

## Experimental and theoretical studies on propeller chirality and toroidal interaction in heptaaryldipyrromethenes and hexaarylbenzenes

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Among various types of chiral molecules such as point chirality, axial chirality,<sup>1</sup> planar chirality,<sup>2</sup> helical chirality,<sup>3</sup> as well as other types of chirality (e.g., Möbius chirality),<sup>4</sup> propeller chirality, as in hexaarylbenzenes, is additional unique category of chiral molecules. An alignment of sterically congested aryl moieties on the benzene-like core exhibited unique propeller shape in their 3D structures, analogous to profiles of windmill or doughnut. Although the geometries of aryl moieties in such molecules are rather dynamic, they cooperatively arrange into either clockwise or counter-clockwise manner, exhibiting unique chiroptical behaviors through the domino-like axial chirality.

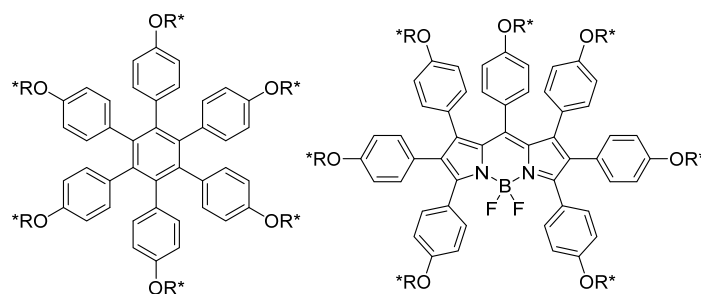


Figure 1. Structures of propeller-shaped hexaarylbenzenes and heptaaryldipyrromethenes

These molecules indeed have been extensively investigated as model systems to study the interactions between the  $\pi$ -stacked propeller blades to rationally design the liquid crystals, molecular capsules/rotors, redox materials, nonlinear optical materials, as well as molecular wires. However, the investigations on chiral aspects have been rather limited. Accordingly, we have systematically investigated the nature of propeller chirality of hexaarylbenzenes<sup>5</sup> and heptaaryldipyrromethenes,<sup>6</sup> focusing on their circular dichroisms and circularly polarized luminescence (Figure 1). The signals of chiroptical properties were found significantly enhanced than those of molecules with simple axial chirality, demonstrating the effective cooperativity and high sensitivity of propeller architecture for, e.g., chirality sensing.

More interestingly, the dynamics of toroidal interactions between the propeller blades have been extensively studied through the changes of chirality signal under given conditions, with an aid of combined theoretical and experimental investigation (Figure 2). Accordingly, lowering the temperature induces the preferred formation of counter-clockwise propeller in hexaarylbenzenes when the groups of point chirality of *R* configuration were appended at the periphery of blades. Increasing temperature changes the equilibrium between clockwise and counter-clockwise isomers, but additional conformation became apparent above the critical temperature. The contribution of such structurally unique conformer, whizzing toroids, becomes substantial in polar solvents (as well as higher temperature) to impact the observed (chir)optical properties.

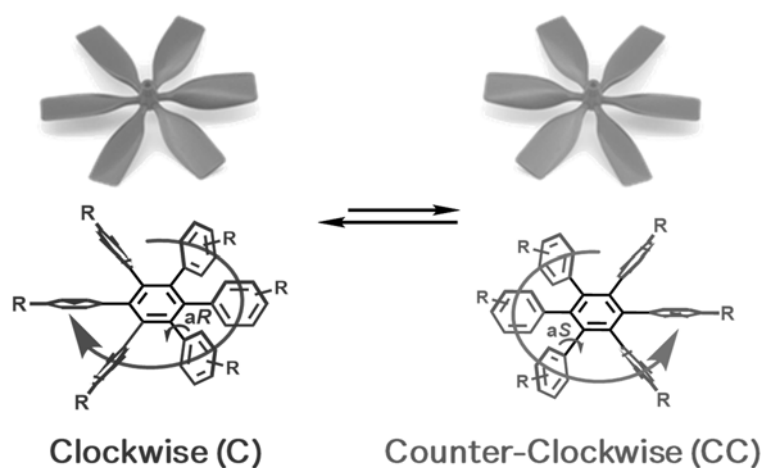


Figure 2. Equilibrium and dynamics between clockwise and counter-clockwise propellers in hexaarylbenzenes.

In the presentation, we will report the details of propeller inversion dynamics and application of such toroidal interaction in precisely controlling the properties of advanced optical materials.

**Funding:** Grant-in-Aids for Scientific Research, Challenging Exploratory Research, and on Innovative Areas "Photosynergetics" (Grant Numbers JP15H03779, JP15K13642, JP15H01087) from Japan Society for the Promotion of Science.

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