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Chiral molecular face-rotating sandwich structures constructed through restricting the phenyl flipping of tetraphenylethylene†

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Chiral tetraphenylethylene (TPE) derivatives have great potential in chiral recognition and circularly polarized luminescence. However, they were mainly constructed through introducing chiral substituents at the periphery of the TPE moiety, which required additional chemical modifications and limited the variety of chiralities of products. Herein, we constructed a series of chiral face-rotating sandwich structures (FRSs) through restricting the phenyl flipping of TPE without introducing any chiral substituents. In FRSs, the complex arrangements of TPE motifs resulted in a variety of chiralities. We also found that non-covalent repulsive interactions in vertices caused the facial hetero-directionality of FRSs, and the hydrogen bonds between imine bonds and hydroxy groups induced excited-state intramolecular proton transfer (ESIPT) emission of FRSs. In addition, the fluorescence intensity of FRSs decreases with the addition of trifluoroacetic acid. This study provides new insights into the rational design of chiral assemblies from aggregation-induced emission (AIE) active building blocks through restriction of intramolecular rotation (RIR).

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Introduction

Tetraphenylethylene (TPE), as an aggregation-induced-emission chromophore (AIEgen),¹ has been extensively applied in fluorescent probes,² optoelectronic materials,³ and bioimaging agents.⁴ As a pseudo- C_4 symmetric building block, TPE has been assembled into covalent-organic frameworks (COFs),⁵ molecular cages⁶ and supramolecular fibres.⁷ Among those TPE-based materials, the chiral ones are particularly interesting because they exhibit extensive functions such as chiral recognition⁸ and circularly polarized luminescence.⁹ Generally, chiral TPE derivatives are constructed through introducing chiral substituents at the periphery of the TPE moiety.¹⁰ Nevertheless, such strategies required additional chemical modifications on TPE, and the chiral substituents limited the variety of chiralities of products. Interestingly, the propeller-like TPE core can exhibit inherent two-dimensional (2D) chirality in *P* or *M* helical configurations¹¹ through the restriction of intramolecular rotation (RIR).¹² In addition, the spatial orientation of vinyl

bonds (Fig. 1a), either vertical or horizontal, also influences the chirality of assembled structures. Therefore, the complex arrangements of the four TPE motifs (Fig. 1b) could generate numerous chiral diastereoisomers without introducing any chiral substituents. But such a strategy to construct chiral TPE-based assemblies was rarely investigated and challenging due to difficulties in chiral separation.

Recently, we have constructed a series of molecular face-rotating polyhedra (FRP),¹³ which display a special form of



Fig. 1 (a) TPE motif exhibits two rotational modes (*P* or *M*) of the phenyl groups and two orientational modes (horizontal or vertical) of the vinyl bonds in two dimensions. (b) Four 2D motifs of TPE could generate numerous diastereoisomers through special arrangements. (c) Structural formula of THFPE, TREN and the corresponding sandwich structures formed by dynamic imine chemistry.

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supramolecular chirality originating from the arrangements of 2D chiral building blocks. In TPE-based FRP,¹⁴ we found that the phenyl flipping of TPE faces was significantly restricted and hence FRP exhibited remarkable stability of chirality and fluorescence in diluted solution. To further control the chirality of FRP, we modulated the rotational patterns of faces with several features. On one hand, the subtle difference in building blocks could bring a huge change in the resultant assemblies and their chirality. For instance, Fujita *et al.* demonstrated that only a 3° difference in the bending angles of two ligands can critically switch achiral Platonic or Archimedean structures into chiral Goldberg polyhedra.¹⁵ More recently, our group reported that different positions of aldehyde in triazatruxene (TAT) lead to distinct assembly behaviour and geometry.¹⁶ On the other hand, vertices also determined the chirality of FRP. We reported that chiral vertices sufficed to control the facial directionality and the conformations of other achiral vertices in FRP assembled from truxene.¹⁷ Nevertheless, how achiral vertices influence the rotational patterns of TPE units remains unclear.

Herein, we assemble the meta-aldehyde TPE (THFPE, Fig. 1c) with tris(2-aminoethyl)amine (TREN) to form a series of chiral face-rotating sandwich structures (FRSSs) without introducing any chiral substituents on TPE. The subtle difference in TPE (the positions of aldehyde groups) changes the resultant structures from previously reported molecular cubes¹⁴ into FRSSs, wherein only four FRSSs emerge as products out of twelve possible diastereoisomers. In FRSSs, three TPE units exhibit hetero-directional configurations, which are controlled by the repulsive interactions in TREN vertices as indicated by theoretical calculations. In addition, the hydroxyl groups form hydrogen bonds with imine bonds and induce the excited-state intramolecular proton transfer (ESIPT) phenomenon. In addition, the fluorescence intensity of FRSSs decreases with the addition of trifluoroacetic acid.

Results and discussion

The facial building block THFPE was prepared from 4,4'-hydroxybenzophenone through multi-step synthesis (Fig. S1†). In the Schiff-base condensation, THFPE (3 equiv.) was mixed with TREN (4 equiv.) and catalytic amounts of trifluoroacetic acid in chloroform at ambient temperature (Fig. 1c). High-resolution mass spectrometry identified the molecular weight to be 1894.21 (Fig. S2†), corresponding to THFPE₃TREN₄. However, the initial nuclear magnetic resonance (NMR) spectrum showed notable overlap of proton signals in the aromatic region (Fig. S3†), suggesting that more than one stereoisomer existed in the products.

High-performance liquid chromatography (HPLC) was employed to separate the mixed products by using a chiral column (Daicel Chiralpak IE) and a mixed solvent as the mobile phase (toluene/chloroform/methanol). After 24 hours of reaction, the HPLC spectrum confirmed that only four fractions eluted in a 1 : 2 : 2 : 1 ratio (Fig. 2a, top). Further characterization revealed that the four fractions correspond to two pairs of hetero-directional enantiomers, *i.e.*, *PMP-1*, *MPM-1*, *PMP-2* and *MPM-2*, which respectively eluted at 17.5, 32.9, 15.5 and 44.7



Fig. 2 Chiral-HPLC and CD analyses of **1** and **2**. (a) Chiral HPLC spectra of the kinetic products (top) synthesised at ambient temperature revealing two pairs of diastereoisomers, (*i.e.*, *MPM-1* and *PMP-1*, *PMP-2* and *MPM-2*) that changed into the thermodynamic products (*MPM-1* and *PMP-1*) when heated at 50 °C for five days (bottom). (b) CD spectra of *PMP-2*, *MPM-1*, *MPM-1* and *MPM-2* (10 μM) in dichloromethane.

min. However, as the reaction was heated at 50 °C for five days, the fraction of FRS **2** gradually decreased (Fig. S4†) and eventually disappeared (Fig. 2a, bottom), suggesting that FRS **2** was a kinetic product which finally converted into thermodynamic FRS **1**. The reaction yield of THFPE₃TREN₄ was calculated to be 97.6% according to the full HPLC spectrum (Fig. S5†).

Slow evaporation of FRSSs in chloroform was allowed to afford prismatic crystals after a month. Although we used enantiopure fractions to grow crystals, single-crystal X-ray diffraction analysis revealed a pair of enantiomers co-crystallized in a unit cell, indicating racemization of FRSSs **1** or **2** during the crystallization process. Further time-dependent chiral-HPLC analyses revealed that only 2% of *MPM-1* or *MPM-2* can change into their enantiomers after five days in solution (Fig. S6†), indicating that the racemization of each enantiopure fraction was quite slow in solution. All crystal structures of FRSSs bear a tetra-capped hetero-directional sandwich structure, wherein one TPE unit was stuck between the other two TPE units with a different rotational configuration and TREN occupied four vertices to link three TPE units.

The crystal structure of *PMP-1* is *C*₂ symmetric according to the central axis of each TPE face (Fig. 3a). The *M* face in the middle is 5.29 Å from two *P* faces (Fig. 3b). The vinyl orientations of *P* faces are parallel whereas they form a 51° angle with the vinyl bond of the middle *M* face (Fig. 3a, inset). In addition, three phenyl rings linked by the same TREN have highly twisted conformations, wherein two phenyl rings from two *P* faces are nearly parallel and they are perpendicular to that from the *M* face as shown in Fig. S7.† Similar to *PMP-1*, *PMP-2* has only a subtle difference in the vinyl orientations of two *P* faces (Fig. 3c): they are noncoplanar perpendicular to each other and form a 45° angle with the vinyl bond of the middle *M* face (Fig. 3d and more structural details are in Fig. S7†).

The imine bonds in FRSSs form hydrogen bonds (O–H⋯N) with hydroxyl groups and are conjugated with phenyl rings, resulting in complete coplanarity with the adjacent phenyl rings. In our previous work, the imine bonds and the adjacent phenyl rings, without the assistance of hydrogen bonds, have a 7° dihedral angle.¹⁴ To investigate the role of hydrogen-bonding interactions, we substituted the hydroxyl groups in



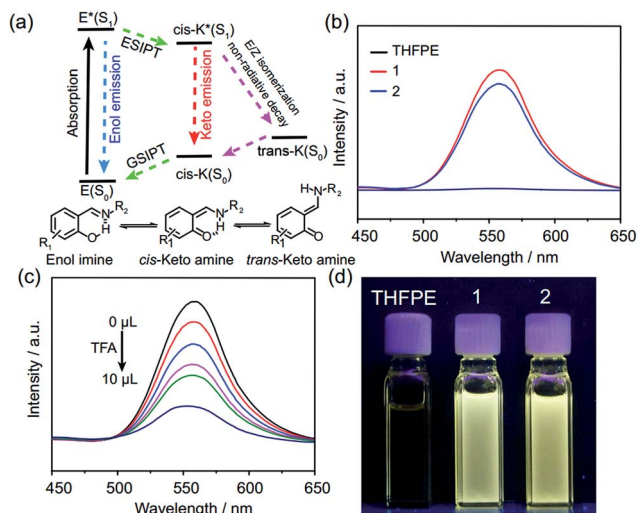


Fig. 4 (a) The ES IPT mechanism of enol-imine compounds through a four-level photo-cycle. (b) Fluorescence spectra of THFPE (30 μM , black), FRSs 1 (10 μM , red) and 2 (10 μM , blue) in chloroform, excited at 360 nm. (c) pH-dependent fluorescence spectra of FRS 1 in chloroform. (d) Fluorescence images of THFPE (1.2 mM, left), 1 (400 μM , middle) and 2 (400 μM , right) under 365 nm UV-irradiation.

aggregation and it will increase the intensity of ES IPT emission.²⁰ In FRSS, the rigidity of TREN vertices can also prevent the *E/Z* isomerization of *cis*-K* and strong ES IPT emission of FRSS can be observed in diluted solution. In addition, the ES IPT emission of FRSS can be tuned by pH and solvent, which can remarkably block the enol-keto tautomerism in the excited state.²¹ By adding TFA into FRSS 1 in chloroform incrementally, the fluorescence intensity decreased dramatically at 550 nm (Fig. 4c), whereas the fluorescence can recover to the initial intensity by using trimethylamine to neutralize TFA (Fig. S19c†). As expected, increasing the solvent polarity can also switch off emission at 550 nm with a red shift (Fig. S19b†).

Conclusions

To conclude, we have constructed a series of FRSS with emergent chirality and fluorescence through restricting the phenyl flipping of TPE units in diluted solution. Due to the non-covalent repulsive interactions, TREN vertices exhibited rotational configurations and transmitted their chirality to the TPE entities, resulting in facial hetero-directionality of FRSS. In addition, the hydrogen bonds between imine bonds and hydroxy groups induced ES IPT properties, which can be tuned by pH and solvents. This study provides a strategy to construct chiral supramolecular assemblies from AIEgens by restricting intramolecular rotation, which can be applied in luminescent materials, molecular recognition or asymmetric catalysis.

Conflicts of interest

There are no conflicts to declare.

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