

Tuning and Shaping Liquid Crystal-Like Ordering in Self-Assembled Structures of Pillar-[5]-arenes and Perfluorinated Diacids

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The interaction of perfluorinated molecules with their environment remains an important, yet poorly understood topic that has garnered much recent attention. Many to-date researched interactions with perfluorinated compounds have focused on their behavior with large polymers, but it has recently been observed that pillar-[5]-arenes—large barrel-shaped aromatic macrocycles much smaller than typical polymers—can interact with perfluorinated substances [1], creating interest in elucidating with what molecules can these pillararenes interact and how they do so.

In our work, we show that complexation between pillar-[5]-arenes and perfluorinated diacids leads to the almost instantaneous formation of a self-assembled film (Figure 1) through a combination of electrostatic and fluorophilic phase separation-induced interactions [2]. The stability of these structures is governed by size-matching effects between the host and guest molecules that produce smectic-like ordering: in systems where this ordering cannot be imposed, stable films cannot be achieved. This rapid complexation enabled by quasi-smectic ordering allows us to template the shape of films through microfluidic production techniques, creating a wealth of hollow shells that could be used for encapsulation.

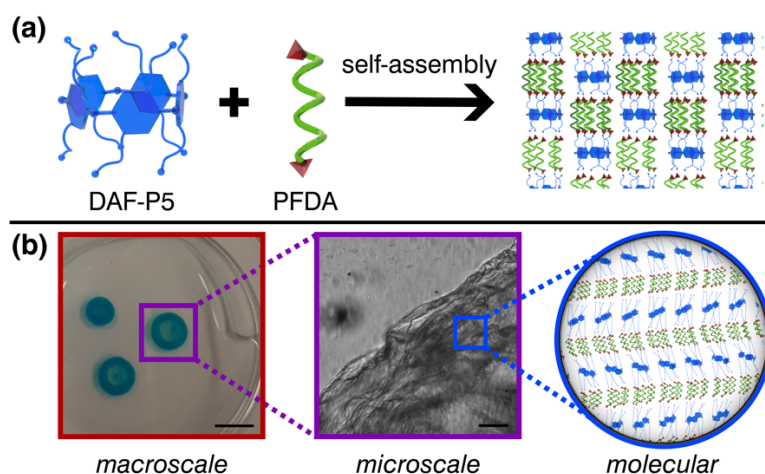


Figure 1. (a) The combination of pillar-[5]-arenes and perfluorinated diacids enable the formation of assemblies through electrostatic and fluorophilic interactions. (b) If the sizes of molecules are well-matched, this enables smectic-like layering that produces solid films and potentially vesicles.

References

[1] T.N. Gao et al, *Angew Chemie Int Ed*, **63**, e202403474 (2024)

[2] L.W. Honaker, T.N. Gao, K.R. de Graaf et al, *Adv Sci*, **11**, 2401807 (2024)

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