Diastereoselective Synthesis of Topological Chiral Pillar[5]arenes: Unveiling the Unit and Macrocyclic Chirality Interplay

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Molecular topology, such as mechanically interlocked and entangled molecular architectures, has increasingly attracted attention in materials science and nanotechnology due to its fascinating topological features.[1] Herein, we present a series of topological chiral pillar[5]arenes (P5As) formed by combining two different planar chiralities (Figure 1a): paracyclophanes (S_p and R_p) and P5As (*pS* and *pR*). The topological chiral P5As were diastereoselectively synthesized using different paracyclophane units (Figure 1b). Topological P5As **a** and **b** were selectively formed from **1** or **2** racemates, while the chiral paracyclophane **2**-S_p selectively gave topological chiral P5A **a**-5(S_p-*pS*). From achiral paracyclophane **1'**, only topological P5A **b** was obtained due to the lack of hydroxymethyl directing groups. All the topological chiral molecules exhibited distinct CD spectra corresponding to the chiral units (Figure 1c), but closely resembled that of planar chiral P5A, indicating that macrocyclic chirality predominantly governs the chiroptical properties of these topological structures. TD DFT calculations revealed that the magnetic (***m***) and electric (***μ***) transition dipole moments, along with their angles (θ), of the chiral paracyclophane units were rearranged and altered within the topological P5A structures (Figure 1d). This rearrangement significantly increased the overall magnitude of $|\boldsymbol{m}|$, reduced the θ angle, and resulted in tunable rotatory strength (*R*) and CD intensity of the topological chiral structures.

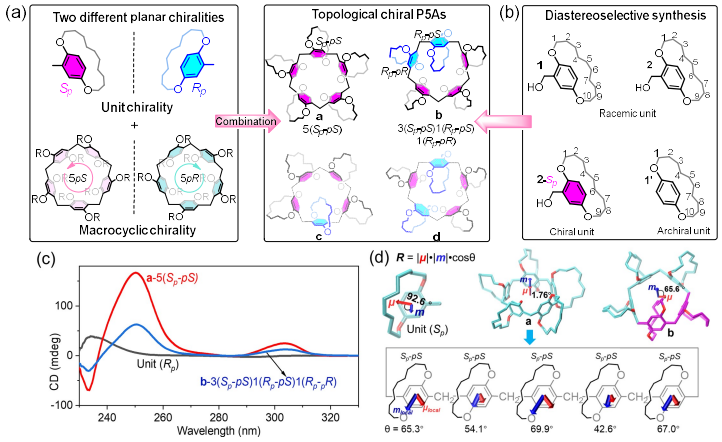

Figure 1. (a) Combination of two different planar chiralities. (b) Paracyclophane monomers. (c) CD spectra and (d) DFT calculation results of these topological chiral P5As.

1) W. Wang, S. Zhou, X. Yu *et al.*, *CCS Chem.* **2024**, *6*, 2084–2109.