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Editorial

TPE-embedded functional macrocycles: From structural design to photophysical property and application

Macrocyclic hosts play a crucial role in supramolecular chemistry and the development of supramolecular functional materials. Their well-defined cavities and diverse host-guest interactions endow macrocycles with excellent stimuli responsiveness, facilitating efficient assembly construction. However, the limited availability of functional groups in conventional macrocycles restricts their ability to meet the demand for fabricating materials with multiple functionalities. To address this limitation, several research groups have introduced tetraphenylethylene (TPE), a well-known building block renowned for its remarkable aggregation-induced emission (AIE) effect, into the macrocycle framework. Herein, this paper summarizes the combination strategies and synergistic approaches that achieve multi-functionality by integrating TPE and macrocyclic architectures. The emission characteristics of TPE-embedded macrocycles are elucidated, and it is anticipated that more AIE-type macrocycles with innovative backbones and broad applications will emerge.

1. Synthetic strategies of TPE-embedded macrocycles

How to identify and leverage the correlation between the structure of TPE and macrocycles is a critical aspect in the rational design of TPE-embedded macrocycles. By utilizing the torsion angle within the TPE unit, Huan Cong's group innovatively incorporated the TPE core into the pillararene skeleton through the introduction of dimethoxybenzene followed by classical intramolecular macrocyclization (Fig. 1A) [1]. The resulting pentagon-shaped dimacrocycle, termed as bowtiearene, features both pillar-like cavities and AIE properties, serving as an exemplary model for the design and synthesis of TPE-embedded macrocycles. Similarly, starting with the TPE unit, Yan-Song Zheng's group conducted extensive research on TPE-based dicycles and tetracycles [2,3]. Following the cyclization of the propeller-like TPE core with short and rigid linkers, the phenyl rings in TPE were immobilized, enabling the isolation of *P*- and *M*-enantiomers and achieving circularly polarized luminescence.

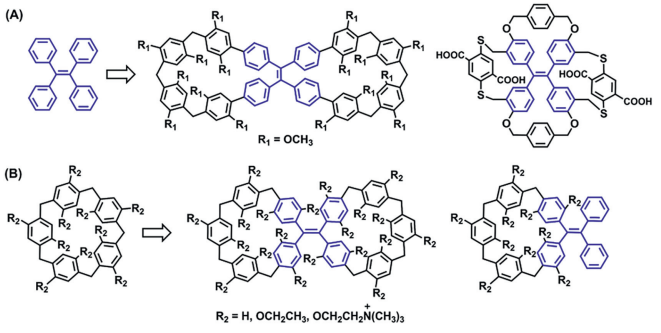

Fig. 1. TPE-embedded macrocycle (A) synthesized from TPE moiety and (B) synthesized from macrocycle moiety.

Various macrocycles, such as pillararenes and calixarenes, consist of repeated aryl rings connected by methylene groups. The inconspicuous diphenylmethylene units within the macrocycle skeleton can be regarded as integral parts of the TPE core. Following this concept, Xiao-Yu Hu's group focused on the derivatization of macrocycles at the *meso*–position. By introducing a ketone structure and subsequently performing asymmetric McMurry coupling with diphenyl ketone or symmetric McMurry coupling with another macrocycle, the pillararene moiety was finely integrated with the TPE unit, yielding TPE-embedded monocycles or dicycles, respectively (Fig. 1B) [4]. Building on these findings, Xiao-Yu Hu's group explored the feasibility of merging other kinds of macrocycles with the TPE unit. A series of butterfly-like TPE-cored dicrown ethers were successfully synthesized *via* intramolecular McMurry coupling of cyclic diketones containing long glycol chains [5]. It should be highlighted that the cavities of the macrocycles are preserved, and their host-guest properties remain intact after TPE functionalization. Consequently, various unique characteristics and applications can be realized when combining these structures with the AIE properties from the TPE unit.

2. Fluorescence regulation of TPE-embedded macrocycles

Due to the proximity of the macrocyclic cavity to the TPE unit, the fluorescence emission of the macrocycle may undergo significant changes following host-guest interactions. Xiao-Yu Hu's group found that TPE-embedded [1_5]paracyclophanes exhibited fluorescence quenching upon cation-π and charge transfer interactions with Ni^{2+} [6]. Fluorescence recovery was then achieved through the precipitation of Ni^{2+} by hydroxide ions. This reversible fluorescence switching behavior suggests potential application of [1_5]paracyclophanes in fluorescent ink. This research clearly demonstrates that the host-guest complexation of TPE-embedded macrocycles is an effective method for controllable fluorescence tuning, providing new insights into the design of luminescent macrocycles.

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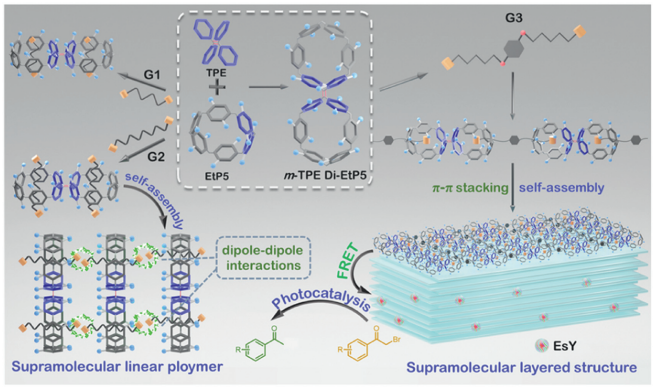

Fig. 2. The assembly of TPE-embedded di-pillar[5]arene with guest molecules for photocatalysis. Copied with permission [7]. Copyright 2023, Wiley-VCH.

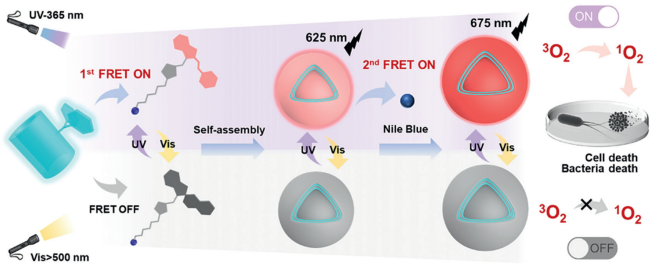

Fig. 3. TPE-functionalized water-soluble pillar[5]arene for switchable FRET process. Copied with permission [8]. Copyright 2023, Royal Society of Chemistry.

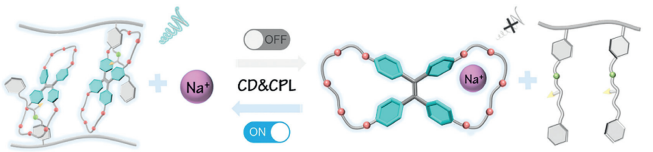

Fig. 4. The modulation of CPL signal by Na^+ competitive association. Copied with permission [5]. Copyright 2024, Springer Nature.

Apart from host-guest properties, the rigid macrocyclic skeleton itself also exerts a significant influence on the AIE effect of the TPE unit. Yan-Song Zheng's group demonstrated that, with the TPE unit immobilized through cyclization, both TPE-cored dicycles and tetracycles exhibited bright fluorescence in both aggregation state and solution. This phenomenon was ascribed to the restriction of intramolecular rotation (RIR) mechanism. By synthesizing various *cis*-dicycles and *gem*–dicycles, they clarified the impact of cyclization on the AIE property [2]. Specifically, *cis*-dicyclization effectively inhibited the double bond rotation in the excited state, which was crucial for the fluorescence enhancement. Without this inhibition, the TPE-cored dicycle would exhibit only negligible emission. In addition to affecting emission intensity, macrocyclization also alters the fluorochromism of TPE. For instance, bowtiearene, existing in single crystal form and soluble in THF, exhibits distinct packing modes characterized by multiple non-covalent interactions, leading to different TPE conformations with varying degrees of twist [1]. These subtle structural changes resulted in blue emission of bowtiearene in the single crystal form and yellow emission in its THF solution.

3. Potential application of TPE-embedded macrocycles

The host-guest interactions of macrocycles serve as a potent tool for inducing self-assembly and have broad applications in biomedicine, adsorption and separation, light harvesting, and other fields. The additional AIE property endows TPE-embedded macrocycles with outstanding superiority in energy transfer process. Specifically, Xiao-Yu Hu's group constructed a supramolecular polymer through the host-guest interaction between TPE-embedded di-pillar[5]arene and dinitrile guest bearing a bulky phenyl group, which further stacked through π-π interaction to form a layered assembly (Fig. 2) [7]. This assembly functioned as an ideal donor in Förster resonance energy transfer (FRET) process due to the intense blue emission of TPE in its aggregated state. Upon incorporating Eosin Y (ESY) as an acceptor, a nanoreactor was fabricated, enabling highly efficient photocatalytic dehalogenation reactions of 2–bromo-1-phenylethanone derivatives. Subsequently, the self-assembly and FRET process in aqueous media were investigated. In aqueous solution, TPE-functionalized pillar[5]arene could bind with sulfonate-modified spiropyrans, assembling into nanoparticles (Fig. 3) [8]. UV-induced isomerization from non-emissive spiropyran to emissive merocyanine activated the energy transfer process between the host and guest due to their close spatial proximity. Further encapsulation of Nile blue as a secondary acceptor within the nanoparticles triggered sequential energy transfer. Additionally, this energy transfer process was accompanied by the generation of reactive oxygen species (ROS), which can be utilized for efficient anticancer and antibacterial treatments. The reversible "on-off" switchability of the FRET process and ROS generation, driven by UV–vis light irradiation-induced isomerization of spiropyrans, underscores the potential of AIE macrocycles with host-guest recognition in photodynamic therapy.

On the other hand, the AIE effect and helical chirality make TPE an ideal candidate for circularly polarized luminescence (CPL), which can be significantly amplified through the assembly process by introducing a macrocycle skeleton. In a study by Xiao-Yu Hu's group, butterfly-like TPE-cored di-crown ether assembled into nanohelices upon complexation with chiral polymer guests, activating its chiral luminescence, which was further well-regulated *via* competitive association with sodium ion (Fig. 4) [5]. On the basis of helical chirality of TPE motif, Yan-Song Zheng's group prepared a TPE-embeded tetracycle tetracid to introduce planar chirality of macrocycle for enhancing CPL performance [3]. Upon addition of octadecylamine, the CPL signal of the chiral tetracycle increased by 64-fold due to nanohelix formation. Continued addition of phenylenediamine led to aggregation into large bundles, achieving a dissymmetry factor (g_{lum}) as high as 0.386. These studies underscore the significant role of TPE-based macrocycles in constructing CPL materials, attributed to their facile synthesis, large g_{lum} values, and ease of regulation.

In conclusion, TPE-embedded macrocycles, characterized by their unique structures and host-guest properties, are anticipated to exhibit reversible switchability and controllable self-assembly with corresponding guests. The development of TPE-embedded macrocycles enhances our understanding of the mechanisms underlying the AIE effect as well as chirality transfer and amplification, thus opening new avenues for rapid advancement in bioimaging, photodynamic therapy, and chiral luminescence.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in the paper.

CRediT authorship contribution statement

Jianmin Jiao: Writing – original draft. **Jiehao Yu:** Writing – review & editing, Conceptualization. **Xueqi Tian:** Writing – review & editing. **Xiao-Yu Hu:** Writing – review & editing, Supervision.

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