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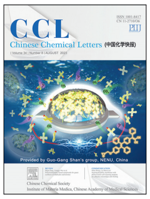

Editorial

Construction of a sequential light-harvesting system *via* supramolecular copolymerization

The current energy crisis is a worldwide problem and the search for clean and economic energy production is a global challenge. In this context, the exploitation and utilization of solar energy is becoming more and more popular. Photosynthesis in nature sets an outstanding example to harvest, transfer and store solar energy [1]. In most of the photosynthetic organisms such as purple photosynthetic bacteria, the rigid protein scaffolds serve as key elements to bind pigments and control their excitation energy transfer. Sequential energy transfer is especially intriguing in this field to make full use of full-band solar energy. To mimic natural photosynthesis [2], a variety of artificial light harvesting systems with two-step sequential energy transfer have been reported recently [3,4]. To realize such a process in artificial systems, donor/acceptor (D/A) chromophores are usually incorporated into useful scaffolds, such as nanoparticles, macrocycles, DNA and proteins. However, the overall energy transfer efficiency (Φ_{overall}) of the most successful artificial LHSs is lower than 70%; a value much lower than that of purple photosynthetic bacteria (almost 100%). It is possibly ascribed to the disordered D/A organization in these scaffold-supported artificial systems.

The light harvesting system of green photosynthetic bacteria provides another natural prototype [5]. In this case, bacterialchlorophyll (BChl) pigments (*e.g.*, BChl *c*) are densely packed *via* supramolecular interactions in a hydrophobic environment provided by chlorosomes (Fig. 1). These individual pigments have intense exciton coupling, resulting in highly efficient light harvesting capabilities. Such a supramolecular architecture facilitates efficient energy transfer from the BChl *c* antenna through BChl *a* in the baseplate of a chlorosome, and ultimately to the reaction center.

Inspired by this natural process, Feng Wang and co-workers from University of Science and Technology of China constructed a sequential energy transfer system with a high Φ_{overall} value *via* supramolecular copolymerization of three different σ-platinated (hetero)acenes [6]. The chemical structure of the donors and acceptors are shown in Fig. 2. These σ-platinated (hetero)acene monomers can undergo supramolecular polymerization in apolar solvent owing to their strong intermolecular packing tendency. The introduction of two amide groups into the three monomers can further enhance the non-covalent packing strength through hydrogen bonding. It is noteworthy that the large Pt(II) groups allow sufficient space between the monomers, avoiding aggregation-caused quenching and maintaining sufficient emission intensity in the supramolecular polymer state. Moreover, on account of their structural similarity, these donor (D) and acceptor (A) monomers can aggregate with each other to form supramolecular copolymers, guaranteeing D/A energy transfer capability. Due to the dense packing properties of the ternary copolymers, they exhibit long diffusion length of excitation energy and high exciton migration rates, which gives rise to a very high Φ_{overall} of 87.4%; much higher than previously reported scaffold-supported supramolecular systems ($\Phi_{\text{overall}} < 70\%$).

The authors first studied the photophysical properties of **1**–**3** in the monomeric state through absorption and emission spectra. The absorption and emission spectra displayed a significant red-shift from **1** to **3**, and density functional theory (DFT) calculations were used to explain this phenomenon. The supramolecular homopolymerization of **1**–**3** was also investigated where the results of circular dichroism (CD) spectroscopy and transmission electron microscopy (TEM) confirmed that monomers **1**–**3** can easily form 1D supramolecular homopolymers in methylcyclohexane (MCH) *via* the nucleation- elongation self-assembly mechanism. Subsequently, the supramolecular copolymerization of **1**/**2** was studied as well as their one-step energy transfer behavior. The structural similarity of **1** and **2** facilitates their aggregation behavior where the copolymerization of **1**/**2** was again studied by CD spectra, DFT calculations and TEM. Furthermore, the energy transfer process of **1**/**2** was monitored by both steady-state and transient-state fluorescence spectroscopy. As a result, Φ_{ET} of this polymer was determined to be 95.8%, corresponding to the energy transfer rate (k_{ET}) of 1.23×10^{10} s^{-1}. Moreover, the exciton migration rate constant of **1**/**2** was calculated to be 6.69×10^{14} L mol^{-1} s^{-1}; a value much higher than previously reported. The authors rationalized this to the long-range-ordered supramolecular copolymers and 1D structural anisotropy.

The two-step sequential energy transfer in a supramolecular copolymer of **1**/**2**/**3** was further investigated where the exciton migration rate from **2** to **3** was calculated to be 9.73×10^{13} L mol^{-1} s^{-1}, indicating an efficient energy transfer ascribed to their spatial proximity. The Φ_{overall} from **1** to **3** was determined to be 87.4%, which is also significantly higher than previously reported sequential energy transfer systems ($\Phi_{\text{overall}} < 70\%$).

Interestingly, the process of the sequential energy transfer could be adjusted by photo-irradiation, thought to be a result of a photo-induced endoperoxidation of the acenes and σ-platinated acenes in the presence of oxygen. The experiment showed that supramolecular copolymerization could facilitate acceleration of the photo-chemical reaction. When irradiated from 460 nm to

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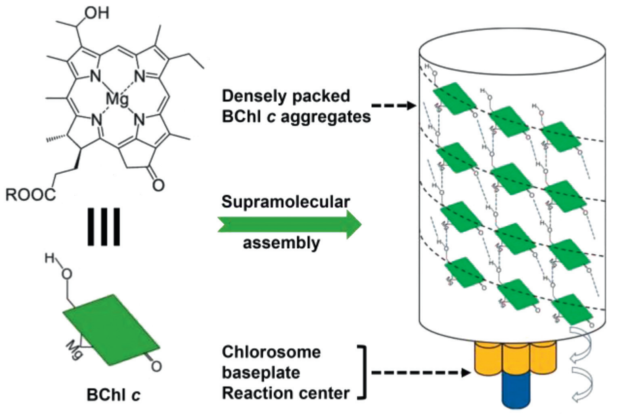

Fig. 1. Schematic illustration of the direct supramolecular alignments of bacteriochlorophyll *c* (BChl *c*) into a light-harvesting antenna, and the sequential energy transfer process in green photosynthetic bacteria.

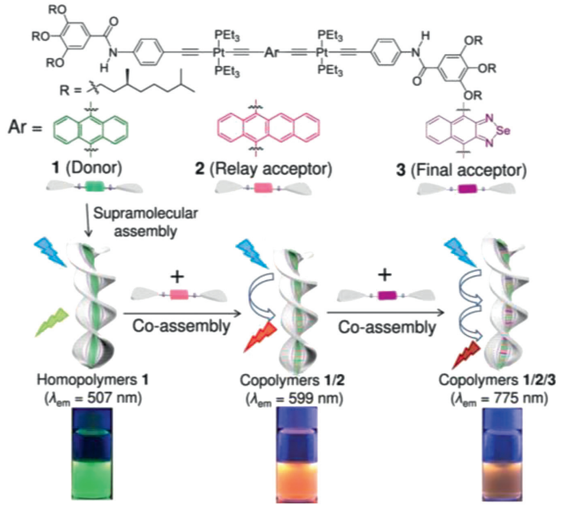

Fig. 2. Cartoon representation of the supramolecular copolymerization of **1**, **2**, and **3** with sequential energy transfer behavior. The supramolecular homopolymers of **1** emit green fluorescence at 507 nm. The binary supramolecular copolymers **1/2** with one-step energy transfer display orange emission at 599 nm. The ternary supramolecular copolymers **1/2/3** with sequential energy transfer show emission at 775 nm.

525 nm, the sequential energy transfer in the supramolecular copolymer system could be inhibited. In addition, the ternary supramolecular copolymers showed time-dependent color changes upon light irradiation. This type of light-triggered modulation of energy transfer may be useful for programmable tuning of emission color.

Feng Wang's work takes inspiration from the natural light-harvesting systems of green photosynthetic bacteria and has provided an artificial two-step energy transfer system based on supramolecular copolymerization of σ-platinated (hetero)acenes. Taking advantage of well-established supramolecular principles, the copolymer is ordered on the nanoscale and exhibits highly efficient energy transfer behavior. The strategy described provides extremely useful insight and their work will be greatly beneficial for the further development of artificial photosynthetic system.

It is worth noting that the supramolecular copolymerization method for constructing artificial light-harvesting systems is a universal and important strategy. Besides π-stacking interaction employed in Feng Wang's work, quadruple hydrogen bonding [7] and host-guest interaction [8] were also used to drive supramolecular copolymerization for the fabrication of light-harvesting systems. It is anticipated that more and more supramolecular copolymers driven by various non-covalent interactions will be created for light-harvesting purposes. In addition, as the efficiency of artificial light-harvesting system continues to improve, it will show potential applications in many fields such as photocatalysis, luminescent materials, bio-imaging and photoelectronic devices, *etc.*

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References

[1] G.D. Scholes, G.R. Fleming, A. Olaya-Castro, et al., Nat. Chem. 3 (2011) 763–774.
[2] T. Xiao, W. Zhong, L. Zhou, et al., Chin. Chem. Lett. 30 (2019) 31–36.
[3] M. Hao, G. Sun, M. Zuo, et al., Angew. Chem. Int. 59 (2019) 10095–10100.
[4] T. Xiao, L. Zhang, H. Wu, et al., Chem. Commun. 57 (2021) 5782–5785.
[5] A. Egawa, T. Fujiwara, T. Mizoguchi, et al., Proc. Natl. Acad. Sci. U. S. A. 104 (2007) 790–795.
[6] Y. Han, X. Zhang, Z. Ge, et al., Nat. Commun. 13 (2022) 3546.
[7] H.Q. Peng, J.F. Xu, Y.Z. Chen, et al., Chem. Commun. 50 (2014) 1334–1337.
[8] H.-J. Kim, P.C. Nandajan, J. Gierschner, et al., Adv. Funct. Mater. 28 (2018) 1705141.