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# Acetal-based spirocyclic skeleton bridged tetraphenylethylene dimer for light-harvesting in water with ultrahigh antenna effect



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Keywords: Light-harvesting Self-assembly Nanoparticles TPE Spirocyclic skeleton	Herein an aqueous-phase artificial light-harvesting platform has been constructed based on the self-assembly of three small organic molecules: a rigid acetal-based spirocyclic skeleton bridged tetraphenylethylene dimer as donor, a hydrophobic dye molecule Nile Red as acceptor, and the surfactant cetyltrimethyl ammonium bromide as amphiphile to enwrap the donor and acceptor and disperse them in water. Due to the rigid skeleton of the tetraphenylethylene dimer that can well accommodate and distribute Nile Red inside the self-assembled nano-spheres, the system shows ultrahigh light-harvesting antenna effects. Moreover, by simply tuning the donor/ acceptor molar ratio, tunable emission including a bright white-light emission could be realized.

#### 1. Introduction

Light-harvesting and energy transfer are extremely important processes in photosynthesis, which is the foundation for life to gain solar energy [1-4]. The light-harvesting units are complex supramolecular systems which organize a large number of chromophores like chlorophylls and carotenoids to collect light and transfer the energy to an acceptor in reaction center [5–10]. Notably, the chromophores are fixed inside rigid protein scaffolds with densely packed alignments, which largely enhances the photon capture efficiency even in low light environments [11–13]. Therefore, an efficient light-harvesting and energy transfer process requires: firstly, a large number of antenna chromophores (donor) with a specific alignment and which need to be located in a confined space but can avoid aggregation-caused quenching (ACQ); secondly, a rigid skeleton is more advantageous to align acceptor chromophores, which can promote effective interchromophoric interaction [11], for example, the so-called Förster resonance energy transfer (FRET) process [14]. To meet the first requirement, aggregation-induced emission (AIE) molecules reported by Tang and co-workers shed a shining light on this research area [15,16]. For the second requirement, various artificial light-harvesting scaffolds have been constructed in recent years, such as porphyrin arrays [5,17-19], supramolecular coordination complexes [20-22], hydrogels [23,24], hybrid assemblies [7, 25], conjugated polymers [26], and self-assembled nanoparticles [27–32]. These artificial systems are usually used for bioimaging [28,33, 34], fluorescent sensors [35,36], and organic luminescent materials [37, 38]. The antenna effect (AE) [39,40], an empirical value for measuring light capture ability, of these systems reported in the past is usually below 40 within a solution system. Therefore, exploiting new type of scaffolds to further improve the light-capturing ability of the artificial platform is highly desirable and remains a big challenge.

Generally, rigid molecules with contorted structures, which can prevent the molecule from densely packing in a confined space, are necessary to create a high free volume inside the nanoparticles (NPs). Therefore, some rigid molecules, which might contain non-planar molecular conformations, are used as a donor (D) scaffold [41]. The spiro-centered and rotation-hindered structure is often employed for microporous organic polymers [42,43], for example, acetal-based spirocyclic skeleton synthesized from pentaerythritol and aromatic acetyl derivatives. Inspired by this, we have prepared a Zn(II) fluorescent probe by using such spirocyclic skeleton bridged Schiff base dimer [44]. Based on our previous works on supramolecular self-assembly [45-49] and a recent work on supramolecular polymer-based light-harvesting system [50], we envisioned that the combination of pentaerythritol-based acetal spirocyclic skeleton with AIE group would be a useful idea to create a more efficient and concise light-harvesting system. Hence, we designed and synthesized such a simple molecule DTPE, an acetal-based spirocyclic skeleton bridged tetraphenylethylene (TPE) dimer, to serve as antenna donors (Fig. 1). By employing a so-called mini-emulsion strategy [51,52], supramolecular NPs based on

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Fig. 1. Schematic illustration of the self-assembly of an artificial light-harvesting system based on DTPE and Nile Red.

**DTPE** in water can be constructed with the assistance of cetyltrimethyl ammonium bromide (**CTAB**). Notably, the hydrophilic head of **CTAB** located on the outer surface of the NPs plays the role not only for dispersing the organic molecules in water, but also mimicking the membrane in real photosynthetic system. Upon loading a hydrophobic dye Nile Red (**NR**) as an acceptor (A), an efficient energy transfer system in water was achieved with an ultrahigh antenna effect (AE = 66), which is much larger than recent reports on artificial light-harvesting system in solution [26,27]. Moreover, the emission of the NPs can be tuned by simply adjusting D/A ratio, which includes an accurate white-light emission. As a result, the **DTPE/NR** system appeared to be a novel and outstanding light-harvesting system with potential applications in luminescent materials.

## 2. Experimental section

## 2.1. Materials and methods

Unless otherwise noted, all chemical reagents and solvents were commercially available and were used without further purification. If needed, solvents were dried by literature known procedures. All yields were given as isolated yields. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker AVANCE III (300 MHz) spectrometer and calibrated against the residual proton signal or natural abundance carbon resonance of the used deuterated solvent from tetramethylsilane (TMS) as the internal standard. The chemical shifts  $\delta$  are indicated in ppm and the coupling constants *J* in Hz. The multiplicities are given as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), and m (multiplet). High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass. SEM investigations were carried out on a JSM-6360LA instrument. TEM



Scheme 1. Synthesis of DTPE.

investigations were carried out on a JEM-2100 instrument. DLS measurements were carried out on a Brookhaven BI-9000AT system, equipped with a 200 mW polarized laser source ( $\lambda = 514$  nm) at a scattering angle of 90°. All samples were prepared according to the corresponding procedures mentioned above. The UV–Vis absorption spectra were measured on a PerkinElmer Lambda 35 UV–Vis Spectrometer. Fluorescence measurements were performed on an Agilent Cary Eclipse spectrofluorometer. The fluorescence lifetimes were measured employing time correlated single photon counting on a FS5 instrument with a pulsed xenon lamp. Analysis of fluorescence decay curves were subjected to fit a bi-exponential decay. The instrument response function (IRF) measures the scattering of laser excitation from



Fig. 2. (a) Fluorescence spectra of DTPE versus H<sub>2</sub>O fraction in THF/H<sub>2</sub>O mixtures. Inset: photographs of DTPE in pure THF (left) and mixed solvent with 95% H<sub>2</sub>O (right). (b) Fluorescence spectra of molecule DTPE in CHCl<sub>3</sub> and NPs of DTPE in water. Inset: the Tyndall effect of (1) DTPE in CHCl<sub>3</sub> and (2) NPs of DTPE in water; photographs of (3) DTPE in CHCl<sub>3</sub> and (4) NPs of DTPE in water under UV lamp irradiation.  $\lambda_{ex} = 365$  nm, [DTPE] =  $5 \times 10^{-5}$  M.

non-fluorescent control samples to determine the fastest possible response of the detectors. The quantum yields were carried out on a FS5 instrument with the integrating sphere. The CIE (Commission Internationale de l'Eclairage) 1931 coordinates were calculated with the method of color matching functions.

# 2.2. Synthesis

As shown in Scheme 1, compound **DTPE** was synthesized by Suzuki coupling reaction of bromotriphenylethylene and 4-formylphenylboronic acid followed by acetalization of the resulting intermediate **1** with pentaerythritol under nitrogen protection.

# 2.2.1. Synthesis of 1

Compound 1 was synthesized according to literature report [53]. To a flask equipped with a magnetic stirrer, bromotriphenylethylene (1.34 g, 4.0 mmol), 4-formylphenylboronic acid (0.90 g, 6.0 mmol), and THF (40 mL) were charged under a nitrogen atmosphere. A solution of tetrabutylammonium bromide (0.01 g) and  $K_2CO_3$  (0.66 g, 4.8 mmol) in water was added dropwise to the mixture. The mixture was stirred at room temperature for 30 min. Tetrakis (triphenylphosphine) palladium (0.23 g, 0.2 mmol) was added quickly and the reaction mixture was heated to reflux at 90 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate (50 mL × 3). The organic layer was combined and dried with anhydrous MgSO<sub>4</sub>. The crude product was purified by silica gel chromatography (PE: EA = 3 : 1,  $\nu/\nu$ ) to afford compound 1 as a yellow solid (1.35 g, 93%). Mp. 156–157 °C [54]; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 9.90 (s, 1H, CHO), 7.63–7.60 (m, 2H, ArH), 7.20–7.18 (m, 2H, ArH), 7.14–7.11 (m, 9H, ArH), 7.03–7.01 (m, 6H, ArH) (Fig. S7).

# 2.2.2. Synthesis of DTPE

To a flask equipped with a magnetic stirrer, compound 1 (1.89 g, 5.2 mmol), p-toluenesulfonic acid (0.03 g, 0.1 mmol), and toluene (50 mL) were charged under an argon atmosphere. A suspension of pentaerythritol (0.35 g, 2.6 mmol) in toluene (50 mL) was added to the mixture. The reaction mixture was heated to reflux for 6 h. After cooled down to room temperature, the reaction mixture was extracted with DCM (50 mL  $\times$  3). The organic layer was dried with anhydrous MgSO<sub>4</sub>. The crude product was purified by silica gel chromatography (PE: EA =  $2:1, \nu/\nu$ ) to afford compound DTPE as a white solid (0.82 g, 38%). Mp. 149.6–151.3 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.21 (d, J = 8.2 Hz, 4H, ArH), 7.10–6.96 (m, 34H, ArH), 5.35 (s, 2H, CH), 4.80 (d, J = 10.8 Hz, 2H, CH<sub>2</sub>), 3.78 (d, J = 11.6 Hz, 4H, CH<sub>2</sub>), 3.59 (d, J = 11.6 Hz, 2H, CH<sub>2</sub>) (Fig. S8); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ (ppm): 144.7, 143.7, 143.6, 143.5, 141.3, 140.4, 135.8, 131.4, 131.3, 127.8, 127.6, 126.5, 126.4, 125.5, 102.4, 71.1, 70.6, 32.5 (Fig. S9); HRMS (ESI): m/z calcd. for  $C_{59}H_{49}O_4$  821.3625 [M + H]<sup>+</sup>, found: 821.3606 (Fig. S10).

## 2.3. Preparation of the NPs

Different types of **DTPE/NR** in a certain molar ratio (80:1, 100:1, 150:1, 200:1, 250:1, 500:1, 750:1, and 1000:1) were dissolved in a small amount of chloroform (250  $\mu$ L) with a constant **DTPE** concentration (2 mM). This organic solution was emulsified in water (10 mL) by ultrasonication with **CTAB** as a surfactant (0.8 mM). By centrifuging and decanting the supernatant, the obtained NPs could be observed by SEM.

# 3. Results and discussion

#### 3.1. AIE property and preparation of NPs

To ensure the AIE property of **DTPE**, the emission of **DTPE** in THF/ H<sub>2</sub>O solutions were tested. As shown in Fig. 2a, there is no emission when it was dissolved in pure THF (a good solvent). When the water (a poor solvent) content was gradually increased to 65%, a moderate emission was observed. As H<sub>2</sub>O increased to 90%, the fluorescence intensity shows a prominent continuous increase. This excellent AIE property encourages us to prepare fluorescent NPs based on DTPE, which were prepared by the mini-emulsion method [51,52]. To an aqueous solution of CTAB (10 mL, [CTAB] = 0.8 mM), DTPE (2 mM) in CHCl3 (250 µL) was added, followed by ultrasonication for 30 min to afford the NPs. The formation of luminescent NPs was first evidenced by the Tyndall effect and AIE phenomenon. The aqueous solution of DTPE dispersed by CTAB shows a clear Tyndall effect, indicating the formation of nanoaggregates (Fig. 2b, inset: (2)). By contrast, the solution of DTPE in CHCl<sub>3</sub> has no Tyndall effect owing to its molecular dissolution in CHCl<sub>3</sub> (Fig. 2b, inset: (1)). Furthermore, the NPs exhibited strong blue fluorescence due to AIE under UV lamp irradiation (Fig. 2b, inset: (4)). On the contrary, the solution of DTPE in CHCl3 has no fluorescence



Fig. 3. (a) Normalized emission spectra of DTPE NPs in water and NR in CHCl<sub>3</sub>, respectively ( $\lambda_{ex} = 365$  nm), and normalized absorption spectrum of both DTPE and NR in water. (b) DLS data of DTPE/NR NPs in water at 25 °C. (c) SEM image of DTPE/NR NPs. (d) TEM image of DTPE/NR NPs. Composition of the NPs: CTAB micelles including DTPE and NR, molar ratio of DTPE/NR = 80/1 ([DTPE] = 5 × 10<sup>-5</sup> M).

under the same condition (Fig. 2b, inset: (3)). These phenomena can also be observed from fluorescence spectra (Fig. 2b). The absolute fluorescence quantum yield of the resultant NPs was determined to be 36.72% by employing an FS5 fluorescence spectrometer (Edinburgh Instrument) (Fig. S3a). The remarkable emission of **DTPE** NPs in water should be due to the restriction of motion of TPE group in a confined space.

## 3.2. Absorption and emission spectra and morphologies of DTPE/NR NPs

Considering the excellent AIE property and the potential nanochannels inside the NPs due to the rigid acetal-based spirocyclic skeleton of DTPE, the NPs would be an ideal candidate for fabricating artificial light-harvesting platform. Therefore, the commercially available dye NR was selected as an energy acceptor owing to the good overlap between emission spectrum of the DTPE and absorption spectrum of NR (Fig. 3a). It should be noting that the absorption spectrum of NR in Fig. 3a was normalized. The actual absorption intensity of the acceptor (NR) at the donor excitation wavelength (365 nm) was negligible, especially at low acceptor concentrations (a maximum of 1.25 mol % was used, D/A = 80/1), which ruled out the possibility for direct excitation of NR on excitation of the donor (Fig. S1). Thus, it is more negligible when the quantity of NR is further reduced (D/A = 100/1-1000/1). Moreover, there is no emission when individual NR NPs in water was excited at 365 nm. Due to the potential nano-channels inside the NPs, the hydrophobic NR can be easily loaded into the hydrophobic micro-environment of the NPs by mini-emulsifying DTPE and NR simultaneously. In this case, the distance between the donor and the acceptor will be greatly shortened, which guarantees an efficient FRET process. The size and morphologies of DTPE/NR NPs were characterized by dynamic light scattering (DLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). DLS measurements

suggested that the NPs are well-defined nano-assemblies with a narrow distribution, presenting an average hydro-dynamic diameter of 174 nm (Fig. 3b). The SEM and TEM images of the NPs showed a regular spherical morphology with diameters around 150 nm (Fig. 3c and d).

# 3.3. The energy transfer process and antenna effect of DTPE/NR NPs

With the DTPE/NR NPs in hand, the energy transfer process and antenna effect were thoroughly studied. Titration of NR gradually lowered the emission of DTPE (donor, D) at 471 nm while enhanced that of the NR (acceptor, A) at 583 nm when excited at 365 nm (Fig. 4a). Meantime, the fluorescent color was changed from blue to red (Fig. 4a, inset). These observations clearly indicate that energy transfer has occurred from the donor to the acceptor. Simultaneously, the fluorescence quantum yield of DTPE/NR NPs (37.67%; Fig. S3b) shows a similar value to individual DTPE NPs, suggesting that the ternary NPs maintained a good fluorescence stability in water. To evaluate the energy transfer process more deeply, the energy-transfer efficiency ( $\Phi_{ET}$ ) of this system is measured. The calculation of  $\Phi_{ET}$  is based on the fluorescence quenching rate of DTPE. With D/A ratios of 80:1, 100:1, 150:1, 200:1, 250:1, 500:1, 750:1, and 1000:1, the  $\Phi_{\text{ET}}$  resulted in 75.9%, 71.0%, 62.5%, 56.6%, 46.9%, 36.4%, 27.8%, and 15.3%, respectively (Fig. S4 and Table S3).

In addition to evaluating the energy transfer process by employing  $\Phi_{ET}$ , the light-harvesting ability is evaluated by the "antenna effect (AE)", the definition of which is the ratio of the fluorescence intensity of the acceptor upon excitation of the donor to that of the direct excitation of the acceptor [39]. In our case, the AE was calculated based on the fluorescence enhancement ratio of **NR**:

$$AE = (I_{DA, 365} - I_{D,365}) / I_{DA,471}$$
 (eq. 1)



Fig. 4. (a) Fluorescence spectra of DTPE/NR NPs in water with different concentrations of NR. Inset: photographs of NPs of DTPE ([DTPE] =  $5 \times 10^{-5}$  M) and DTPE/NR ([DTPE] =  $5 \times 10^{-5}$  M, [NR] =  $6.25 \times 10^{-7}$  M). (b) Fluorescence decay profiles of NPs of DTPE and DTPE/NR. [DTPE] =  $5 \times 10^{-5}$  M, [NR] =  $6.25 \times 10^{-7}$  M.

Where  $I_{DA,365}$  and  $I_{DA,471}$  are the fluorescence intensities of NR at 583 nm upon excitation of the NPs at 365 nm (excitation of the donor) and at 471 nm (the direct excitation of NR), respectively.  $I_{D,365}$  is the residual fluorescence intensity of the individual DTPE NPs at 583 nm when excited at 365 nm, which was normalized with the DTPE-NR assembly at 471 nm. Due to the fluorescence intensity of NR at 583 nm includes the residue of DTPE, the actual fluorescence intensity of NR at 583 nm should be adjusted by subtracting  $I_{D,365}$ .

With increasing D/A ratios from 80:1 to 100:1, 150:1, 200:1, 250:1, 500:1, 750:1, and 1000:1, the AE were calculated to be 46, 51, 55, 62, 66, 58, 48, and 44, respectively (Fig. S5 and Table S4). It is worth noting that the AE can reach 66 when D/A is 250:1 ( $\Phi_{\rm ET}$  = 46.9%). To the best of our knowledge, this is the highest AE in an aqueous system compared to previous reports [26,27]. In a control experiment, by employing a monomer compound tetraphenylethylene (TPE), which is without the rigid spirocyclic structure, as donor to construct NPs (Scheme S1), the fluorescence intensity of TPE decreased upon the addition of NR (Fig. S6), suggesting that the energy could be absorbed by NR. However, there is no emission peak from NR, indicating that the AE is 0. It may be because NR cannot be well distributed in such NPs and

aggregation-caused quenching therefore occurs. Thus, the acetal-based spirocyclic skeleton is a key factor for the realization of efficient light-harvesting capability.

In order to further investigate the energy transfer behavior inside the NPs, time-resolved fluorescence experiments were carried out. The transient fluorescence profiles were fitted by a double exponential decay. The NPs with individual **DTPE** showed the fluorescence lifetimes of  $\tau_1 = 3.29$  ns and  $\tau_2 = 7.52$  ns when detecting at 471 nm (Fig. 4b and Table S1). On the contrary, the fluorescence lifetimes of the **DTPE/NR** NPs (D/A = 80/1) decreased to  $\tau_1 = 1.62$  ns and  $\tau_2 = 3.62$  ns, demonstrating that the energy was successfully transferred from **DTPE** donor to the **NR** acceptor, which is consistent with steady-state fluorescence spectroscopy. These data suggest that the resultant **DTPE/NR** NPs can act as an ideal light-harvesting platform in aqueous solution.

## 3.4. The tunable emission property of DTPE/NR NPs

Thanks to the flexibility of the construction strategy, the tunable emission property of the DTPE/NR NPs was further investigated. As we can see from the CIE 1931 chromaticity diagram (Fig. 5a), the systems exhibited D/A ratio-dependent fluorescence variations. The NPs with individual DTPE locates in the blue area. With the D/A ratio decreased from 1000:1 to 80:1, the fluorescence color changed from blue to red gradually (Fig. 5a and c) due to the different extent of the energy transfer. It is noteworthy that a white-light emission was achieved when the molar ratio of D/A = 150:1 (Fig. 5a and c). The white-light fluorescence color was tested to be (0.33, 0.32) in the CIE coordinate (Fig. 5a), which is in line with the pure white color coordinate (0.33, 0.33). At this moment, the  $\Phi_{ET}$  is 62.5% and the antenna effect is up to 55. Moreover, the white fluorescence quantum yield is 42.63%, which was continuously enhanced with the increasing acceptor (Fig. S3c). The fluorescence lifetimes of the white-light NPs were determined to be  $\tau_1 =$ 2.62 ns and  $\tau_2 = 5.72$  ns, which were shorter than individual **DTPE** but longer than NPs with D/A = 80:1. This artificial light-harvesting system is not only stable in solution but also stable in the solid-state, which is evidenced by the application of such system for security ink. Upon writing the pre-prepared solutions on an art paper, no colorful letter was observed under natural light (Fig. 5b, upper), but obvious colorful letters including a white letter "W" were clearly observed under a UV lamp irradiation (Fig. 5b, down). Compared to conventional fluorescent inks, the resultant fluorescent ink is an aqueous system with AIE property. It can emit bright fluorescence both in aqueous solution and in the solid state (eg. words on paper). Furthermore, the color (emission) of such fluorescent ink could be continuously tuned from blue through white to red just by simply adjusting the D/A ratio. As a result, we successfully use this energy transfer system to achieve data encryption and anticounterfeiting functions.

#### 4. Conclusions

In conclusion, a highly efficient light-harvesting system in water has been self-assembled by employing three small organic molecules: **CTAB** as surfactant, **DTPE** as donor, and **NR** as acceptor. Owing to the special rigid spirocyclic structure of the donor, the acceptor could be distributed rationally inside the NPs to avoid ACQ and induce efficient FRET process. By simply adjusting the D/A ratio, tunable emission including a white-light emission can be realized. Notably, an ultrahigh antenna effect of 66 was achieved at a higher donor/acceptor ratio of 250/1. Moreover, such NPs are also stable in the solid state, endowing it with the capability as security inks for anti-counterfeiting techniques. The



**Fig. 5.** (a) The CIE chromaticity diagram of photoluminescence color changes by varying the ratios of chromophores, and the white-light emitting coordinate. (b) Letters written by the fluorescent inks: photographs under natural light (upper) and UV light (down). (c) Photographs of NPs in water with different D/A ratios.

current system opens a new window for mimicking light-harvesting and developing new dynamic luminescent materials by employing the selfassembly of simple organic molecules.

# 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 this paper.

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# Appendix A. Supplementary data

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#### References

- [1] Wigginton NS. Artificial photosynthesis steps up. Science 2016;352(6290):1185-6.
- [2] Schulze M, Kunz V, Frischmann PD, Würthner F. A supramolecular ruthenium macrocycle with high catalytic activity for water oxidation that mechanistically mimics photosystem II. Nat Chem 2016;8(6):576–83.
- [3] Gust D, Moore TA. Mimicking photosynthesis. Science 1989;244(4900):35–41.
- [4] Arnon DI. Conversion of light into chemical energy in photosynthesis. Nature 1959; 184(4679):10–21.
- [5] Otsuki J. Supramolecular approach towards light-harvesting materials based on porphyrins and chlorophylls. J Mater Chem 2018;6(16):6710–53.
- [6] Peng H-Q, Niu L-Y, Chen Y-Z, Wu L-Z, Tung C-H, Yang Q-Z. Biological applications of supramolecular assemblies designed for excitation energy transfer. Chem Rev 2015;115(15):7502–42.
- [7] Rao KV, Datta KKR, Eswaramoorthy M, George SJ. Light-harvesting hybrid assemblies. Chem Eur J 2012;18(8):2184–94.

- [8] Collini E, Wong CY, Wilk KE, Curmi PMG, Brumer P, Scholes GD. Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature. Nature 2010;463(7281):644–7.
- [9] Xiao T, Zhong W, Zhou L, Xu L, Sun X-Q, Elmes RBP, et al. Artificial lightharvesting systems fabricated by supramolecular host–guest interactions. Chin Chem Lett 2019;30(1):31–6.
- [10] Kundu S, Patra A. Nanoscale strategies for light harvesting. Chem Rev 2017;117 (2):712–57.
- [11] Wu G, Huang Z, Scherman OA. Quantitative supramolecular heterodimerization for efficient energy transfer. Angew Chem Int Ed 2020;59(37):15963–7.
- [12] Guo S, Song Y, He Y, Hu XY, Wang L. Highly efficient artificial light-harvesting systems constructed in aqueous solution based on supramolecular self-assembly. Angew Chem Int Ed 2018;57(12):3163–7.
- [13] Pullerits T, Sundström V. Photosynthetic Light-harvesting pigment-protein complexes: toward understanding how and why. Acc Chem Res 1996;29(8):381-9.
- [14] Wu PG, Brand L. Resonance energy transfer: methods and applications. Anal Biochem 1994;218(1):1–13.
- [15] Hong Y, Lam JWY, Tang BZ. Aggregation-induced emission. Chem Soc Rev 2011; 40(11):5361–88.
- [16] Luo J, Xie Z, Lam JWY, Cheng L, Chen H, Qiu C, et al. Aggregation-induced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem Commun 2001;(18): 1740–1.
- [17] Li W-S, Aida T. Dendrimer porphyrins and phthalocyanines. Chem Rev 2009;109 (11):6047–76.
- [18] Pruchyathamkorn J, Kendrick WJ, Frawley AT, Mattioni A, Caycedo-Soler F, Huelga SF, et al. A complex comprising a cyanine dye rotaxane and a porphyrin nanoring as a model light-harvesting system. Angew Chem Int Ed 2020;132(38): 16597–600.
- [19] Đorđević L, Demitri N, Bonifazi D. Solvent-dependent moulding of porphyrin-based nanostructures: solid state, solution and on surface self-assembly. Supramol Chem 2016;28(9–10):753–61.
- [20] Qin Y, Liu X, Jia P-P, Xu L, Yang H-B. BODIPY-based macrocycles. Chem Soc Rev 2020;49(16):5678–703.
- [21] Zhang Z, Zhao Z, Hou Y, Wang H, Li X, He G, et al. Aqueous platinum(II)-cagebased light-harvesting system for photocatalytic cross-coupling hydrogen evolution reaction. Angew Chem Int Ed 2019;58(26):8862–6.
- [22] Acharyya K, Bhattacharyya S, Sepehrpour H, Chakraborty S, Lu S, Shi B, et al. Selfassembled fluorescent Pt(II) metallacycles as artificial light-harvesting systems. J Am Chem Soc 2019;141(37):14565–9.
- [23] Ji L, Sang Y, Ouyang G, Yang D, Duan P, Jiang Y, et al. Cooperative chirality and sequential energy transfer in a supramolecular light-harvesting nanotube. Angew Chem Int Ed 2019;58(3):844–8.
- [24] Zhao Q, Chen Y, Li SH, Liu Y. Tunable white-light emission by supramolecular selfsorting in highly swollen hydrogels. Chem Commun 2018;54(2):200–3.

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- [25] Inagaki S, Ohtani O, Goto Y, Okamoto K, Ikai M, Yamanaka K-i, et al. Light harvesting by a periodic mesoporous organosilica chromophore. Angew Chem Int Ed 2009;48(22):4042–6.
- [26] Xu L, Wang Z, Wang R, Wang L, He X, Jiang H, et al. A conjugated polymeric supramolecular network with aggregation-induced emission enhancement: an efficient light-harvesting system with an ultrahigh antenna effect. Angew Chem Int Ed 2020;59(25):9908–13.
- [27] Sun G, Qian W, Jiao J, Han T, Shi Y, Hu X-Y, et al. A highly efficient artificial lightharvesting system with two-step sequential energy transfer based on supramolecular self-assembly. J Mater Chem 2020;8(19):9590–6.
- [28] Zhu X, Wang J-X, Niu L-Y, Yang Q-Z. Aggregation-induced emission materials with narrowed emission band by light-harvesting strategy: fluorescence and chemiluminescence imaging. Chem Mater 2019;31(9):3573–81.
- [29] Wang XH, Song N, Hou W, Wang CY, Wang Y, Tang J, et al. Efficient aggregationinduced emission manipulated by polymer host materials. Adv Mater 2019;31(37): 1903962.
- [30] Li JJ, Chen Y, Yu J, Cheng N, Liu Y. A supramolecular artificial light-harvesting system with an ultrahigh antenna effect. Adv Mater 2017;29(30):1701905.
- [31] Xu Z, Peng S, Wang YY, Zhang JK, Lazar Alexandra I, Guo DS. Broad-spectrum tunable photoluminescent nanomaterials constructed from a modular lightharvesting platform based on macrocyclic amphiphiles. Adv Mater 2016;28(35): 7666–71.
- [32] Sun Y, Guo F, Zuo T, Hua J, Diao G. Stimulus-responsive light-harvesting complexes based on the pillararene-induced co-assembly of β-carotene and chlorophyll. Nat Commun 2016;7:12042.
- [33] Wang P, Miao X, Meng Y, Wang Q, Wang J, Duan H, et al. Tetraphenylethene-based supramolecular coordination frameworks with aggregation-induced emission for an artificial light-harvesting system. ACS Appl Mater Interfaces 2020;12(20): 22630–9.
- [34] Chen XM, Cao Q, Bisoyi HK, Wang M, Yang H, Li Q. An efficient near-infrared emissive artificial supramolecular light-harvesting system for imaging in the Golgi apparatus. Angew Chem Int Ed 2020;59(26):10493–7.
- [35] Xiao T, Zhou L, Wei X, Li Z, Sun X. Supramolecular copolymers driven by quadruple hydrogen bonding and host-guest interactions. Chin J Org Chem 2020; 40(4):944–9.
- [36] Jia L, Niu LY, Wang LY, Wang X, Yang QZ. A FRET-based supramolecular nanoprobe with switch on red fluorescence to detect SO<sub>2</sub> derivatives in living cells. J Mater Chem B 2020;8(7):1538–44.
- [37] Li JJ, Zhang HY, Dai XY, Liu ZX, Liu Y. A highly efficient light-harvesting system with sequential energy transfer based on a multicharged supramolecular assembly. Chem Commun 2020;56(44):5949–52.
- [38] Li C, Zhang J, Zhang S, Zhao Y. Efficient light-harvesting systems with tunable emission through controlled precipitation in confined nanospace. Angew Chem Int Ed 2019;58(6):1643–7.
- [39] Dutta PK, Varghese R, Nangreave J, Lin S, Yan H, Liu Y. DNA-directed artificial light-harvesting antenna. J Am Chem Soc 2011;133(31):11985–93.

- [40] Miller RA, Presley AD, Francis MB. Self-assembling light-harvesting systems from synthetically modified tobacco mosaic virus coat proteins. J Am Chem Soc 2007; 129(11):3104–9.
- [41] Li Y, Dong Y, Cheng L, Qin C, Nian H, Zhang H, et al. Aggregation-induced emission and light-harvesting function of tetraphenylethene-based tetracationic dicyclophane. J Am Chem Soc 2019;141(21):8412–5.
- [42] Zhao Y-C, Zhang L-M, Wang T, Han B-H. Microporous organic polymers with acetal linkages: synthesis, characterization, and gas sorption properties. Polym Chem 2014;5(2):614–21.
- [43] Han Y, Zhang L-M, Zhao Y-C, Wang T, Han B-H. Microporous organic polymers with ketal linkages: synthesis, characterization, and gas sorption properties. ACS Appl Mater Interfaces 2013;5(10):4166–72.
- [44] Li Z-Y, Su H-K, Zhou K, Yang B-Z, Xiao T, Sun X-Q, et al. Oxo-spirocyclic structure bridged ditopic Schiff base: a turn-on fluorescent probe for selective recognition of Zn(II) and its application in biosensing. Dyes Pigments 2018;149:921–6.
- [45] Xiao T, Zhong W, Yang W, Qi L, Gao Y, Sue ACH, et al. Reversible hydrogenbonded polymerization regulated by allosteric metal templation. Chem Commun 2020;56(92):14385–8.
- [46] Xiao T, Zhong W, Qi L, Gu J, Feng X, Yin Y, et al. Ring-opening supramolecular polymerization controlled by orthogonal non-covalent interactions. Polym Chem 2019;10(24):3342–50.
- [47] Xiao T, Xu L, Wang J, Li Z-Y, Sun X-Q, Wang L. Biomimetic folding of small organic molecules driven by multiple non-covalent interactions. Org Chem Front 2019;6 (7):936–41.
- [48] Xiao T, Xu L, Götz J, Cheng M, Würthner F, Gu J, et al. Supramolecular polymerization and cyclization of dioxynaphthalene motif bridged bifunctional UPys: minor variations in the molecular skeleton and drastic differences in selfassembly. Mater Chem Front 2019;3(12):2738–45.
- [49] Xiao T, Qi L, Zhong W, Lin C, Wang R, Wang L. Stimuli-responsive nanocarriers constructed from pillar[n]arene-based supra-amphiphiles. Mater Chem Front 2019; 3(10):1973–93.
- [50] Xiao T, Wu H, Sun G, Diao K, Wei X, Li ZY, et al. An efficient artificial lightharvesting system with tunable emission in water constructed from a H-bonded AIE supramolecular polymer and nile red. Chem Commun 2020;56(80):12021–4.
- [51] Peng HQ, Xu JF, Chen YZ, Wu LZ, Tung CH, Yang QZ. Water-dispersible nanospheres of hydrogen-bonded supramolecular polymers and their application for mimicking light-harvesting systems. Chem Commun 2014;50(11):1334–7.
- [52] Zhu Y, Xu L, Wang L, Tang H, Cao D. Effect of scaffold structures on the artificial light-harvesting systems: a case study with an AIEE-active pillar[5]arene dyad. Chem Commun 2019;55(42):5910–3.
- [53] Li C, Zhang J, Zhang S, Zhao Y. Efficient light-harvesting systems with tunable emission through controlled precipitation in confined nanospace. Angew Chem Int Ed 2019;58(6):1643–7.
- [54] Jayaram DT, Ramos-Romero S, Shankar BH, Garrido C, Rubio N, Sanchez-Cid L, Gómez SB, Blanco J, Ramaiah D. In vitro and in vivo demonstration of photodynamic activity and cytoplasm imaging through TPE nanoparticles. ACS Chem Biol 2016;11(1):104–12.