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Artificial Light-Harvesting Systems Based on AlEgen-branched Rotaxane Dendrimers for Efficient Photocatalysis

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Abstract: Aiming at the construction of novel platform for efficient light harvesting, the precise synthesis of a new family of AlEgenbranched rotaxane dendrimers was successful realized from an AlEgen-functionalized [2]rotaxane through a controllable divergent approach. In the resultant AlE macromolecules, up to twenty-one AlEgens located at the tails of each branches, thus making them the first successful example of AlEgen-branched dendrimers. Attributed to the solvent-induced switching feature of the rotaxane branches, the integrated rotaxane dendrimers displayed interesting dynamic feature upon the aggregation-induced emission (AIE) process. Moreover, novel artificial light-harvesting systems were further constructed based on these AlEgen-branched rotaxane dendrimers, which revealed impressive generation-dependent photocatalytic performances for both photooxidation reaction and aerobic cross-dehydrogenative coupling (CDC) reaction.

Introduction

Inspired by the natural photosynthesis process, great efforts have been paid on the construction of novel artificial light harvesting systems (LHSs) aiming at not only the indepth understanding of some key aspects of the natural photosynthetic process such as photoinduced electron transfer and energy transfer but also developing clean and sustainable energy to combat global energy issues.¹ In particular, to achieve satisfactory energy collection efficiency, in addition to the relatively high donor to acceptor ratio, the other prime factor is the densely packed arrangements of donors.² However, such tight and compact arrangements usually lead to the quenching of the fluorescence of the donors due to the aggregation-caused quenching (ACQ) effect, which might result in reduced energy collection efficiencies.³ Over the past few years, to suppress such ACQ effect, a growing interest in the construction of novel artificial LHSs based on luminogens with aggregation-induced emission (AIE) characteristics (i.e. AIEgens) has been witnessed.⁴ In contrast to traditional fluorescent molecules with ACQ characteristics, AIEgens reveal high emission in aggregated states because of the restricted intramolecular motion (RIM), thereby making them excellent candidates as donors for the construction of novel artificial LHSs.⁵ Moreover, besides the choices of suitable donors, the accurate positioning of these donors, which will directly influence the key energy transfer process, are also crucial for efficient light harvesting.⁶ To achieve this goal, dendrimers have evolved to be privileged and most frequently used platforms for the constructions of artificial LHSs due to their unique highly branched and starshaped feature as well as well-tuned structures for well-defined arrangements of chromophores.⁷ During the past few decades, pioneered by Fréchet, Aida, Vögtle, and Balzani *et al.*, diverse light-harvesting dendrimers have been successfully constructed, which have shown great potentials for practical applications beyond just solar energy conversion.⁸

Considering the aforementioned attractive photophysical feature of AIEgens and unique structural feature of dendrimers, the integrated AIEgen-based dendrimers are expected to be ideal and promising platforms for the construction of novel artificial LHSs. However, to our surprise, compared with the widely-investigated AIEgen-based polymers,⁹ AIEgen-based dendrimers have been rarely explored and the research in their applications for light-harvesting have never been conducted. In particular, possibly due to the lack of suitable AIEgen units with specific substituent functional groups for dendrimer growth, currently no reports on dendrimers with AIEgens at either the branches or the branching points, which could be defined as AlEgen-branched dendrimers, have been demonstrated. Notably, compared with AIEgen-cored or AIEgen-terminated dendrimers with the AIEgens units located at either cores¹⁰ or peripheries¹¹ of the dendrimers (Figure 1a-b), respectively, in AIEgenbranched dendrimers (Figure 1c-d), the AIEgen units are precisely arranged with the skeleton of dendrimers in a monodispersed manner. Such well-defined skeleton of AIEgenbranched dendrimers thus results in a higher density of AIEgens, which is crucial for light harvesting. Moreover, based on such high density of AlEgens, the dendrimer skeleton should inherently impose more pronounced steric hindrance effect on the free motion of the embedded AIEgen units, which might lead to an enhanced AIE effect and better AIE performance. Attributed to these attractive features, the design and synthesis of AlEgen-branched dendrimers and the further exploration of their applications in light harvesting will be of great importance.

Herein, based on our on-going interests in mechanically (MIMs),¹² molecules especially interlocked rotaxane dendrimers,¹³ a new family of interlocked AIEgen-branched dendrimers, i.e. rotaxane dendrimers with multiple AIEgens at the branches (Figure 1e), were designed and synthesized for the first time. In particular, the unique structural and dynamic features of the rotaxane dendrimers endowed the resultant AIEactive macromolecules with interesting AIE behaviors. Moreover, these AIE macromolecules were further employed for the construction of novel artificial LHSs, which were proven to be highly efficient photocatalysts for both photooxidation reaction and aerobic cross-dehydrogenative coupling (CDC) reaction.

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strategy of this work. AlEgen-cored dendrimers (a), AlEgen-terminated dendrimers (b), AlEgen-branched dendrimers (c and d), and AlEgen-branched rotaxane dendrimers presented in this work for the construction of novel artificial light harvesting systems (e).

Results and Discussion

Synthesis and Characterization of the TPE-branched Rotaxane Dendrimers. In this study, a new TPE-functionalized [2]rotaxane¹⁴ TPE-R was designed as the key building block (Figure 2). In the [2]rotaxane, the pillar[5]arene macrocycle S3 functionalized with two TIPS-protected alkynes was employed as the wheel components.¹⁵ It should be noted that the TIPSprotected alkynes could be gently converted to the alkyne group that further serves as reactive sites for dendrimer growth. In addition, the bulky TPE moiety, one of the most typical AIEgens, was chosen as one stopper in the axle component, and the monosubstituted platinum-acetylide moiety was selected as not only another stopper but also the dendrimer growth sites.¹⁶ More importantly, to endow the targeted AIEgen-branched rotaxane dendrimers with dynamic features, the urea moiety¹⁷ was introduced as the stimuli-responsive site into the axle component. According to such design strategy, the targeted [2]rotaxane TPE-R was successfully prepared in 80% yield on a gram scale through the threading-followed-by-stoppering strategy (Scheme S1).

With the obtained TPE-functionalized [2]rotaxane TPE-R in hand, the targeted AIEgen-branched rotaxane dendrimers were then prepared through a controllable divergent approach. As outlined in Figure 2, the reaction of TPE-R with 1, 3, 5triethynylbenzene as the core module using Cul as catalyst resulted in the first-generation TPE-branched rotaxane dendrimer TG1 in 83% yield. The subsequent deprotection of TG1 with tetrabutylammonium fluoride trihydrate (Bu₄NF·3H₂O) gave rise to the intermediate TG1-YNE with six alkyne groups, which was further employed as the starting material for the synthesis of the second-generation TPE-branched rotaxane dendrimer TG2 with nine TPE moieties in 70% yield through the reaction with TPE-R. By repeating such deprotection-coupling process, the synthesis of the third-generation TPE-branched rotaxane dendrimer TG3 with twenty-one TPE moieties was then successfully achieved.

The resultant TPE-branched rotaxane dendrimers TG1-TG3 was investigated by extensive characterizations including 1-D multinuclear (1H, 13C, and 31P) and MALDI-TOF-MS analysis (Figures S14-S26). For instance, for TG1 and TG2, by the means of mass analysis, the successful synthesis of the targeted rotaxane dendrimers was confirmed (Figures S25-S26). However, in the case of TG3, continuous attempts for MS analysis has been failed possibly due to its large molecular mass (M = 48917 Da) and low ionization efficiency. Thus GPC experiments were then performed to evaluate the monodispersity of these TPE-branched rotaxane dendrimers. To our delight, as shown in the GPC curves, for each rotaxane dendrimer, only a single peak with narrow distribution for the number-averaged molecular weight (M_n) was observed (Figures S27-S29). Notably, the polydispersity index (PDI) values of all rotaxane dendrimers were around 1.02, suggesting the successful formation of monodisperse TPE-branched rotaxane dendrimers TG1-TG3.

Moreover. two-dimensional (2-D) diffusion-ordered spectroscopy (DOSY) analysis provided additional indirect supports for the successful synthesis of the targeted rotaxane dendrimers (Figures S30-S32). Only one set of signals corresponding to the existence of sole specie was founded in all DOSY spectra of TG1-TG3. More importantly, as revealed by the significant decrease of the diffusion coefficients (D) along with the increase of generations of these rotaxane dendrimers: for TG1, (5.76 \pm 0.12) × 10^{-10} m^2 s^{-1}; for TG2, (2.69 \pm 0.13) × 10^{-10} m² s⁻¹; for **TG3**, (1.58 ± 0.10) × 10^{-10} m² s⁻¹, the monodispersity and progressive size increase of the obtained rotaxane dendrimers were clearly confirmed. Such size changes were further determined by atomic force microscopy (AFM) analysis. According to the AFM images shown in Figure S33, all rotaxane dendrimers TG1-TG3 revealed a uniform sphere-like morphology. Moreover, the gradual increase of the average heights from 4.0 ± 0.1 nm (TG1) to 8.1 ± 0.2 nm (TG2) and 12.5± 0.3 nm (TG3) was observed. According to all these results described above, the successful synthesis of the targeted TPEbranched rotaxane dendrimers TG1-TG3 was confirmed.

AlE Behaviors of the TPE-branched Rotaxane Dendrimers. With the targeted TPE-branched rotaxane dendrimers in hand, their AlE behaviors were then evaluated. In this study, CH_2Cl_2 was selected as the good solvent and MeOH was chosen as the poor solvent, respectively. Due to the existence of the urea moiety in each branch of these rotaxane dendrimers as the stimuli-responsive site, the addition of MeOH was supposed to

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Figure 2. (a) Synthesis of TPE-branched rotaxane dendrimer **TG1** by a Cul-catalyzed coupling reaction of **TPE-R** and 1, 3, 5-triethynylbenzene. (b) Schematic representation of a controllable divergent strategy for the synthesis of TPE-branched rotaxane dendrimers **TG2** and **TG3**. Reaction conditions: (I) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2 h; (b) **TPE-R**, Cul, DCM/Et₂NH, rt, overnight, 70%; (II) (a) Bu₄NF·3H₂O, THF, rt, 2

play dual roles. On one hand, the increase amount of MeOH could significantly change the polarity of the solvent, which might further induce the movement of the pillar[5]arene rings away from the urea moiety to the alkyl chain moiety through the interaction between the urea moiety with the MeOH molecules.¹⁸ On the other hand, such solvent-induced motions of the wheel component would further lead to the modulation of the AIE behaviors of the integrated TPE-branched rotaxane dendrimers, making them attractive as smart AIE-active macromolecules.

To test such hypothesis, the stimuli-responsive behavior of [2]rotaxane TPE-R was firstly evaluated. With the assistance of 2-D ¹H-¹H COSY analysis, the signals of the methylene protons of the alkyl chain were clearly identified. By changing the volume ratios of CD₂Cl₂/CD₃OD that could adjust the solvent polarity, a series of ¹H NMR spectra were recorded. As expected, upon the increase of the fractions of CD₃OD in CD₂Cl₂, obvious downfield shifts of the signals of the methylene protons (H₈₋₁₂) nearby the urea moiety were observed. Meanwhile, the signals of the methylene protons near the platinum-acetylide moiety (H₃₋₇) underwent the obvious upfield shifts (Figure 3a). Such interesting solvent-induced motions of the wheel component of the [2]rotaxane was possibly due to the breaking of the hydrogen bonding between the pillar[5]arene ring and the urea moiety that led to the translational motion of the pillar[5]arene ring, which was in accord with our previous reports on solventinduced switching of similar rotaxanes.13b,13d To confirm such hypothesis, the model [2]rotaxane TPE-RC without the urea moiety was synthesized (Scheme S9). As expected, upon the addition of equivoluminal CD_3OD to the CD_2Cl_2 solution of **TPE-RC**, almost no changes of the ¹H NMR spectra were observed, indicating the urea moiety did act as the stimuli-responsive site (Figure S39).

Similar with [2]rotaxane TPE-R, as revealed by the ¹H NMR study, the resultant TPE-branched rotaxane dendrimers TG1-TG3 displayed similar solvent-induced switching motions of the pillar[5]arene rings located at both the branches and branching points (Figures S41-S46). More importantly, along with such switching process, the arrangements as well as the density of the TPE moieties within the integrated rotaxane dendrimers were further modulated, which might influence the AIE behaviors. To evaluate such effect, the AIE behaviors of the resultant TPEbranched rotaxane dendrimers were then investigated in detail. As revealed by the fluorescence spectra, for all rotaxane dendrimers, they only displayed very weak fluorescence in pure CH₂Cl₂ solution. Upon the gradual increase of the fraction of MeOH (f, vol%) from 30% to 65%, only slight increase of the emission intensity was revealed. By further increasing the f to 65% and finally to 98%, the remarkable enhancement in the emission intensity was observed, thus indicating that all TPEbranched rotaxane dendrimers TG1-TG3 are typical AIEgens. Notably, as the generation of the rotaxane dendrimers increased, the extent of the enhancement in the fluorescence intensity when f increased from 65% to 98% decreased progressively from 31-fold for TG1 and 14-fold for TG2 to 9-fold for TG3 (Figure 3b, d, f). Such trend might be attributed to the more

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Figure 3. AIE behaviors of TPE-branched rotaxane dendrimers TG1-TG3. (a) Cartoon representation of the AIE behaviors of TG3 during which both the arrangements and the density of the TPE moieties within the integrated rotaxane dendrimers were modulated through the solvent-induced switching motions of the pillar[5]arene rings (*top*) and ¹H NMR spectra (CD₂Cl₂, 298 K, 400 MHz) of solvent-induced switching behavior of [2]rotaxane TPE-R (*bottom*); Fluorescence spectra of TG1 (b), TG2 (d), and TG3 (f) in CH₂Cl₂/MeOH with various MeOH fractions ([TPE units] = 30 μ M, λ_{ex} = 345 nm), *inset* photographs of TGn (n = 1, 2, 3) in CH₂Cl₂/MeOH with 50% (*left*) and 98% (*right*) MeOH fractions upon UV lamp excitation (λ_{ex} = 365 nm); TEM images of TG1 (c), TG2 (e), and TG3 (g) in aggregate states.

pronounced depression of free motions of the incorporated TPE units due to the more remarkable steric hindrance effect of the higher-generation dendrimer skeleton, which thus led to a relatively reduced AIE efficiency upon the further aggregation.

To provide additional supports for such AIE phenomenon described above, transmission electron microscopy (TEM) and dynamic light scattering (DLS) analysis were further performed to investigate the aggregation of TG1-TG3. As revealed by the TEM images, the formation of homogenous spherical particles in the aggregated state for all TPE-branched rotaxane dendrimers TG1-TG3 was observed (Figures 3c, e, g). In addition, the DLS results further suggested the formation of nanoscale aggregates of TG1-TG3 in the aggregated state (Figures S73-S75). Notably, the values of the average diameters of the spherical particles in TEM analysis fitted very well with that of the average hydrodynamic diameters (D_h) determined by the DLS analysis (for TG1: 88.0 \pm 5.0 nm from TEM analysis and 81.2 \pm 4.3 nm from DLS analysis; for TG2: 106.0 ± 6.0 nm from TEM analysis and 104.6 ± 8.8 nm from DLS analysis; for TG3: 133.0 ± 4.0 nm from TEM analysis and 126.5 ± 4.9 nm from DLS analysis). Notably, the DLS analysis also indicated an interesting two-step aggregation behaviors of TPE-branched rotaxane dendrimers (Figure S76). The existence of low fraction of MeOH only led to the contraction of the rotaxane dendrimers by driving the translational motion of the pillar[5]arene ring in each branches. With the further increase of the MeOH fractions, the resultant contracted rotaxane dendrimers started to aggregate, thus leading to the formation of larger aggregates.

To evaluate the unique role that the structural and dynamic feature of the rotaxane dendrimers played in their AIE behaviors, two model first-generation dendrimers, *i.e.* **C1** without the pillar[5]arene rings and **C2** without the urea moieties, were synthesized (Scheme S8 and S10). For **C1**, it displayed AIE behavior only if the *f* were above 90%, possibly due to its better

solubility in MeOH compared with **TG1** (Figure S50). While in the case of **C2**, attributed to the absence of urea moieties, ¹H NMR study suggested that it did not show stimuliresponsiveness upon the addition of equivoluminal CD₃OD (Figure S40). It also behaved typical AIE feature similar with **TG1** (Figure S51). However, regarding to the fluorescence quantum yield (Φ_F), both **C1** (0.28%) and **C2** (1.56%) revealed smaller values than that of **TG1** (4.29%) (Table S1), thus highlighting that not only the important role of the dendritic rotaxane skeleton but also the solvent-switching feature of the TPE-branched rotaxane dendrimers, both of which could lead to the restriction of intramolecular rotations (RIR) of the TPE units that contributed to the improvement of the AIE performances.

Construction of Artificial Light-Harvesting Systems Based on the TPE-branched Rotaxane Dendrimers. To further explore the potential applications of these novel AIE macromolecules, the construction of artificial LHSs¹⁹ based on TPE-branched rotaxane dendrimers TG1-TG3 was then investigated. In this study, the fluorescent dye eosin Y (ESY) was chosen as the fluorescence energy acceptor (Figure 4a). First of all, the successful formation of the integrated aggregate of TGn (n = 1, 2, 3) and ESY was confirmed by DLS, TEM, elemental mapping analysis, and fluorescence imaging (Figures S77-S78). For instance, upon mixing ESY and TGn (n = 1, 2, 3) (ESY and the TPE units in a 1:3 ratio) in the aggregate state, remarkable increase of the average hydrodynamic diameters (D_h) was determined by DLS, respectively (Figures S73-S75). Similar trend was also observed from the TEM analysis, from which homogenous spherical particles with increased average diameters were observed (Figure 4b, e, h).

To check the possibility of efficient energy transfer from the rotaxane dendrimers **TGn** (n = 1, 2, 3) to ESY, the adsorption spectrum of ESY and the emission spectra of the rotaxane dendrimer **TG1** were recorded. As show in Figure S53, these

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Figure 4. The construction of artificial LHSs based on TPE-branched rotaxane dendrimers TGn (donor, n = 1, 2, 3) and ESY (acceptor). Cartoon representation of LHSs based on TPE-branched rotaxane dendrimers TG3 and ESY, ET: energy transfer (a); TEM images of TG1-ESY (b), TG2-ESY (e) and TG3-ESY (h) in aggregate states; Fluorescence spectra of TG1 (c), TG2 (f) and TG3 (i) with different ratios of TPE units in TGn-ESY ([TPE units] = 30 μ M, λ_{ex} =345 nm); *inset*: photograph of TGn-ESY in CH₂Cl₂/MeOH with 98% MeOH fractions upon UV lamp excitation (λ_{ex} = 365 nm); Time-resolved fluorescence decay curves of TG1 and TG1-ESY (d), TG2 and TG2-ESY (g), and TG3 and TG3-ESY (j) in the aggregate states (375 nm excitation and 480 nm detection).

two spectra overlap well, suggesting the feasibility for the construction of targeted LHSs. To confirm this hypothesis, the gradual increase of the ratios of ESY in the integrated systems TGn-ESY (n = 1, 2, 3) were performed. To our delight, for all TPE-branched rotaxane dendrimers TG1-TG3, along with such process, the emission intensity at around 480 nm originated from the TPE units in rotaxane dendrimers **TGn** (n = 1, 2, 3) was found to be decreased as indicated by their fluorescence spectra, while a new emission band at around 555 nm derived from ESY appeared and increased upon the excitation at 345 nm (Figure 4c, f, i). According to these phenomena, efficient energy transfer (ET) from the rotaxane dendrimers **TGn** (n = 1, 2, 3) to ESY was suggested. Moreover, as revealed by the fluorescence spectra, slight hypochromic shifts and bathochromic shifts were observed for TPE units and ESY, respectively, indicating the interactions between the rotaxane dendrimers and ESY in the resultant aggregate state.

In addition, such process was further evidenced by the decrease of the fluorescence lifetimes (τ) of the rotaxane dendrimers upon the mixing with ESY as determined by time-correlated single-photon counting (TCSPC) technique (Figure 4d,

g, j). For instance, when the molar ratio of TPE/ESY was kept at 3:1, the fluorescence lifetime of **TG1** was reduced from 1.77 ns to 1.36 ns for **TG1-ESY**. And for **TG2** and **TG3**, the values were from 1.68 ns to 0.91 ns and 1.72 ns to 0.91 ns, respectively. More importantly, according to the ratios of fluorescence intensities of TPE units for rotaxane dendrimers, the energy-transfer efficiencies (Φ_{ET}) were calculated to be 42.5% for **TG1-ESY**, 68.2% for **TG2-ESY**, and 71.6% for **TG3-ESY**, respectively (Figures S57-S59), which are relatively high compared with the previously-reported supramolecular light-harvesting systems.^{19b-f}

Such high energy-transfer efficiencies of these **TGn-ESY** (n = 1, 2, 3) systems encouraged us to further explore their lightharvesting properties. As expected, the fluorescence intensity of ESY excited at 345 nm (absorption wavelength for TPE) was stronger than that obtained by direct excitation at 480 nm (absorption wavelength for ESY), which was in accord with typical light harvesting antenna effect. More importantly, the antenna effects of these **TGn-ESY** (n = 1, 2, 3) systems were calculated to be 1.1 (**TG1-ESY**), 2.3 (**TG2-ESY**), and 4.1 (**TG3-ESY**), respectively, which became larger along with the increase of the generation of the TPE-branched rotaxane dendrimer

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(Figures S62-S64). Such interesting generation effect might be originated from the increasing density of TPE moiety within the skeletons of rotaxane dendrimers **TGn** (n = 1, 2, 3), thus highlighting the unique structural feature of AIEgen-branched dendrimers.



Figure 5. Artificial LHSs based on the TPE-branched rotaxane dendrimers as efficient photocatalysts for photooxidation reaction. (a) The artificial LHSs **TGn-ESY** (n = 1, 2, 3) serve as photosensitizers that can produce ${}^{1}O_{2}$ for photooxidation reaction of 2-(ethylsulfanyl)ethanol to 2-(ethylsulfinyl)ethan-1-ol. The singlet energy was determined by the absorption onset on the lower energy side (345 and 525 nm for the TPE donor and ESY acceptor, respectively), the triplet energy of ESY was copied from a recent report (*Anal. Bioanal. Chem.* **2020**, *412*, 7595.). ET: energy transfer, ISC: intersystem crossing; Kinetic plot for photooxidation of sulfides under UV irradiation (b), fitting of the pseudo-first order kinetic rate constant (c) and the normalized kinetic rate constants (d) catalyzed by **TGn-ESY** (n = 1, 2, 3) and model ones **C1-ESY** and **C2-ESY**. (e) The normalized ${}^{1}O_{2}$ quantum yield of **TGn-ESY** (n = 1, 2, 3) and **C1-ESY** and **C2-ESY**.

Generation Effect of the TPE-branched Rotaxane Dendrimers on Photocatalysis. Towards the mimicking of the nature LHSs as the entry gate of photosynthesis, the resultant TPE-branched rotaxane-dendrimer-based LHSs TGn-ESY (n = 1, 2, 3) were further utilized as photocatalysis for chemical transformations. The photocatalytic processes were monitored by ¹H NMR spectra. Herein, to evaluate the scope of the artificial LHSs as photocatalysts, both photooxidation reaction and aerobic CDC reaction were chosen as the reactions.

Based on the energy transfer process, the artificial LHSs **TGn-ESY** (n = 1, 2, 3) were supposed to be capable of producing singlet oxygen ($^{1}O_{2}$), making them promising photosensitizers for diverse types of reactions especially photooxidation reactions (Figure 5a). Thus the photooxidation of 2-(ethylsulfanyl)ethanol to 2-(ethylsulfinyl)ethan-1-ol was selected as the model reaction.²⁰ Only 3.0 mol % artificial LHSs (based on the TPE units in the rotaxane dendrimers) were employed as photocatalysts. As monitored by ¹H NMR, when using **TG1-ESY**

as the catalyst, full conversion from sulfide to sulfoxide was achieved after 10.0 h of photoirradiation. Moreover, for TG2-ESY and TG3-ESY, the reaction times reduced to 8.0 h and 4.0 h, respectively, to reach the full conversion, thus indicating an impressive generation effect of the TPE-branched rotaxane dendrimers on photocatalysis. Notably, additional artificial LHSs based on the corresponding model dendrimers C1 and C2 were also constructed and tested as photocatalysts, for both of which around 15.0 h of photoirradiation was needed to trigger the full conversion due to their reduced ¹O₂ generation efficiencies and the lower antenna effects, highlighting the superiority of the **TPE-branched** rotaxane dendrimers (Figure 5b). All photocatalytic processes were quantified by their kinetic equations as listed in Table S3, from which the kinetic rate constants k were calculated. Remarkably, the k values of artificial LHSs catalysts TG2-ESY (0.336 h⁻¹) and TG3-ESY (0.685 h⁻¹) were 2.2-fold and 4.4-fold of that of TG1-ESY (0.154 h^{-1}) (Figure 5c, d). In addition, the normalized ${}^{1}O_{2}$ generation efficiency (Φ_0) values of artificial LHSs catalysts **TG2-ESY** and TG3-ESY were 2.3-fold and 4.2-fold of that of TG1-ESY, which was almost identical with the enhancement of the k values (Figure 5e). According to these values, when keeping the amounts of the TPE units the same, artificial LHSs based on higher generation TPE-branched rotaxane dendrimers were proven to display boosted photocatalytic performance, offering a new platform for the construction of efficient photocatalysts.

Table 1. Catalyst comparison data using artificial LHSs as photocatalysts for the aerobic CDC reaction of *N*-phenyl-1, 2, 3, 4-tetrahydroisoquinoline with indole.

1a	+ E	1.0 mol% cat. MeOH, air, 365 nm	
Entry	Catalyst	Time	Yield (%) ^[a]
1	TG3-ESY	4 h	89
2	TG2-ESY	8 h	90
3	TG1-ESY	11 h	95
4	TG1	24 h	trace
5	ESY	24 h	trace
6	No cat.	24 h	none

[a] Isolated yields of products after column chromatography.

In the case of aerobic CDC reaction,²¹ the typical crosscoupling of *N*-phenyl-1, 2, 3, 4-tetrahydroisoquinoline with indole was chosen as the model reaction. To our delight, by using only 1.0 mol % artificial LHSs (based on the TPE units in the rotaxane dendrimers) as catalysts, full conversion was achieved within 11.0 h for **TG1-ESY**, 8.0 h for **TG2-ESY**, and 4.0 h for **TG3-ESY** with the isolated yields of 95%, 90%, and 89%, respectively, again suggesting an attractive generation effect. Control experiments using either sole **TG1** or ESY as catalyst under the same reaction condition only resulted in a trace conversion, indicating that the integrated artificial LHSs did serve as the catalysts (Table 1). Encouraged by such high catalytic activity of the resultant LHSs, the scope of the LHS-

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catalyzed coupling reaction was further examined by using **TG1-ESY** as the photocatalyst. According to the results shown in Figure S88, for indoles with both electron-withdrawing and electron-donating groups, the desired coupling products could be obtained in good to excellent yields. In addition, other nucleophilic substrates such as nitromethane and dimethyl malonate were also applicative for such photocatalyzed aerobic CDC reaction, making the current TPE-branched rotaxane dendrimer-based LHSs excellent candidates as efficient photocatalysts for diverse chemical transformations.

Conclusion

For the first time, the precise synthesis of TPE-branched rotaxane dendrimers as a new family of AIE macromolecules was successfully realized, in which up to twenty-one TPE units were distributed within the dendrimer skeletons in a monodispersed manner. Moreover, due to their unique structural and dynamic features, the resultant TPE-branched rotaxane dendrimers displayed a typical AIE behavior. The addition of MeOH molecules as poor solvent not only induced the motions of the DEP[5]A rings within the dendrimer skeletons but also triggered the aggregation process, jointly leading to the enhancement of the emission. Moreover, by choosing ESY as the acceptor, novel artificial LHSs based on these resultant AIE macromolecules were successfully constructed through multiple energy transfer process, which featured interesting generationdependent antenna effects. Impressively, these LHSs were proven to be efficient photocatalysts for both photooxidation and aerobic CDC reactions, and ones based on higher-generation TPE-branched rotaxane dendrimers revealed the enhanced catalytic performances. The study herein not only realized the first successful synthesis of AIEgen-branched dendrimers but also provided a feasible and promising platform for the construction of novel artificial LHSs for practical applications such as photocatalysis.

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Keywords: light harvesting • aggregation-induced emission • mechanically interlocked molecules • rotaxane dendrimers • photocatalysis

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A novel artificial light-harvesting system based on AIEgen-branched rotaxane dendrimers has been successfully constructed which displayed impressive generation-dependent photocatalytic performances for both photooxidation reaction and aerobic crossdehydrogenative coupling reaction.