ADVANCED FUNCTIONAL MATERIALS
www.afm-journal.de

Artificial Light-Harvesting Material Based on Self-Assembly of Coordination Polymer Nanoparticles

Fang Pu, Li Wu, Enguo Ju, Xiang Ran, Jinsong Ren, and Xiaogang Qu**

Artificial light-harvesting antenna materials as potential mimics for photosynthetic systems have attracted intense attention recently. Herein, a new modular approach to construct light-harvesting material, which involves the self-assembly of coordination polymer nanoparticles (CPNs) at room temperature, is presented. Fluorescence resonance energy transfer (FRET) occurs between donor and acceptor molecules encapsulated in the CPNs, and the emission signal of acceptor is amplified significantly. To the best of our knowledge, this is the first example of artificial light-harvesting material generated from biomolecule-based coordination polymer nanoparticles. The modularity of the material makes it convenient to manipulate the system by changing the composite of CPNs and the type and amount of dyes confined, implying it is a general strategy. The material functions not only in fluid medium, but also in the form of solid state, which extends its application areas greatly. Furthermore, photocurrent generation can be realized by the dye-encapsulated CPNs system upon irradiation with visible light, implying the potential usefulness in light-energy conversion and photoelectronic applications. Besides, the creation of FRET system provides a platform to mimic dual-channel logic gate at nanoscale level, which is beneficial to the construction of integrated logic devices with multiple functions.

1. Introduction

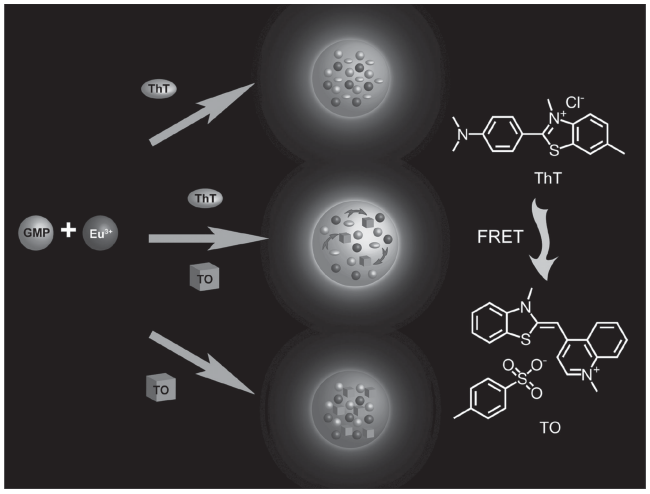
Light-harvesting antenna materials have attracted great interest owing to their applications for sensors,[1–3] photocatalysis,[4] photosynthesis,[5] and optoelectronic devices.[6,7] This kind of systems absorbs solar light and transfers the excitation energy to a reaction centre by highly efficient energy transfer. Fluorescence resonance energy transfer (FRET) plays a key role in the design of light-harvesting antenna molecules. For that, appropriate pair of energy donor and acceptor needs to be organized efficiently. So far, many attempts have been made to mimic natural light-harvesting antenna systems using various materials,[8] including organic molecules,[9] micelles,[10] dendrimers,[11] hydrogels,[12] and porphyrin assemblies.[13] Among them, complex organic molecules or dendrimers provide stable and precise structures by integrating donor and acceptor molecules through covalent interaction. However, the synthesis processes are relatively complicated and organic solvents are needed, which add to the cost and time. Recently, biomolecules have been demonstrated as excellent scaffolds for the construction of artificial light-harvesting systems.[14–16] For example, Zou et al. prepared porous microspheres based on hierarchical co-assembly of dipeptides and porphyrins, which serve as light-harvesting antennae with a relatively broad spectral cross-section and considerable photostability.[17] Nucleic acids offer the unique ability to scaffold chromophores at precise locations and orientations to construct light-harvesting antenna. Kumar et al. demonstrated the first example of light-harvesting units based on DNA-protein complexes.[18] Dutta et al. employed DNA nanotechnology to create a structurally well-defined, DNA-templated light-harvesting antenna.[19] Light-harvesting system consisting of DNA scaffolds, intercalated donor dyes and a porphyrin acceptor anchored to a lipid bilayer was also mimicked.[20] However, these strategies are compromised by the requirement for protein modification or DNA labelling. Lately, metal-organic frameworks (MOFs), also known as coordination polymers generated from assembly of metal ions and organic ligands, have been explored as light-harvesting materials.[21,22] Nevertheless, the macroscopic crystalline MOFs do not always fulfill specific needs for some applications due to limited solution-based behaviour. Miniaturization of these materials to nanoscale therefore affords an important strategy for the development of new light-harvesting materials.[23–25]

Recently, numerous biomolecules have been shown to serve as building blocks linked by metal ions through primary coordination interactions and further grow into nanostructures.[26–29] Although promising, the nanoscale metal-biomolecules coordination polymer-based light-harvesting materials have not been reported. Nucleotides, the building blocks of nucleic acids, are very attractive ligands for fabricating coordination polymers as they contain multiple high affinity metal binding sites and chirality.[30] Many guest materials, such as dyes, metal nanoparticles, and proteins, can be encapsulated in the CPNs generated from nucleotides.[30–32] Very recently, we employed the encapsulation ability of nucleotide-based CPNs and fluorescence

F. Pu, L. Wu, E. Ju, X. Ran, Prof. J. Ren, Prof. X. Qu
State Key Laboratory of Rare Earth Resource Utilization and Laboratory of Chemical Biology
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
Changchun, Jilin 130022, P. R. China
E-mail: jren@ciac.ac.cn; xqu@ciac.ac.cn
L. Wu, E. Ju, X. Ran
University of Chinese Academy of Sciences
Beijing 100039, P. R. China

DOI: 10.1002/adfm.201400276

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim



Scheme 1. Construction of an artificial light-harvesting system by encapsulating two dyes into the coordination polymer nanoparticles through self-assembly.

properties of guest molecule confined in CPNs to construct various logic gates and imaging probe.[33] In the present work, for the first time, we constructed a mimic of light-harvesting system using nucleotide-based CPNs which could encapsulate donor and acceptor molecules simultaneously. Efficient FRET occurred between non-covalently bound donor and acceptor molecules mediated by self-assembly of CPNs. Upon irradiation with visible light, photocurrent generation could be achieved by the dye-encapsulated CPNs system. Furthermore, we constructed a logic system involving multiple fluorescent output modes using the obtained material. This proof of concept is an important step in construction of nanoscale logic systems with multiple functions.

2. Results and Discussion

Scheme 1 presents the construction of the light-harvesting system by encapsulating dyes into the CPNs through self-assembly. The highly hydrophilic dyes Thioflavin T (ThT) and thiazole orange (TO) are nucleic acid binders, which associate with nucleic acids through different mechanisms.[34–36] They were selected as FRET donor–acceptor pair in the model due to their suitable optical properties and commercial availability. In the experiment, guanosine 5′-monophosphate (GMP), ThT and TO were dissolved and mixed in pure water at room temperature. Then $Eu(NO_3)_3$ solution was added to the above mixture under moderate stirring. Solid product of quaternary complex GMP/ThT/TO/Eu formed immediately. Meanwhile, the ternary complexes GMP/ThT/Eu and GMP/TO/Eu were produced for control under the same experimental condition. Scanning electron microscopy (SEM) images show that the shape of GMP/ThT/Eu and GMP/TO/Eu was nanoparticles with an average diameter of 30 nm (Figure S1, Supporting Information). The size of nanoparticles including both ThT and TO was a little bigger. The chemical composition of the CPNs was determined by energy-dispersive X-ray (EDX) analysis, which demonstrated the presence of Eu, as well as GMP (Figure S2, Supporting Information). Fourier transform infrared (FTIR) experiment was carried out to understand the assembly of these CPNs. As shown in Figure S3 (Supporting Information), upon addition of Eu^{3+} into GMP, two characteristic antisymmetric and symmetric stretching bands of GMP associated with the phosphate group at 1084 and 981 cm^{-1} shifted slightly. It indicated that phosphate group was involved in the coordination bonds. In addition, C8-N7 stretching vibrations at 1493 cm^{-1} were shifted after complexation, suggesting nucleobase moiety was also involved in the coordination. The FTIR spectrum of GMP/ThT/TO/Eu is similar to that of GMP/Eu, indicating encapsulation of ThT and TO did not change the self-assembly behaviour of CPNs. It is worth to note that Kimizuka et al. reported that anionic dyes could be effectively incorporated into CPNs through coordination of their carboxyl groups to lanthanide ions, whereas most of cationic dyes were left in the supernatants.[30] Differently, ThT and TO are both positively charged and can be encapsulated by CPNs in the present study. It suggests that the inclusion ability of CPNs is not only dependent on the coordination interaction. It is most likely due to the stacking with the bases.[34,36]

ThT and TO are virtually nonfluorescent in aqueous solution, while they have high absorption coefficient and fluorescence quantum yield when bound to nucleic acids.[34–36] Moreover, we found that the fluorescence intensity of ThT and TO was enhanced when they were incorporated in GMP/lanthanide ions CPNs, respectively. As shown in Figure S4 (Supporting Information), GMP/ThT/Eu CPNs emitted an intense light with a peak centered at 488 nm upon excitation with 440-nm light. GMP/TO/Eu CPNs presented emission centered at 535 nm with excitation wavelength at 490 nm. The increase of fluorescence intensity can be attributed to the restriction of conformational rotation of ThT and TO by the surrounding coordination networks.[34,36] It is the prerequisite to achieve efficient FRET between the two dyes. The FRET process requires the spectral overlap between the emission band of the donor and the absorption band of the acceptor, the distance between them within the Förster radius, and the appropriate orientation of transition dipoles. Herein, ThT was chosen as the energy donor and TO served as the acceptor. As can be seen in **Figure 1**A, the large spectra overlap between the emission spectrum of ThT and the absorption spectrum of TO satisfies one of the requirements for efficient FRET. The self-assembly of GMP and Eu^{3+} ion into CPNs can bring ThT and TO into close proximity and result in an appropriate orientation between them, allowing for the FRET from ThT to TO. Therefore, a significant signal amplification (emission increase) of TO and/or fluorescence quenching of ThT could be observed after encapsulating the two dyes into GMP/Eu CPNs simultaneously (Figure 1B). Compared to the weak fluorescence emission from direct excitation of GMP/TO/Eu at 490 nm, the TO emission was significantly amplified when ThT was excited at 440 nm. The over 3-fold more signal amplification clearly indicates an efficient FRET from ThT to TO. The resonance energy transfer was further supported by the excitation spectrum of GMP/ThT/TO/Eu at 535 nm. As shown in Figure S5 (Supporting Information), a maximum peak at 440 nm was observed, which corresponds

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

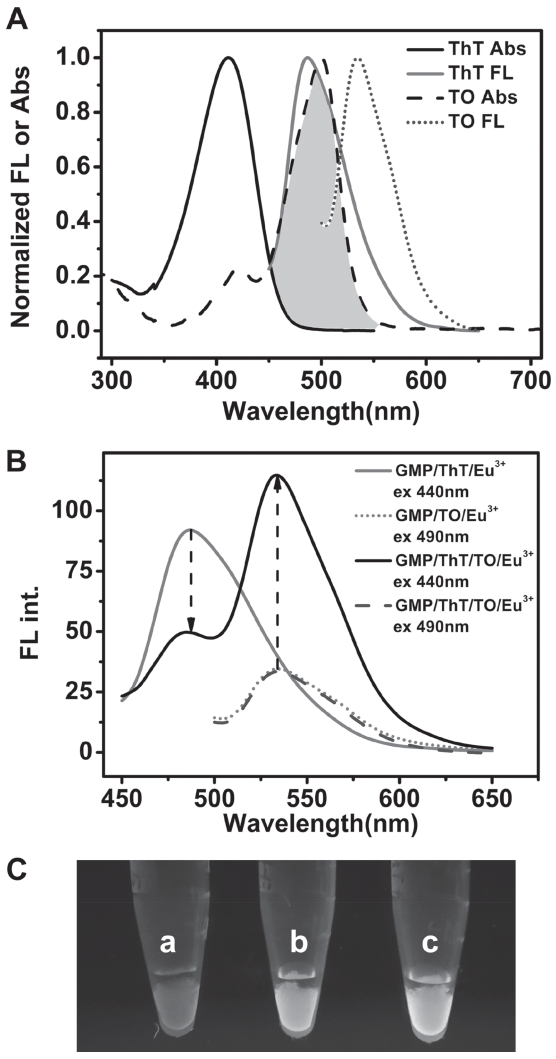


Figure 1. A) Normalized absorption spectra of ThT and TO, and normalized fluorescence spectra of GMP/ThT/Eu and GMP/TO/Eu. B) Fluorescence spectra of GMP/ThT/Eu and GMP/ThT/TO/Eu, upon excitation at 440 nm. Direct excitation of GMP/TO/Eu at 490 nm is also shown. [ThT]:[TO] = 25:1. C) Images of a) GMP/TO/Eu, b) GMP/ThT/Eu, and c) GMP/ThT/TO/Eu under UV lamp.

to the excitation spectrum of GMP/ThT/Eu recorded in the absence of the acceptor. In addition, the emission of a mixture of two ternary complexes GMP/ThT/Eu and GMP/TO/Eu was measured as the control. As shown in Figure S6 (Supporting Information), no FRET occurred when the mixture was excited at 440 nm. It resulted from the barrier property of the coordination networks of nucleotide/lanthanide ions. ThT and TO were limited by the existing dense coordination networks, respectively. It demonstrates that the donor and acceptor are indeed brought within Förster distance in the coordination polymer nanoparticles. Besides fluorescence spectrum measurement, the fluorescence difference of these CPNs could be readily distinguished by the naked eye under UV illumination. As shown in Figure 1C and Figure S7 (Supporting Information), the tube containing GMP/TO/Eu CPNs was dim and the tube containing GMP/ThT/Eu CPNs presented green light. Bright yellow emission was observed for the GMP/ThT/TO/Eu complex. The fluorescence image is consistent with the fluorescence spectra and strongly supports our fluorescence amplification system. It should be mentioned that GMP/Eu CPNs have three principal functions in the light-harvesting system. First, they result in the fluorescence enhancement of donor and acceptor molecules, which are nonfluorescent in aqueous solution. This behaviour enables self-confirmation of formation of CPNs and encapsulation of dyes. Second, they provide necessary Förster donor–acceptor separation distance and orientation for FRET. Third, they act as a barrier to protect the dyes from leakage into the aqueous solution. As stated above, they play an indispensable role in the construction of our system.

It has been reported that the light-harvesting ability is related to the amount of donor and acceptor. The ratio of emission intensity at 535 and 488 nm ($I_{535\ nm}/I_{488\ nm}$), which is associated with the amplification, was studied as a function of acceptor TO concentration (**Figure 2**A). It was found that the emission intensity of TO at 535 nm gradually increased, and that of ThT at 488 nm gradually decreased with the increase of TO concentration when excited at 440 nm (Figure 2B). The ratio values of $I_{535\ nm}/I_{488\ nm}$ increased, although the amount of ThT was the same in all the CPNs (Figure 2C). It implies that more TO molecules accepted energy from a fixed amount of ThT with increasing acceptor loading. Then the amount of TO was fixed and the variation in fluorescence intensity of dyes with the amount of ThT incorporated was studied (Figure 2D). It was observed that both emissions at 488 and 535 nm increased with the increase of ThT concentration (Figure 2E). The amplification multiple of TO fluorescence also increased. It implies more energy was contributed by ThT and transferred to a certain amount of acceptor with increasing donor loading. However, the ratio values of $I_{535\ nm}/I_{488}$ increased slightly (Figure 2F). The system displayed efficient FRET and significant antenna effect. Antenna effect (AE) could be calculated by dividing the area of emission (centered at 535 nm) from the TO upon excitation at 440 nm by the area of emission from direct excitation of TO at 490 nm.[37] Overall transfer efficiency (*E*) from donor to acceptor could be measured using Equation 1.[20] These results were collected in **Figure 3**, suggesting the antenna effect and transfer efficiency of the system depend on the concentration ratio of donor and acceptor. Although there was an increase in AE with the increase of ratio of ThT and TO, the efficiency of energy transfer increased and reached a maximum at the ratio of 2. Increasing the ratio further resulted in a decrease in efficiency. This is most likely caused by the fact that the system was saturated with ThT at high concentration ratio. Excess ThT absorbed light but could not transfer energy to the acceptor, thereby decreased the overall transfer efficiency. A proper equilibrium between AE and E can be found by changing the amount or ratio of dyes in the future applications. Furthermore, we examined the influence of temperature and ion strength on the light-harvesting ability of the CPNs. The fluorescence spectra were recorded at approximately 10 °C increases from 20 to 60 °C. As shown in Figure S8A (Supporting Information), both emissions at 488 and 535 nm decreased with the increase of temperature. The ratio values of $I_{535\ nm}/I_{488\ nm}$ increased slightly (Figure S8B, Supporting Information). To investigate

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

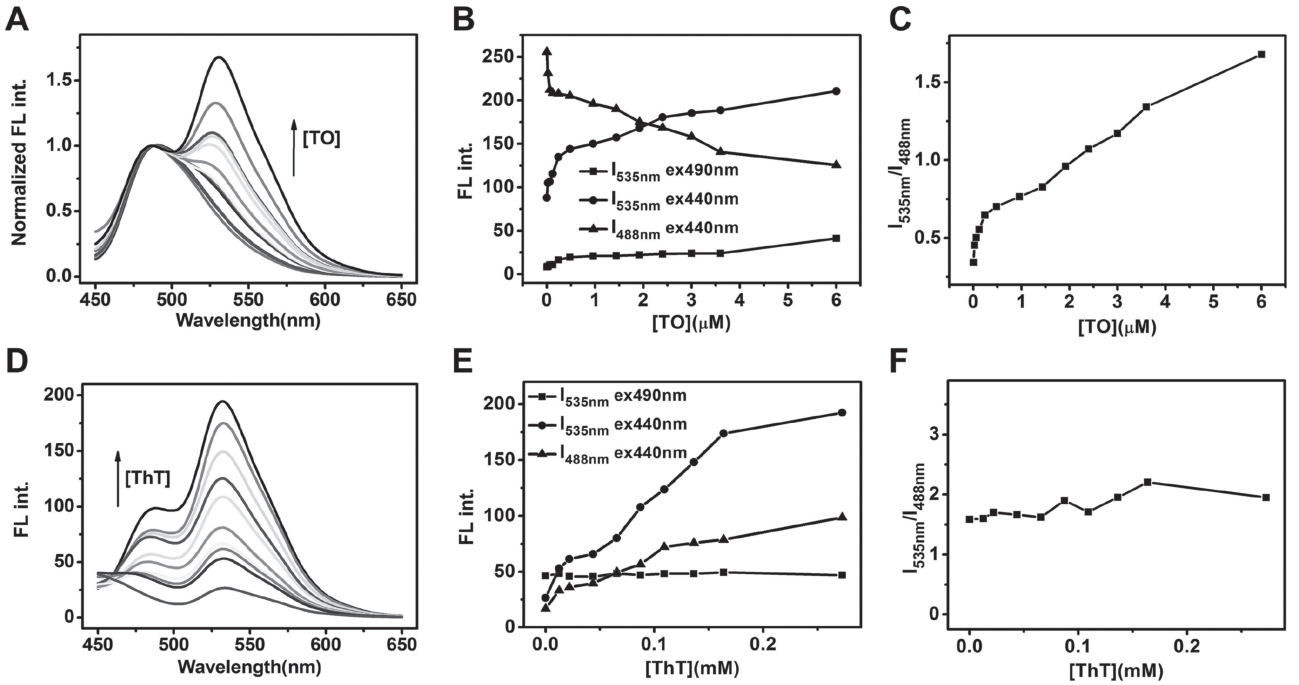


Figure 2. A) Fluorescence spectra of GMP/ThT/TO/Eu with various amount of TO and fixed concentration of ThT ([ThT] = 1.1×10^{-4} M), upon excitation at 440 nm. The spectra are normalized relative to the ThT emission at 488 nm. B) The fluorescence intensities of GMP/ThT/TO/Eu at 535 and 488 nm versus TO concentrations. C) The ratio $I_{535\ nm}/I_{488\ nm}$ versus TO concentrations. D) Fluorescence spectra of GMP/ThT/TO/Eu with various amount of ThT and fixed concentration of TO ([TO] = 6 μM), upon excitation at 440 nm. E) The fluorescence intensities of GMP/ThT/TO/Eu at 535 and 488 nm versus ThT concentrations. F) The ratio $I_{535\ nm}/I_{488\ nm}$ versus ThT concentrations.

the effect of ion strength, we took KCl as the example. Emissions at 488 and 535 nm decreased when the concentration of KCl was raised, while the ratio values of $I_{535\ nm}/I_{488\ nm}$ decreased slightly (Supporting Information, Figure S8C,D). These results showed that temperature and KCl could slightly suppress the emission intensity of the system and affect FRET to a certain extent. However, most of light-harvesting ability was still maintained.

For many light-harvesting systems based on organic assemblies, the emission of several luminophores is often quenched in the solid state in comparison to that in solution, due to aggregate formation in the condensed phase.[38] Interestingly, the dyes-encapsulated GMP/Eu CPNs preserved their fluorescent property even in the form of solid state in our system. The powder samples of GMP/ThT/Eu, GMP/TO/Eu, and GMP/ThT/TO/Eu CPNs were separated from aqueous solution by centrifugation and freeze-dried. As shown in Figure S9A (Supporting Information), GMP/ThT/Eu emitted green fluorescence and GMP/TO/Eu emitted weak light when they were irradiated under UV light. Differently, bright yellow light could be observed for the GMP/ThT/TO/Eu CPNs. The equal quantities of solid dyes alone gave negligible fluorescence under the same conditions (data not shown). Furthermore, fluorescence spectra of these solid CPNs were obtained. As shown in Figure S9B (Supporting Information), GMP/ThT/Eu exhibited emission at 495 nm upon excitation of 440 nm, while GMP/TO/Eu presented emission at 545 nm upon excitation of 490 nm. The maximum peaks were red-shifted compared to those in aqueous solution, which might be caused by the change of local environments of coordination polymer networks. When solid powder of GMP/ThT/TO/Eu was excited at 440 nm, fluorescence enhancement at 535 nm was observed. The excitation spectrum of GMP/ThT/TO/Eu with emission at 535 nm was similar to that of GMP/ThT/Eu with emission at 495 nm, as shown in Figure S9C (Supporting Information). These results demonstrated that FRET from ThT to TO and amplification of acceptor signal could also occur in solid phase. In previous reports, some light-harvesting materials based on biomolecules were fabricated in solution.[17,19] These studies did not specify their light-harvesting property in the form of solid. The

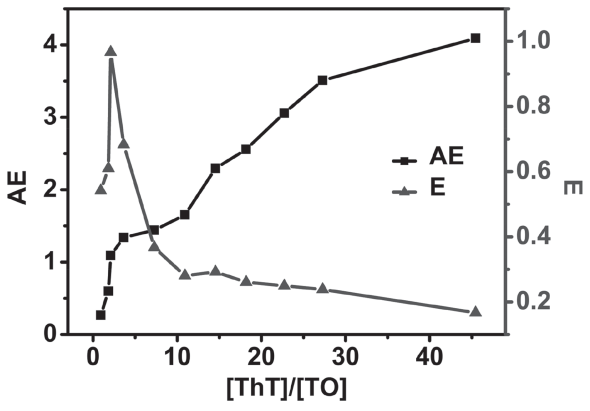


Figure 3. Antenna effect and overall transfer efficiency of the light-harvesting system as a function of ThT: TO ratio.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

3D spatial organization and conformation of the biopolymers are essential to support energy transfer. Optimized buffers are always needed to retain the relative distance and orientation of the donor and acceptor molecules. Different from these systems, our material involves the self-assembly of coordination polymer nanoparticles. Owing to the close proximity of the donor and acceptor molecules in the co-assembled aggregates, the CPNs in the solid state showed a similar FRET behaviour to that dispersed in the solution. Therefore, our material gets out of the boundary of the solution. It can function not only in fluid medium, but also in the form of solid, which extends its application area greatly.

Due to the modularity of the material, it is convenient to vary the combination of donor and acceptor molecules. Another pairs of energy donor and acceptor can be incorporated into CPNs conveniently to result in new light-harvesting systems. Herein, we chose Hoechst 33342 (Hoe)/TO and ThT/Genefinder (GF) as models to confirm the universality of the strategy. Hoechst 33342, whose structure is shown in Figure S10 (Supporting Information), is one of the most commonly used DNA dyes. Figure S11 shows normalized absorption and fluorescence spectra of Hoe and TO. The shaded overlap between Hoe fluorescence and TO absorption allows efficient FRET. After being encapsulated into CPNs, the donor Hoe and the acceptor TO were held in close proximity. The function of GMP/Hoe/TO/Eu CPNs as light-harvesting system was examined by exciting donor at 352 nm. As shown in Figure S12A (Supporting Information), in the absence of acceptor TO, strong emission of Hoe centered at 475 nm was observed. Excitation of GMP/Hoe/TO/Eu resulted in fluorescence decrease at 475 nm and emission increase of TO. Compared with that by direct excitation of GMP/TO/Eu at 490 nm, TO signal was amplified. Moreover, due to the difference of excitation wavelengths of donors, the Stokes shifts of these CPNs are different. GMP/Hoe/TO/Eu CPNs presented much larger Stokes shift than that of GMP/ThT/TO/Eu CPNs. It implies this light-harvesting system can extend the Stokes shift and facilitate the separation of excitation and emission light. Meanwhile, it provides the possibility to adjust the excitation to the powerful and inexpensive light sources. Besides fluorescence spectra analysis, the fluorescence difference for the CPNs could also be visualized using UV transilluminator (Figure S12B, Supporting Information). Similarly, since the emission spectrum of ThT overlaps with the absorbance spectrum of GF (Figure S13, Supporting Information), efficient FRET between donor ThT and acceptor GF occurred through self-assembly of GMP and Eu^{3+} (Figure S14, Supporting Information). Compared to the weak fluorescence emission from direct excitation of GF at 490 nm, the dye signal was significantly amplified. Meanwhile, the fluorescent property was preserved in the solid state (Figure S15, Supporting Information). In addition to tuning the donor–acceptor combinations, the general approach for the design of light-harvesting materials involves the mixing of different nucleotides and lanthanide ions. As shown in Figure S16 (Supporting Information), as expected, FRET from ThT to TO occurred in the CPNs generated from adenosine 5′-monophosphate (AMP)/Gd^{3+} and deoxyguanosine 5′-monophosphate (dGMP)/Eu^{3+}. These results suggest that our strategy can facilitate the construction of arrays of light-harvesting systems. It provides a simple and universal approach by changing the combination of donor and acceptor dyes and constituents of CPNs. Indeed, the lack of precision in positioning the dyes in the CPNs is a limitation in comparison to organic dendrimers. The limitation exists commonly in light-harvesting systems with hybrid scaffolds.[8] On the other hand, the relatively easy one-step synthetic procedure offers a guideline for the design of a new class of light-harvesting nanomaterials.

In natural photosynthetic systems, solar photons are harvested by antenna molecules. Then the collected photoenergy is converted to electric current by photo-induced charge separation. As one of photoelectronic molecular functions, photocurrent generation by photo-induced charges separation and transfer has been studies extensively.[39] Herein, we also measured the photocurrent generation of CPNs deposited on an indium tin oxide (ITO) glass in $NaNO_3$ solution upon irradiation with a visible light (450 nm). The time courses of the photocurrents for the respective samples are shown in **Figure 4**A. The photoinduced response of CPNs containing dyes could be observed upon illumination under visible light, implying the electrons excited by light energy were efficiently separated and transferred. Moreover, the photocurrent of GMP/ThT/TO/Eu

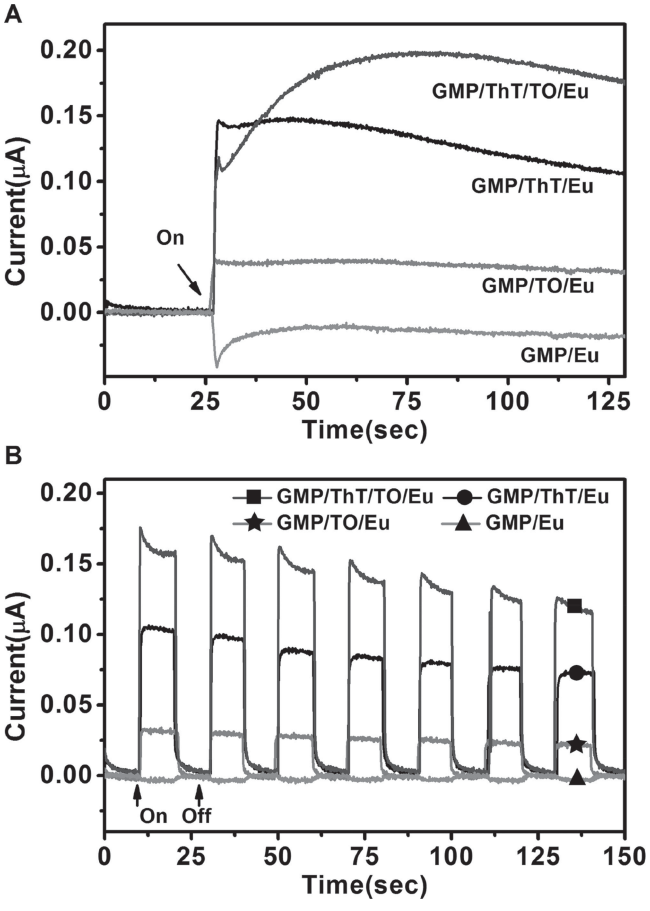
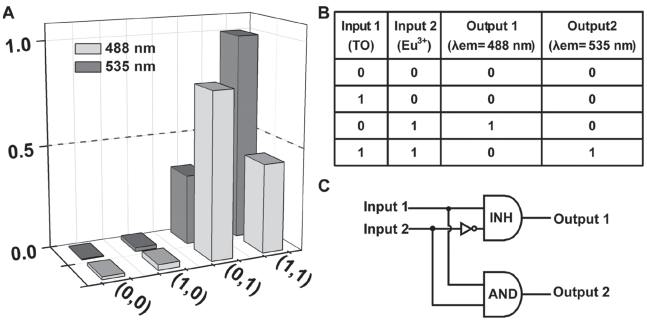


Figure 4. A) Photocurrents of CPNs under visible light (450 nm, 35 mW cm^{-2}) illumination. B) Photocurrent on-off cycles of CPNs samples as a function of time under visible light illumination. "On" represents the electrode under light irradiation, while "Off" means the light was turned off.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

was higher than that of GMP/ThT/Eu under the same experimental conditions. It implies that the presence of an energy acceptor would promote the photoinduced electron transfer, resulting in promotion of the photocurrent generation. Since the photocurrent response is wavelength-dependent and the wavelength of light source used in the present study is near to the absorption band of TO, GMP/TO/Eu displayed a weak photocurrent response. In contrast to the CPNs containing dyes, the CPNs without dyes did not display significant photoactivity as expected. Free ThT or TO also did not generate photocurrent upon illumination under the same light, as shown in Figure S17 (Supporting Information). These results demonstrated the necessity of encapsulating dyes in CPNs for photocurrent generation. Photocurrent on-off cycles of CPNs as a function of time showed the current was generated only when the light was on (Figure 4B). The photocurrent dropped instantly when the illumination was cut off. Photocurrent generation measurement presents the potential usefulness of our material in light-energy conversion and photoelectronic applications.

Recently, there has been great interest in the development of molecular logic systems.[40,41] Several organic molecules, biomolecules and nanomaterials have been used to design and construct various logic gates.[42–44] However, most of the reported logic systems relied on only one output mode. Shiraishi et al. have demonstrated that a simple-structured molecule behaved as a fluorescent molecular logic gate with multiply-configurable dual outputs.[45] Bhowmik et al. constructed multifunctional and multiply-configurable logic gates based on small molecule G-quadruplex DNA recognition.[46] We have reported dual-channel logic gates based on conjugated polymer/dye/DNA system.[47] However, the development of dual-channel logic gates in a simple, green, and cost-effective manner still remains a challenge. The behaviours of light-harvesting make our system suitable for mimicking logic gates at two different wavelengths. Herein, GMP/ThT was viewed as the gate while TO and Eu^{3+} acted as the two inputs. The relative fluorescence intensity at 488 and 535 nm were regarded as the outputs with a threshold value of 0.5. In the absence of TO and Eu^{3+} (0, 0), nearly no fluorescence was seen both at 488 and 535 nm, corresponding to logic output 0. The addition of TO into the solution of GMP/ThT (1, 0) could not change the fluorescence behaviour; thus logic value was 0. After adding Eu^{3+} (0, 1), GMP/ThT/Eu CPNs were formed and fluorescence at 488 nm was enhanced, resulting in logic value 1. However, there was no emission at 535 nm due to the lack of TO, corresponding to 0. When TO and Eu^{3+} were added simultaneously (1, 1), GMP/ThT/TO/Eu CPNs were formed and FRET between ThT and TO occurred. Fluorescence decrease of ThT and emission increase of TO were observed. The weak fluorescence at 488 nm was smaller than threshold value of 0.5; thus we regarded it as 0. Due to the amplification of fluorescence by FRET, the intense emission at 535 nm corresponded to logic output 1. The results corresponded to the truth tables of INH and AND logic gates (**Figure 5**), respectively. It indicated that the system worked as a dual-channel output mode. The presence of such dual channels adds to the complexity of the logic system which is a desirable feature.



Input 1 (TO)	Input 2 (Eu^{3+})	Output 1 (λem= 488 nm)	Output2 (λem= 535 nm)
0	0	0	0
1	0	0	0
0	1	1	0
1	1	0	1

Figure 5. A) Relative fluorescence intensities at 488 and 535 nm for dual-channel logic gates. B) Truth table for the logic gates. C) Logic scheme.

3. Conclusion

In summary, for the first time, an artificial light-harvesting material involving biomolecule-based coordination polymer nanoparticles was successfully fabricated by one-pot synthesis at room temperature. The system relies on the significant signal amplification through efficient FRET from ThT to TO mediated by self-assembly of nucleotide and lanthanide ions. By comparison with organic molecule-based covalent systems, our system is much easier to be obtained through direct encapsulation of dyes into the CPNs using a noncovalent principle. Neither complex modification nor labelling process is required, which offers the advantages of simplicity, time-saving and cost efficiency. The modularity of the material makes it convenient to vary the amount of donor and acceptor. Moreover, the work suggests a universal approach to construct arrays of light-harvesting systems by changing the combination of donor and acceptor dyes and constituents of CPNs. It provides the possibility to extend the Stokes shift and adjust the excitation to the more powerful and inexpensive light sources. Photocurrent can be generated upon irradiation with visible light. Furthermore, the generation of FRET system provides a platform to mimic dual-channel logic gate at nanoscale level. It may be beneficial to the construction of more miniaturized and integrated logic devices with multiple functions. Combined together, we expect this work will be helpful in optical, photovoltaic and photosynthetic fields.

4. Experimental Section

Materials: Guanosine 5′-monophosphate (GMP), adenosine 5′-monophosphate (AMP), deoxyguanosine 5′-monophosphate (dGMP), Thioflavin T (ThT), Thiazole orange (TO), and Hoechst 33342 were purchased from Sigma-Aldrich and used without further purification. The extinction coefficient of ThT is 34 000 M^{-1} cm^{-1} at 412 nm. The extinction coefficient of TO is 63 000 M^{-1} cm^{-1} at 500 nm. The extinction coefficient of Hoechst 33342 is 45 000 M^{-1} cm^{-1} at 350 nm. $EuCl_3{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}6H_2O$ was purchased from Aladdin Reagent (Shanghai, China). Genefinder (GF) was purchased from Bio-v Company (Xiamen, China). All other reagents were all of analytical reagent grade and used as received.

Measurements: Fluorescence spectra of CPNs in aqueous solutions were measured on a JASCO FP-6500 spectrophotometer. Fluorescence spectra of solid CPNs were measured on an F-7000 spectrophotometer (Hitachi, Japan). UV/vis absorption spectra were recorded on a JASCO V-550 spectrophotometer. Scanning electron microscopy (SEM) was conducted on an S-4800 field emission scanning microscope. Fourier transform infrared (FTIR) analyses were carried out on a Bruker Vertex 70 FT-IR spectrometer.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Preparation of CPNs: GMP (5 mM) and dyes with different concentrations were dissolved in pure water (1 mL). Then $EuCl_3$ solution (2 mM) was added to the mixture under slight shake. Solid products of GMP/lanthanide ions appeared within one minute. The products were kept at room temperature for 30 min and collected by centrifugation.

Measurement of Antenna Effect and Transfer Efficiency: Antenna effect (AE) and transfer efficiency (E) of the light-harvesting system were calculated by following equation:

$$AE = \frac{I_{A(ex,D)}}{I_{A(ex,A)}} = \frac{n_D \varepsilon_D E}{n_A \varepsilon_A} \quad (1)$$

where $I_{A(ex,D)}$ is the intensity of acceptor emission when exciting the donor, $I_{A(ex,A)}$ is the acceptor emission upon direct excitation of the acceptor, n_D is the number of donors, ε_D is the maximum absorption coefficient of the donor, n_A is the number of acceptors, ε_A is the maximum absorption coefficient of the acceptor, and E is the overall transfer efficiency from donors to acceptor.

Photocurrent Generation Measurement: Photocurrent measurement was carried out using the three-electrode system comprised of a platinum wire as the auxiliary electrode, an Ag/AgCl as the reference electrode and an indium tin oxide (ITO) glass as the working electrode. For the preparation of working electrode, CPNs solutions were dropped on the indium tin oxide grass and dried at room temperature to form film. The three electrodes were immersed into an electrolyte bath containing $NaNO_3$ (100 mM) for photo-electrochemical measurements with a potential of 0.2 V. The working electrode was illuminated with a visible light source (450 nm).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Financial support was provided by National Basic Research Program of China (Grant 2012CB720602, 2011CB936004) and the National Natural Science Foundation of China (Grants 91213302, 21210002, 21303182).

Received: January 24, 2014
Revised: March 6, 2014
Published online: April 14, 2014

[1] L. An, L. Liu, S. Wang, G. C. Bazan, *Angew. Chem. Int. Ed.* **2009**, *48*, 4372.
[2] T. Mayr, S. M. Borisov, T. Abel, B. Enko, K. Waich, G. Mistlberger, I. Klimant, *Anal. Chem.* **2009**, *81*, 6541.
[3] M. Waki, N. Mizoshita, Y. Maegawa, T. Hasegawa, T. Tani, T. Shimada, S. Inagaki, *Chem. Eur. J.* **2012**, *18*, 1992.
[4] C. Wang, Z. Xie, K. E. deKrafft, W. Lin, *ACS Appl. Mater. Interfaces* **2012**, *4*, 2288.
[5] D. Gust, T. A. Moore, A. L. Moore, *Acc. Chem. Res.* **2001**, *34*, 40.
[6] T. Q. Nguyen, J. Wu, V. V. Doan, B. J. Schwartz, S. H. Tolbert, *Science* **2000**, *288*, 652.
[7] Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson, S. R. Forrest, *Nature* **2006**, *440*, 908.
[8] K. V. Rao, K. K. R. Datta, M. Eswaramoorthy, S. J. George, *Chem. Eur. J.* **2012**, *18*, 2184.
[9] V. Garg, G. Kodis, P. A. Liddell, Y. Terazono, T. A. Moore, A. L. Moore, D. Gust, *J. Phys. Chem. B* **2013**, *117*, 11299.
[10] H. Q. Peng, Y. Z. Chen, Y. Zhao, Q. Z. Yang, L. Z. Wu, C. H. Tung, L. P. Zhang, Q. X. Tong, *Angew. Chem. Int. Ed.* **2012**, *51*, 2088.
[11] J. L. Wang, J. Yan, Z. M. Tang, Q. Xiao, Y. Ma, J. Pei, *J. Am. Chem. Soc.* **2008**, *130*, 9952.
[12] K. V. Rao, K. K. Datta, M. Eswaramoorthy, S. J. George, *Angew. Chem. Int. Ed.* **2011**, *50*, 1179.
[13] A. Satake, S. Azuma, Y. Kuramochi, S. Hirota, Y. Kobuke, *Chem. Eur. J.* **2011**, *17*, 855.
[14] K. J. Channon, G. L. Devlin, C. E. MacPhee, *J. Am. Chem. Soc.* **2009**, *131*, 12520.
[15] F. Garo, R. Haner, *Angew. Chem. Int. Ed.* **2012**, *51*, 916.
[16] N. Sancho Oltra, W. R. Browne, G. Roelfes, *Chem. Eur. J.* **2013**, *19*, 2457.
[17] Q. Zou, L. Zhang, X. Yan, A. Wang, G. Ma, J. Li, H. Mohwald, S. Mann, *Angew. Chem. Int. Ed.* **2014**, *53*, 2366.
[18] C. V. Kumar, M. R. Duff, *J. Am. Chem. Soc.* **2009**, *131*, 16024.
[19] P. K. Dutta, R. Varghese, J. Nangreave, S. Lin, H. Yan, Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 11985.
[20] J. G. Woller, J. K. Hannestad, B. Albinsson, *J. Am. Chem. Soc.* **2013**, *135*, 2759.
[21] C. A. Kent, D. M. Liu, L. Q. Ma, J. M. Papanikolas, T. J. Meyer, W. B. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 12940.
[22] H. J. Son, S. Jin, S. Patwardhan, S. J. Wezenberg, N. C. Jeong, M. So, C. E. Wilmer, A. A. Sarjeant, G. C. Schatz, R. Q. Snurr, O. K. Farha, G. P. Wiederrecht, J. T. Hupp, *J. Am. Chem. Soc.* **2013**, *135*, 862.
[23] X. Zhang, Z. K. Chen, K. P. Loh, *J. Am. Chem. Soc.* **2009**, *131*, 7210.
[24] X. Zhang, M. A. Ballem, M. Ahren, A. Suska, P. Bergman, K. Uvdal, *J. Am. Chem. Soc.* **2010**, *132*, 10391.
[25] X. J. Zhang, M. A. Ballem, Z. J. Hu, P. Bergman, K. Uvdal, *Angew. Chem. Int. Ed.* **2011**, *50*, 5728.
[26] I. Imaz, M. Rubio-Martinez, J. An, I. Sole-Font, N. L. Rosi, D. Maspoch, *Chem. Commun.* **2011**, *47*, 7287.
[27] A. Carne, C. Carbonell, I. Imaz, D. Maspoch, *Chem. Soc. Rev.* **2011**, *40*, 291.
[28] Y. Liu, Z. Tang, *Chem. Eur. J.* **2012**, *18*, 1030.
[29] F. Pu, X. Liu, B. Xu, J. Ren, X. Qu, *Chem. Eur. J.* **2012**, *18*, 4322.
[30] R. Nishiyabu, N. Hashimoto, T. Cho, K. Watanabe, T. Yasunaga, A. Endo, K. Kaneko, T. Niidome, M. Murata, C. Adachi, Y. Katayama, M. Hashizume, N. Kimizuka, *J. Am. Chem. Soc.* **2009**, *131*, 2151.
[31] R. Nishiyabu, C. Aime, R. Gondo, T. Noguchi, N. Kimizuka, *Angew. Chem. Int. Ed.* **2009**, *48*, 9465.
[32] R. Nishiyabu, C. Aime, R. Gondo, K. Kaneko, N. Kimizuka, *Chem. Commun.* **2010**, *46*, 4333.
[33] F. Pu, E. Ju, J. Ren, X. Qu, *Adv. Mater.* **2014**, *26*, 1111.
[34] J. Nygren, N. Svanvik, M. Kubista, *Biopolymers* **1998**, *46*, 39.
[35] I. Lubitz, D. Zikich, A. Kotlyar, *Biochemistry* **2010**, *49*, 3567.
[36] J. Mohanty, N. Barooah, V. Dhamodharan, S. Harikrishna, P. I. Pradeepkumar, A. C. Bhasikuttan, *J. Am. Chem. Soc.* **2013**, *135*, 367.
[37] D. W. Brousmiche, J. M. Serin, J. M. J. Frechet, G. S. He, T. C. Lin, S. J. Chung, P. N. Prasad, R. Kannan, L. S. Tan, *J. Phys. Chem. B* **2004**, *108*, 8592.
[38] V. M. Suresh, S. J. George, T. K. Maji, *Adv. Funct. Mater.* **2013**, *23*, 5585.
[39] R. Moritoh, T. Morita, S. Kimura, *Biopolymers* **2013**, *100*, 1.
[40] J. Andreasson, U. Pischel, *Chem. Soc. Rev.* **2010**, *39*, 174.
[41] A. P. de Silva, *Chem. Asian J.* **2011**, *6*, 750.
[42] D. Liu, W. Chen, K. Sun, K. Deng, W. Zhang, Z. Wang, X. Jiang, *Angew. Chem. Int. Ed.* **2011**, *50*, 4103.
[43] H. Z. He, D. S. Chan, C. H. Leung, D. L. Ma, *Nucleic Acids Res.* **2013**, *41*, 4345.
[44] Q. Jiang, Z. G. Wang, B. Ding, *Small* **2013**, *9*, 1016.
[45] Y. Shiraishi, Y. Tokitoh, T. Hirai, *Chem. Commun.* **2005**, 5316.
[46] S. Bhowmik, R. N. Das, B. Parasar, J. Dash, *Chem. Commun.* **2013**, *49*, 1817.
[47] F. Pu, C. Wang, D. Hu, Z. Huang, J. Ren, S. Wang, X. Qu, *Mol. Biosyst.* **2010**, *6*, 1928.

© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim