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Editorial

Supramolecular homo- and hetero-chiral donor–acceptor copolymers with distinct nanomorphology and energy transfer efficiency

Chirality is ubiquitous in many fields such as biology, pharmacology, chemistry, and physics. It therefore is of great significance to research on chirality generation, chirality transfer, and chirality amplification effects, especially in the living process [1]. Supramolecular polymerization has become an efficient tool to organize molecular building blocks based on various chiral motifs [2]. When stereogenic elements are incorporated into the monomeric structures, their stereo-communication prefers the helical supramolecular polymers *via* chirality amplification. Despite several principles proposed, including “sergeants-and-soldiers [3]” and “majority rules [4]”, it remains a key challenge to choose reasonable chiral induction motifs for the chiral supramolecular copolymerization with expected arrangement properties. Moreover, it is intriguing to introduce donor–acceptor (D–A) units instead of the same comonomers into the monomeric structures, which could endow fascinating features to the resulting supramolecular polymers [5–8].

Recently, Wang and co-workers from University of Science and Technology of China reported a novel chirality-controlled supramolecular D–A copolymeric system by using enantiopure benzamide-based comonomers in homochiral and heterochiral organization modes [9]. With the elaborate choice of sterregenic comonomers, they achieved chirality-dependent supramolecular coassembly in a random or alternate organization manner, which brought distinct energy transfer efficiency properties. In this work (Fig. 1), diethynylanthracene-based benzamide serves as the D-type monomer, and diethynyltetracene-based benzamide acts as the A-type monomer. Two enantiopure linkages, locating between the diethynylacene core and the wedge-shaped alkyl chain peripheries, are incorporated into two pairs of comonomers structure. With regard to homochiral supramolecular copolymerization, each monomer can provide intermolecular hydrogen bonds and π-π stacking interactions to drive non-covalent complexation, accompanied by the generation of steric hindrance between the neighbouring methyl groups. Interestingly, this steric effect is relieved for heterochiral supramolecular copolymerization. Consequently, it steers random arrangement for homochiral co-assembly within the nanofibers, and alternate arrangement for heterochiral coassembly within the nanoparticles (Fig. 1). This work creatively utilizes D–A comonomers to construct supramolecular polymers with different nanomorphology and distinct energy transfer efficiency, which is enlightening to the potential applications of supramolecular polymers in chiral photonics and enantioselective detection fields.

In this work, supramolecular copolymerization occurs between D-monomer and A-monomer in apolar methylcyclohexane (MCH), as synergistically driven by π-π stacking and hydrogen bonding interactions. These non-covalent driving forces are firstly confirmed by single crystal analysis (Fig. 2a). Besides, UV−vis and CD spectral results indicate chirality transfer of monomer from the stereogenic centers to the inner anthracene/tetracene core, leading to the formation of single-handed helical aggregates in MCH. When they mixed *R*/*S*-enantiomer equivalently in MCH, obvious color change from green to yellow and higher thermo-stability property were monitored for heterocomplexation (Figs. 2b and c). It preferentially formed an alternate arrangement between the two enantiomers. Furthermore, nanoparticles were obtained for racemates, while nanofibers were encountered for enantiopure compounds. To clarify the origin of the alternate arrangement between racemates, density functional theory (DFT) calculation was employed (Fig. 2d).

Subsequently, they investigated homochiral and heterochiral supramolecular copolymerization behaviors by using the D/A-type monomers. According to UV–vis spectral measurements and mathematical calculation of bonding fractions, homochiral comonomers bias the random arrangement in supramolecular copolymers (Figs. 3a and b). Meanwhile, heterochiral comonomers prefer the alternate arrangement. They further studied the arrangement at the excessive concentration of monomers. Two possible modes might exist. One is attaching the excessive monomers to the end of alternate co-stacks to form triblock supramolecular copolymers, while the other is the narcissistic formation of alternate supramolecular copolymers and homopolymers. The latter mode is demonstrated by both atomic force microscopy and transmission electron microscopy images (Figs. 3c and d), showing the co-existence of nanofibers (derived from homopolmerization) and nanoparticles (derived from alternate copolymerization). Finally, fluorescence and circular polarized luminescence (CPL) experiments indicate that homochiral supramolecular D–A system performs high energy transfer efficiency whilst heterochiral copolymerization displays weak energy transfer (Figs. 3e and f).

In summary, this contribution presents an intriguing chirality-controlled supramolecular D–A copolymerization with different energy transfer features. Wang and co-workers constructed nanofibers and nanoparticles through homo- and heterochiral supramolecular co-assembly modes, which coincided with ran-

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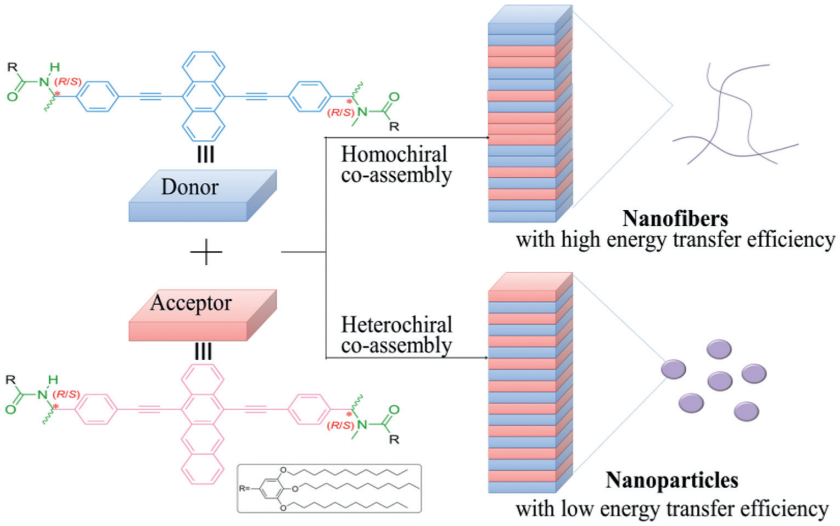

Fig. 1. Chemical structures of D-type and A-type monomers (*R*/*S*), and the schematic representation for chirality-dependent D–A organization in the supramolecular copolymers.

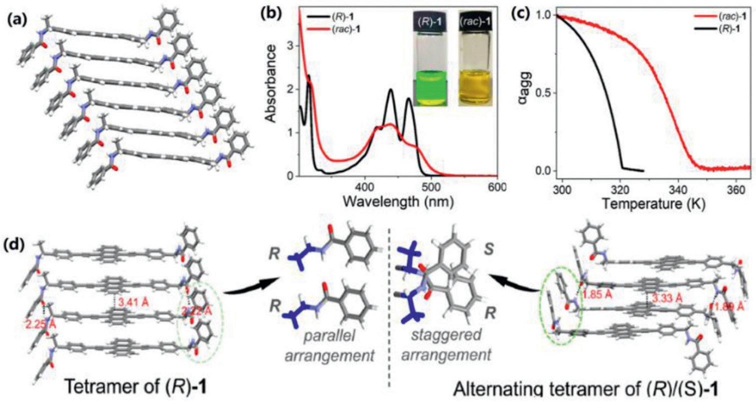

Fig. 2. (a) Single-crystal structure of an analogue comonomer. (b) UV—vis spectra of (*R*)-**1** and (*rac*)-**1**. Inset: photographs of the solutions. (c) The degree of aggregate α_{agg} as a function of temperature. (d) Side view of the optimized structures of the (*R*)-/(*S*)-tetramers with parallel and staggered arrangement by using ωB97XD/6-31G(d) level. Reproduced with permission [9]. Copyright 2022, American Chemical Society.

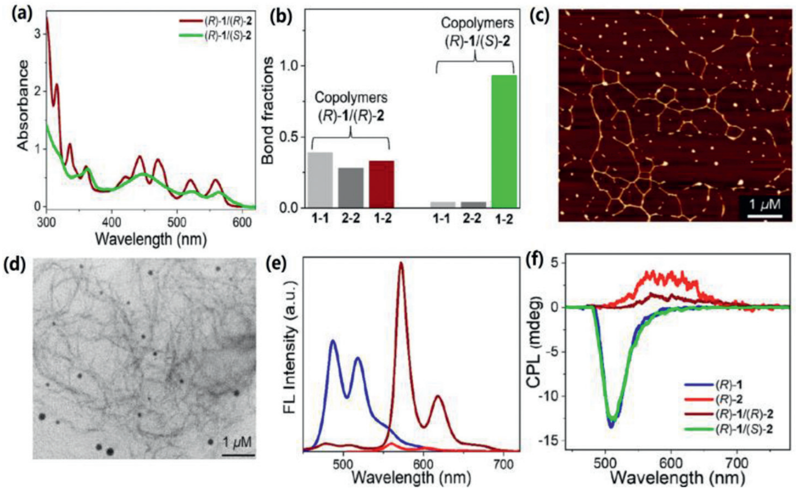

Fig. 3. (a) UV–vis spectra of a 1:1 mixture of copolymers (*R*)-**1**/(*R*)-**2** and (*R*)-**1**/(*S*)-**2**. (b) Calculated homobonding and heterobonding fractions in supramolecular copolymers. (c) AFM image of a 2:1 mixture of (*R*)-**1**/(*S*)-**2** on mica. (d) TEM image of a 2:1 mixture of (*R*)-**1**/(*S*)-**2**. (e) Fluorescent spectra of (*R*)-**1** with the addition of 0 mol% (blue line) and 10 mol% (brown line) amounts of (*R*)-**2**, together with the fluorescence spectrum of (*R*)-**2** (red line). (f) CPL spectra of comonmers and their complexes. Reproduced with permission [9]. Copyright 2022, American Chemical Society.

domly mixed organization and alternate organization, respectively. Their innovative design principle focuses on the introduction of the stereogenic group into the linkage between the π-aromatic core and the alkyl chain peripheries. The steric hindrance not only renders parallel arrangement, but also can be relieved for staggered arrangement. We believe that their judicious choice of stereogenic elements as the chiral induction motifs will bring various organization possibilities (random, alternate, block, periodic, *etc.*) for chiral supramolecular D–A copolymerization. As a result, it will produce a large quantity of supramolecular-level materials in chiral sensing, recognition, and optoelectronic fields.

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