

Molecular Face-Rotating Cube with Emergent Chiral and Fluorescence Properties

Hang Qu, Yu Wang,*[®] Zhihao Li, Xinchang Wang, Hongxun Fang, Zhongqun Tian,[®] and Xiaoyu Cao^{*®}

State Key Laboratory of Physical Chemistry of Solid Surfaces, *i*ChEM and College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

Supporting Information

ABSTRACT: Chiral cage compounds are mainly constructed from chiral precursors or based on the symmetry breaking during coordination-driven self-assembly. Herein, we present a strategy to construct chiral organic cages by restricting the P or M rotational configuration of tetraphenylethylene (TPE) faces through dynamic covalent chemistry. The combination of graph theory, experimental characterizations and theoretical calculations suggests emergent chirality of cages is originated from complex arrangements of TPE faces with different orientational and rotational configurations. Accompanied by the generation of chirality, strong fluorescence also emerged during cage formation, even in dilute solutions with various solvents. In addition, the circularly polarized luminescence of the cages is realized as a synergy of their dual chiral and fluorescence properties. Chirality and fluorescence of cages are remarkably stable, because intramolecular flipping of phenyl rings in TPE faces is restricted, as indicated by calculations. This study provides insight into construct chiral cages by the rational design through graph theory, and might facilitate further design of cages and other supramolecular assemblies from aggregation-induced emission active building blocks.

C age compounds are important in a variety of applications including molecular sensing,^{1,2} separation³⁻⁵ and catal-ysis.⁶⁻⁸ Using metal-organic coordination,⁹⁻¹³ hydrogen bonding¹⁴⁻¹⁶ and dynamic covalent chemistry,¹⁷⁻²⁰ chemists have synthesized many cage compounds. Among these cages, the chiral ones are interesting because chirality increases structural complexity as well as functionality of cage and hierarchical assemblies.^{4,21,22} For instance, many applications of cages are related to chirality, e.g., chiral separation^{3,5} and asymmetric catalysis.⁸

Generally, two strategies have been established to construct chiral cages: by using chiral precursors,^{3,13,19,21} or based on the chirality at metal centers in Δ and Λ configurations.^{8,23} Inspired by the study of Buckminster Fuller, we have reported a strategy to generate emergent chirality of organic cages by assembling achiral two-dimensional truxene building blocks into chiral octahedra through dynamic imine chemistry.²⁴ The truxene faces exhibited either clockwise or anticlockwise rotational patterns on the octahedron faces, resulting in five types of chiral face-rotating polyhedra (FRP) in the thermodynamic and kinetic products. More recently, Fujita et al. reported a more sophisticated

emergent chirality in a tetravalent Goldberg polyhedron,²⁵ and the graph theory analysis suggested cage chirality was generated from asymmetric arrangement of the triangular and square facial patterns. These studies illustrate the complexity of emergent chirality of cages, and indicate importance of introducing graph theory into the investigation of polyhedral cages.

Here, we present how complex cage structures evolve out of simple tetraphenylethylene faces through the combination of graph theory, experimental investigation and theoretical calculations.

Tetraphenylethylene (TPE) is a well-known aggregationinduced emission (AIE) chromophore, $^{26-28}$ and due to the steric hindrance between the phenyl rings, 29 it exhibits either clockwise or anticlockwise rotational patterns in its propeller-like *P* or *M* configurations, respectively (Figure 1A). To further develop the strategy of face-rotating polyhedra, we decided to construct facerotating cubes (FRCs) from six tetragonal TPE faces and eight triamine vertices (Figure 1C), and investigate whether the chiral and fluorescence properties can be emerged simultaneously in the FRCs.

We further scrutinized the structure of TPE and found its rectangle motif presents two orientational configurations of the vinyl bond (i.e., vertical and horizontal as shown in Figure 1A), in addition to the *P* and *M* rotational configurations of the phenyl rings. The two orientational configurations of TPE might also lead to various stereoisomers of the assembled structures, yet this phenomenon has not been reported, despite several metal–organic frameworks,^{30–33} covalent-organic frameworks^{34,35} and cages^{26,36–38} have been assembled from TPE.

When rectangle TPE motifs are patterned onto the cubic faces, the independent orientational and rotational configurations generate numerous stereoisomers. Using the graph theory analysis based on permutation groups (Supplementary Method), we first determined there are eight types of patterned cubes if we only consider the vinyl orientations of TPE, including six achiral cubes and a pair of chiral enantiomers. And when we further consider the P and M rotational configurations, there are 224 types of patterned cubes, among which only four are achiral mesomers and the rest are chiral (Figure 1B). Therefore, there is a great chance to achieve emergent chirality, if the P and M configurations of TPE can be fixed in the cubic structure.

The facial building block 4,4',4",4'"-(ethene-1,1,2,2-tetrayl)tetrabenzaldehyde (ETTBA) consists of a TPE core and four surrounding aldehyde groups for reversible imine formation

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Figure 1. Synthesis of the chiral cubes with different facial rotational and orientational configurations. (A) TPE motif exhibits two rotational modes (*P* or *M*) of the phenyl groups and two orientational modes (horizontal or vertical) of the vinyl group in two dimensions. (B) Rotational and orientational modes of the TPE motif generate 224 types of cubes when they are painted on the six faces of a cube. Nevertheless, only four types of cubes were found in the experimental product (D,E). (C) Schematic of synthesis of organic cubes from six ETTBA faces and eight TREN vertices. (D,E) Cartoons to show the TPE configurations in the homodirectional cubes (6P)-1 and (6M)-1, and the heterodirectional cubes (4P2M)-2 and (2P4M)-2.

(Figure 1C). This facial building block was synthesized from benzopheone within three steps with high yields (Figure S1), whereas the vertex building block (tris(2-aminoethyl)amine, TREN) is commercially available. To form the cubes, the methanol solution of TREN (8 equiv) was layered onto the chloroform solution of ETTBA (6 equiv) at ambient temperature for 10 days without stirring (Figure 1C).

Mass spectrometry analysis confirmed ETTBA₆TREN₈ was formed exclusively, exhibiting a molecular weight of 3403.80 (Figure S2). Nevertheless, we measured more than five single crystals isolated from the reaction solution and found all of them were cocrystals that cannot be precisely solved, suggesting there are more than one stereoisomers in the product. Further separation and characterization revealed two pairs of enantiomers, i.e., the homodirectional (6*P*)-1 and (6*M*)-1, and the heterodirectional (4*P*2*M*)-2 and (2*P*4*M*)-2, as shown in Figure 1D,E.

The product mixture was separated by high-performance liquid chromatography (HPLC) with a chiral column (Daicel Chiralcel IC), resulting in only four fractions of cage isomers in a 3:1:3:1 ratio (Figures 2A and S3). These four fractions were separated and characterized individually. Nuclear magnetic resonance (NMR) analysis was not sufficient to elucidate the structures of the separated stereoisomers (Figure S4), because of the notable signal overlap of various phenyl protons and imine protons, which is a common issue for large empty cages.²⁵ Fortunately, we obtained and analyzed all single crystals of the four separated stereoisomers, confirming HPLC fractions eluting at 16.8, 19.3, 24.5 and 28.9 min are (6*M*)-1, (2*P*4*M*)-2, (6*P*)-1 and (4*P*2*M*)-2, respectively (Figure 2A).

Diffusion of diethyl ether into the chloroform solutions of (6M)-1 and (6P)-1 gave the corresponding cube-shaped single



Figure 2. Chiral-HPLC and CD analyses of the cubes 1 and 2. (a) Chiral HPLC spectrum contains four peaks corresponding to (6M)-1, (2P4M)-2, (6P)-1 and (4P2M)-2 in a 3:1:3:1 ratio. The absorbance for all cubes was recorded at 300 nm. (b) CD spectra of the separated cubes (6M)-1, (2P4M)-2, (6P)-1 and (4P2M)-2 in the mixed solvent of dichloromethane and methanol (v:v = 1:1).

crystals, respectively, whereas the hexagonal-shaped single crystals of (2P4M)-2 and (4P2M)-2 were individually grown by a similar method by changing chloroform into the mixed solvent of dichloromethane and methanol (v:v = 1:1). All FRCs have an eight-capped cubic structure (Figure 3), in which six TPE units occupy six faces linked by eight tripodal TREN-linked vertices.



Figure 3. Single-crystal structures of (6M)-1 and (2P4M)-2. Front and diagonal views of the cubic structures of (6M)-1 (A,B) and (2P4M)-2 (C,D). Carbon atoms are shown in gray, green or pink, nitrogen atoms are shown in blue, and hydrogen atoms are omitted for clarity.

The homodirectional (6M)-1 structure has a high (T) symmetry, and a same M configuration for each TPE faces (Figure 3A,B). The vinyl orientations in each two opposite TPE faces are parallel with a same distance of 11.5 Å, whereas the vinyl orientations in each two adjacent TPE faces are noncoplanar perpendicular. Along the diagonal line (C_3 symmetric axial), the three phenyl rings linked to a same TREN vertex (pink rings in Figure 3B) are evenly distributed, exhibiting the same 60° dihedral angle to each other. In addition, all imine bonds in (6M)-1 are in E conformation and coplanar with the adjacent phenyl rings (Figure S5A), suggesting a strong conjugation between the adjacent imine bond and phenyl ring.

The heterodirectional (2P4M)-2 structure (Figure 3C,D) has a lower (D_2) symmetry in comparison with the homodirectional cubes. As shown in Figure 3C, the distance between two *P* faces (top and bottom) is approximately 14% smaller than the distance between two opposite *M* faces (front and back, or left and right). The vinyl orientations in two opposite *P* faces are noncoplanar perpendicular, whereas the vinyl orientations in each two opposite M faces are parallel. As shown in (Figure 3D), each TREN vertex is linked to one P face and two M faces. Two phenyl rings from the M faces (pink) have a 73° dihedral angle (Figure SSB), whereas the phenyl ring from the P face (green) is nearly parallel to one of the pink phenyl rings. Despite that the vertex configuration is dramatically different from that of (6M)-1, all imine bonds in (2P4M)-2 are still in E conformation and coplanar with the adjacent phenyl rings (Figure SSB).

The (6P)-1 and (4P2M)-2 structures were assigned to be the enantiomers of (6M)-1 and (2P4M)-2, respectively, as shown in Figure S6.

The emergent chirality of the four FRCs in solid state was confirmed by single-crystal analysis. During the HPLC separation, the online optical rotation detection indicated that the four FRCs are also chiroptical active in solution (Figure S7).

Further circular dichroism (CD) analysis of the separated FRCs (Figure 2B) showed a strong positive Cotton effect in the spectrum of (6M)-1, and a negative mirror-image spectrum for (6P)-1. (2P4M)-2 and (4P2M)-2 also showed a pair of mirror-image spectra with a relatively weaker intensity, and their CD spectral signs were dominated by the major faces, i.e., M and P, respectively. Comparing to the CD spectrum of (6M)-1, an extra small peak at 360 nm was shown in the spectrum of (2P4M)-2, which can be rationalized by the extra absorption at the corresponding region as shown in the UV–vis spectra (Figure 4A). All CD spectra of the four FRCs are consistent with the



Figure 4. Fluorescence and CPL analyses of the cubes 1 and 2. (A) UV– vis spectra of ETTBA (50 μ M, black) and the cubes 1 (8 μ M, red) and 2 (8 μ M, blue) in the mixed solvent of dichloromethane and methanol (v:v = 1:1). (B) Fluorescence spectra of ETTBA (50 μ M, black) and the cubes 1 (8 μ M, red) and 2 (8 μ M, blue) in chloroform, excited at 340 nm. (C) Fluorescence images of ETTBA, 1 and 2 solutions under the 365 nm UV light. (D) CPL spectra of ETTBA (0.6 mM, black), (6M)-1 (0.1 mM, magenta), (6P)-1 (0.1 mM, yellow), (2P4M)-2 (0.1 mM, green) and (4P2M)-2 (0.1 mM, cyan) in chloroform, excited at 340 nm.

(ZINDO/S)-predicted CD spectra as shown in Figure S8, further confirming the structures revealed by single-crystal X-ray analysis.

The correlation between TPE configurations and CD spectral signs in FRCs is similar to that in small chiral molecules synthesized from a single TPE unit,²⁹ in which TPE monomers in M or P configurations also generate positive or negative Cotton effects, respectively. Nevertheless, the CD intensities of FRCs, e.g., 1.4×10^6 deg cm² dmol⁻¹ for FRC 1, are 100 times stronger than that of chiral TPE monomers,²⁹ indicating a strong nonlinear effect of the chiroptical properties in FRCs.

In addition, the separated FRCs showed a remarkable stability against racemization. For instance, the CD and HPLC spectra of (6P)-1 remains the same even after being heated in the chloroform solution at 60 °C for 24 h (Figure S9). This indicates *M* or *P* configuration of FRCs is restricted in solution, and there is a high energy barrier in converting (6P)-1 into (6M)-1 through changing rotational configuration of all six faces. The stability of the separated chiral cages provides important potential for their further applications as chiral porous materials.^{39,40}

Comparing with the absorption spectrum of ETTBA monomer, the spectra of FRCs are notably blue-shifted. This can be rationalized by the decrease of the conjugation degree of TPE core, as a result of the restriction of the phenyl flipping in FRCs.⁴¹ In addition, the spectrum of 1 is more blue-shifted than that of 2, which is in accord with the larger twist of the TPE core in 1, as indicated by the analysis of the dihedral angles between the phenyl rings and the vinyl bonds (Figure S5).

The emergent fluorescence property of FRCs also resulted from the restriction of phenyl flipping.^{42–44} In contrast to the low fluorescence activity of the ETTBA solution, strong blue fluorescence with a peak at 427 nm was observed in the solutions of 1 and 2 (Figure 4B,C). In addition, the fluorescence quantum yields in toluene for FRCs 1 and 2 were measured to be 26.0% and 30.9% respectively, by using 9,10-diphenylanthracene as standard. The fluorescence of FRCs can be further tuned by solvent, generally showing an increase in fluorescence intensity upon the decrease of solvent polarity (Figure S10).

On the basis of the emergent chirality and fluorescence of FRCs, we envisioned FRCs would also generate the circularly polarized luminescence (CPL).^{45–47} Indeed, intensive mirrorimage CPL signals of (6*M*)-1 (positive) and (6*P*)-1 (negative) were observed at 450 nm in their chloroform solutions (Figure 4D), with a large CPL dissymmetric factor ($g_{lum}^1 = \pm 1.1 \times 10^{-3}$). The CPL spectra of (2*P*4*M*)-2 and (4*P*2*M*)-2 is similar to that of (6*M*)-1 and (6*P*)-1, respectively, with a slightly smaller dissymmetric factor ($g_{lum}^2 = \pm 9.3 \times 10^{-4}$).

The dual emergent chiral and fluorescence properties of FRCs is unprecedented for cage compounds. Despite few TPE cages have been reported, $^{26,36-38}$ the chiral property of them has not been investigated due to difficulties in separation and characterization. Besides, the emergent fluorescence was mainly presented in the small cages formed from two close-packed TPE faces,^{26,36} in which steric hindrance between the opposite TPE faces is strong enough to restrict intramolecular flipping of TPE phenyl rings. By contrast, the larger TPE cages, in which steric hindrance between the opposite TPE faces is absent, generate much weaker fluorescence in dilute solutions.^{37,38} Further density functional based tight binding plus (DFTB+) calculations suggest that the cooperativity in the six TPE faces of FRCs and the conjugation between imine bonds and phenyl rings work together to realize the restriction of phenyl flipping in FRCs and thus to generate stable chirality and fluorescence (Figures S11 and S12, and Supplementary Method).

To conclude, we haveconstructed a series of cubic cages with stable chirality and strong fluorescence, providing great potential for chiral sensors and luminescent materials. The method we used to restrict the intramolecular flipping of TPE units by the conjugation between imine bonds and phenyl rings might facilitate further design of cages and other supramolecular assemblies from AIE-active building blocks. In addition, this study provides a strategy to construct chiral cages by rational design through graph theory. The mathematic method based on permutation groups is suitable for the analysis of all kinds of polyhedra incorporating different kinds of faces or vertices, and it will become more important as the complexity of the research objects increases.

ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and data (ZIP) Supplementary methods (PDF)

AUTHOR INFORMATION

Corresponding Authors

*roywangyu@gmail.com

*xcao@xmu.edu.cn

ORCID 💿

Yu Wang: 0000-0002-9029-1846 Zhongqun Tian: 0000-0002-9775-8189 Xiaoyu Cao: 0000-0003-0219-1798

Notes

The authors declare no competing financial interest.

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