Figure-eight macrocyclic imines: chiral natural product scaffold-based rapid synthesis and chiroptical modulation

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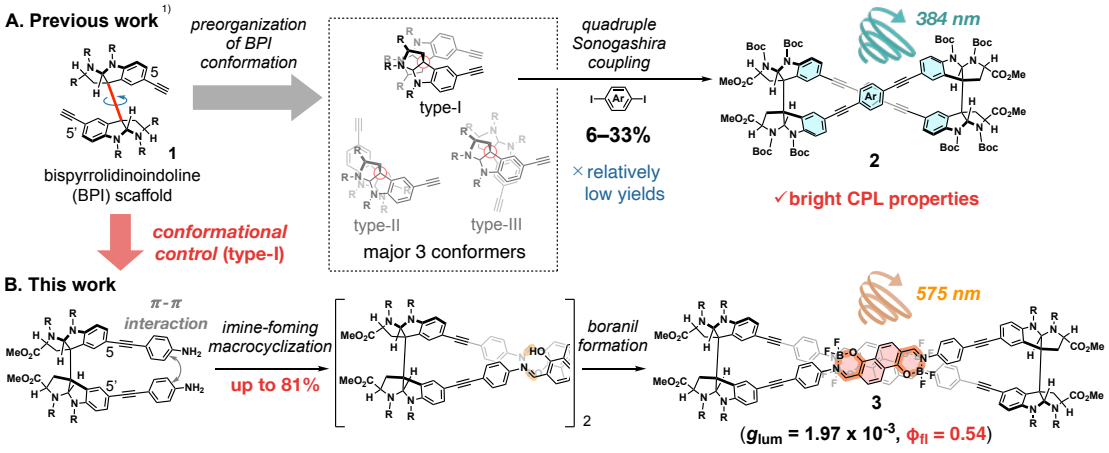
Chiral D_2-symmetric figure-eight macrocycles with intercrossing π-conjugated chromophores are versatile scaffolds for enhancing chiroptical properties. In our previous studies, the chiral C_2-symmetric bispyrrolidinoindoline (BPI) scaffold **1** was employed to synthesize a figure-eight macrocycle **2** exhibiting remarkable circularly polarized luminescence (CPL) at 384 nm (Figure A).[1] Preorganization of the BPI scaffold into the type-I conformation was achieved by introducing bulky substituents on the nitrogen atoms, enabling macrocyclization via quadruple Sonogashira couplings. However, the macrocyclization yield remained limited to 6–33%, highlighting the need for improved conformational control of the macrocyclization precursors and more efficient methods for macrocycle construction.

This study presents an efficient and flexible synthetic approach for chiral macrocyclic frameworks via thermodynamically controlled imine formation (Figure B). A BPI-based macrocyclization precursor, bearing aryl alkynyl substituents at the C5/5' positions, enabled precise conformational control of the BPI scaffold into the type-I through π–π interactions. This method produced figure-eight macrocyclic imines with high efficiency and yields of up to 81%. Subsequent modifications of the intercrossing chromophores, including imine reduction or boranil formation, allowed for the rational tuning of their optical and chiroptical properties. Notably, macrocyclic boranil **3** exhibited bright CPL properties (g_{lum} = 1.97 x 10^{-3}) with orange emission while maintaining a high quantum yield (ϕ_{fl} = 0.54). This approach provides a versatile synthetic platform for figure-eight macrocycles with customizable chiroptical properties.



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