data. In summary,

it is anticipated that this work will have a broad impact on chemical, medicinal, biomedical as well as material sciences including research that focuses on synthesis and exploitation of optoelectronic materials.

Conflict of interest statement. None declared.

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PHYSICS

Raise quantum anomalous Hall states up

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Experimental progress on the quantum anomalous Hall (QAH) effect has been significantly accelerated recently by the discovery of an intrinsic magnetic topological insulator $MnBi_2Te_4$ [1]. The material is natively antiferromagnetic, but an external magnetic field of several tesla can overcome its weak interlayer antiferromagnetic coupling, making it ferromagnetic. Interestingly, ferromagnetic $MnBi_2Te_4$ is predicted to be a magnetic Weyl semimetal, a topological phase hunted for almost a decade but with few cases confirmed experimentally [2]. A characteristic property of a magnetic Weyl semimetal is that its thin films can show the QAH effect with the Chern number (C), i.e. the number of the dissipationless edge channels, increasing with their thicknesses [3]. It provides an elegant way to engineer the QAH edge states for various studies and applications, but has never been experimentally demonstrated.

In a recent work published in *National Science Review*, Prof. Jian Wang from Peking University and his collaborators observed the Hall resistance plateaus of both one quantum resistance ($\sim$25.8 kΩ) and half quantum resistance ($\sim$12.9 kΩ), corresponding to the $C = 1$ and $C = 2$ QAH states, respectively, in $MnBi_2Te_4$ flakes of different

thicknesses under a moderate magnetic field of about 5 tesla (Fig. 1) [4]. This unambiguously confirms the magnetic Weyl semimetal phase in ferromagnetic $MnBi_2Te_4$, and, for the first time, showed us the unique aspect of magnetic Weyl semimetals.

An astonishing observation is that the QAH states can survive rather a high temperature in $MnBi_2Te_4$ flakes. $C = 2$ QAH state is observed at T >13 K. In some $C = 1$ samples, almost quantized anomalous Hall resistance is observed at a temperature even higher than the magnetic ordering temperature (90.4% at 45 K in a seven-septuple-layer device, 96.7% at 30 K in an eight-septuple-layer device). This appears counter-intuitive, but is actually a natural result of the two-dimensional magnetism of $MnBi_2Te_4$. According to the Mermin-Wagner theorem, the ordering temperature of such a 2D magnetic system is not limited by the exchange energy but the magnetic anisotropic energy, which suppresses the magnetic fluctuation resulting from low dimension. A perpendicular magnetic field increases the effective anisotropic energy and thus elevates the effective magnetic ordering temperature. The topological electronic states of $MnBi_2Te_4$ are predicted to have a large magnetically induced gap
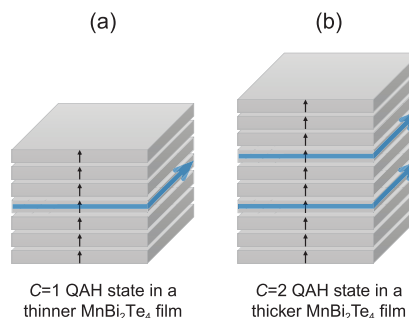
Figure 1. Schematics of the $C = 1$ QAH state (a) and the $C = 2$ QAH state (b) in thinner (7 septuple-layer) and thicker (10 septuple-layer) $MnBi_2Te_4$ films, respectively. The black arrows indicate the magnetization vectors. The blue lines with arrows indicate the chiral edge states.

(several tens of meV), which can, in principle, support the QAH state above room temperature if the magnetic ordering temperature could also reach so high. The present work strongly supports such a robust QAH state in it.

The additional magnetic anisotropy is not necessarily provided by an external magnetic field. Exchange coupling with a neighboring ferromagnetic or antiferromagnetic insulator can also stabilize the long-range magnetic order of $MnBi_2Te_4$. A recent theoretical work showed that in some magnetic van der