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Editorial

Supramolecular assembly-enhanced chiroptical properties of pyrene-modified cyclodextrins

Manipulating the chiroptical activities of chiral chromophores is helpful to expand the potential applications of circularly polarized luminescence (CPL) materials in the fields of chiral sensing, optical displays, biological probe, information storage and so on [1]. In recent years, macrocycles-based supramolecular systems have been continually and extensively applied in the fields of biomedicine, catalysis, optical and electronic materials [2,3]. In particular, supramolecular self-assembly, as an effective strategy to improve chiroptical activities, has attracted great attention [4]. However, the dynamic non-covalent interactions of supramolecular assemblies still make it challenging to restrict the chiral arrangement of chromophores strictly.

Recently, Yang and coworkers from Sichuan University reported a supramolecular strategy through a combination of host–guest complexation and supramolecular aggregation to obtain significant chiroptical properties [5]. They synthesized pyrene di-substituted γ-cyclodextrin (γ-CD) derivates, which self-assembled to supramolecular polymers in an aqueous solution with the pyrene moieties interpenetrating into γ-CD cavities. Subsequently, the self-assembled polymers further aggregated into nanostrips through the periphery of γ-CD (Figs. 1 and 2).

The host-guest complexation of γ-CD with pyrene gives rise to J-type stacking of pyrenes accompanied by apparent excimer fluorescence and the further aggregation restricts pyrene into a rigid chiral environment, thus exhibiting excellent chiral spectral properties. The g_{abs} and g_{lum} values are up to 4.3×10^{-2} and 5.3×10^{-2}, which surpassed the current record of chiral pyrene derivatives obtained in supramolecular aggregates. Due to the protective effect of cavity encapsulation and aggregation against the solvent collision, the fluorescence quantum efficiency Φ_f is up to 64.1% (Table 1). Moreover, temperature, pH and competitive guest can significantly affect the aggregation and manipulate the chiroptical properties (Fig. 2).

In addition, they used a newly proposed parameter $B^i_{CPL} = B_{CPL}/n$ to evaluate the chiral emission performance, where B_{CPL} is the CPL brightness and n is the number of chromophore units in the molecule. Because of the high Φ_f and g_{lum}, the B_{CPL} and B^i_{CPL} of this pyrene di-substituted γ-CD supramolecular system are 338.6 and 169.3 $(mol/L)^{-1}$ cm^{-1}, respectively, in which the B^i_{CPL} value is the highest one obtained with excimer fluorescence (Table 1).

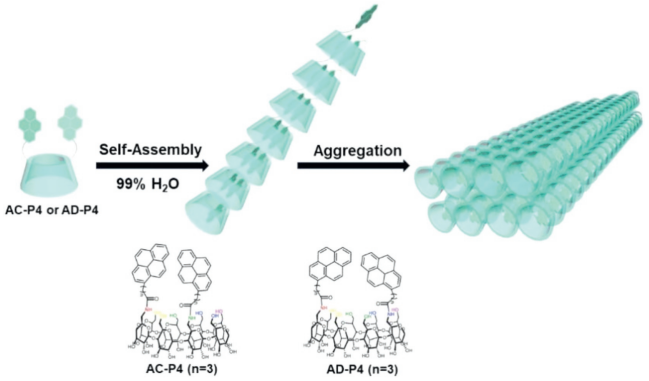

Fig. 1. Scheme illustration of the aggregation process of di-pyrene-substituted γ-CDs.

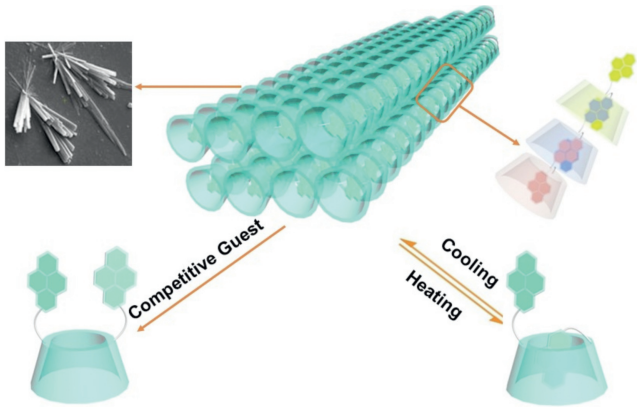

Fig. 2. Schematic diagram of the influence of competitive guest and temperature on the aggregation. Reproduced with permission [5]. Copyright 2022, Wiley-VCH.

Table 1
Photophysical parameters of the pyrene derivatives measured in 99% H_2O at 8 °C.

Pyrenes	AC-P4	AD-P4
ε $((mol/L)^{-1}$ $cm^{-1})$	21,400	20,500
Φ_f (%)	59.7	64.1
g_{abs} (%)	4.5	4.2
g_{lum} (%)	5.3	4.9
B_{CPL} $((mol/L)^{-1}$ $cm^{-1})$	338.6	321.4
B^i_{CPL} $((mol/L)^{-1}$ $cm^{-1})$	169.3	160.7

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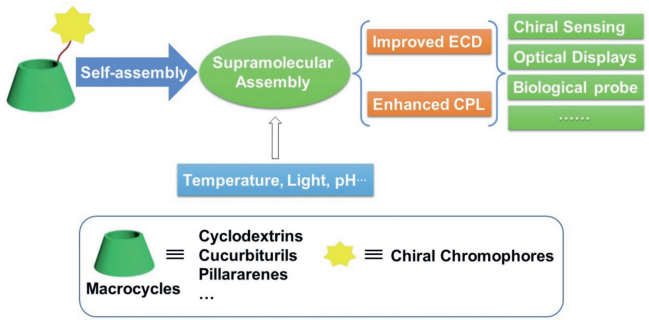

Fig. 3. The construction of assembly-enhanced chiral supramolecular assembly and its modulation and applications.

In summary, Yang and coworkers have developed a supramolecular strategy based on pyrene-modified cyclodextrin by synergistic host-guest complexation-induced aggregation, which effectively confines the two pyrene units to a relatively rigid chiral environment, thus achieving significant enhancement of chiral optical activity. We believed that this strategy could be applied to other macrocyclic compounds, such as cucurbiturils, pillararenes, thus providing us with a novel toolbox to regulate the arrangement of chiral chromophores and enhance the CPL signals, meanwhile which could also be further modulated by temperature, light, pH and solvent change (Fig. 3). To be envisaged, this new strategy will play a more and more important role in the research and development of CPL field.

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References

[1] M. Li, M.Y. Wang, Y.F. Wang, et al., Angew. Chem. Int. Ed. 60 (2021) 20728–20733.
[2] Y. Zhang, L. Wang, J. Wang, et al., Chin. Chem. Lett. 32 (2021) 1902–1906.
[3] X.Y. Dai, Y.Y. Hu, Y. Sun, et al., Adv. Sci. 9 (2022) 2200524.
[4] S. Zheng, J. Han, X. Jin, et al., Angew. Chem. Int. Ed. 60 (2021) 22711–22716.
[5] C. Tu, W. Wu, W. Liang, et al., Angew. Chem. Int. Ed. 61 (2022) e202203541.