



## Continuous intra- and intermolecular energy transfer in light-harvesting gels from natural amino acids-based dendrons

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### ABSTRACT

The gels and co-gels from glycine (**Gly**) and glutamic acid (**Glu**)-based dendrons with either tyrosine (**Tyr**) or tryptophan (**Trp**), two of the luminescent amino acid residues in natural proteins, at the focal point were prepared (**Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>**). It was found that such gels, especially the co-gels from **Tyr-AB<sub>4</sub>**/**Trp-AB<sub>4</sub>**, showed a high efficient energy transfer (ET) and light-harvesting behaviors. Moreover, luminescent gels with tunable emission ranging from blue to green were also observed owing to the cascade intra- and intermolecular ET from dendritic gelators to the guest molecules (**PDNS**) in the host–guest gel sample (co-gel with **PDNS** as the guest molecule), which mimicked the natural light-harvesting systems.

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In natural light-harvesting systems, chlorophyll molecules arrange orderly in the protein matrix through non-covalent interactions. The continuous energy transfer (ET) between the chromophores plays an important role in the photosynthetic process.<sup>1</sup> In order to mimic natural photosynthetic process, various artificial light-harvesting materials and ET systems were developed, including supramolecular complexes,<sup>2</sup> chromophores-linked polymers,<sup>3</sup> unimolecular dendrimers,<sup>4</sup> and self-assembled monolayers.<sup>5</sup> Gel, as an important kind of supramolecular assembly with three dimensional networks, has attracted increasing attention<sup>6</sup> and became an active candidate of ET and light-harvesting materials. The ordered molecular stacking in gel phase facilitates the order orientation of the transition dipole moments of donor and acceptor and shortens the intermolecular distance, leading to the enhancement of ET efficiency.<sup>7</sup>

ET in organogels based on linear molecules has been extensively studied.<sup>8</sup> In recent years, dendrimers and dendrons are of much interest for ET and light-harvesting applications due to their unique interior structures in favor of the energy gradient for energy funneling process and the large numbers of peripheral groups for capturing light. Meijer and co-workers have investigated the energy and electron transfer process between functionalized dendrimer and guest molecules in supramolecular assemblies, such as homogeneous thin films.<sup>9</sup> Moore, De Schryver, Müllen, Aida, Fréchet, et al. have investi-

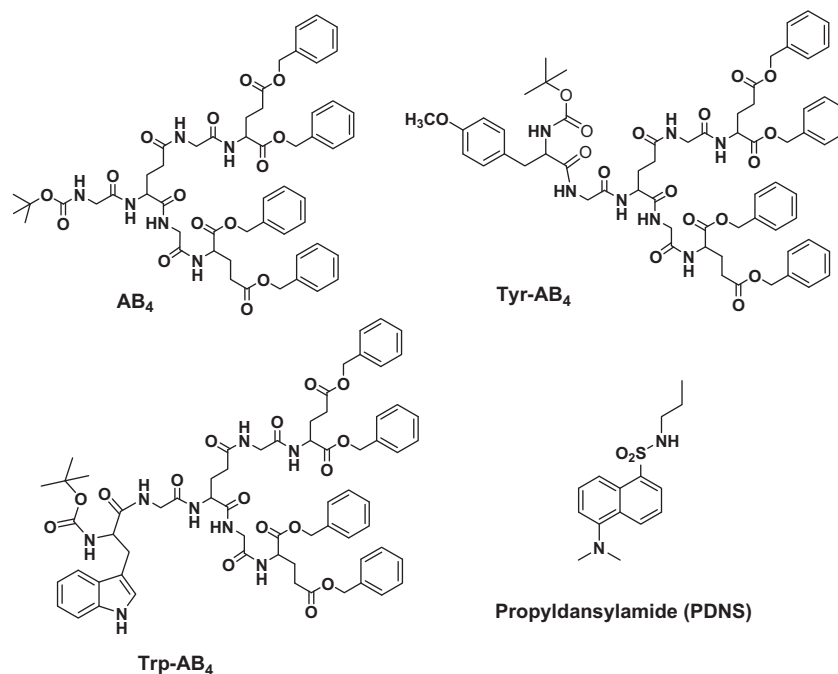
gated the 'light-harvesting' properties of dendrons with conjugated or nonconjugated molecular structures.<sup>10</sup>

However, little attention has been paid to ET and light-harvesting property in gels from dendritic gelators, in particular, the dendrons with modifiable focal point and multi-functional peripheral groups. Compared to common ET process in supramolecular assemblies via an intermolecular way, both intra- and intermolecular light-harvesting and ET processes could occur efficiently, which is a unique feature of dendritic gelators different from linear molecules.

Polypeptides based on natural amino acids, usually regarded as the excellent gelators, can self-assemble into 3D entangled networks composed of fibrillar architectures. The amyloid-like fibers exhibited a high stability in a broad range of physiochemical conditions, making them the promising candidates in the field of biomaterials.<sup>11</sup> In our previous studies, we have reported the natural amino acids-based dendrons that showed strong gelation ability in various organic solvents.<sup>12</sup> In addition, we have also focused our interest in the fluorescent and light-harvesting properties of the dendrimers and dendrons in solution.<sup>13</sup> Recently, we have expanded our sight into the light-harvesting property and ET process of dendritic molecules in the gel state. Herein, we report the gels from glycine (**Gly**)- and glutamic acid (**Glu**)-based dendrons with either tyrosine (**Tyr**) or tryptophan (**Trp**), two of the luminescent amino acid residues in natural proteins, at the focal point. Such gels showed efficient light-harvesting and energy transfer properties. Moreover, luminescent gels with tunable emission ranging from blue to green were also

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**Scheme 1.** Chemical structures of donor model compound **AB<sub>4</sub>**, dendrons **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>**, propyldansylamide (**PDNS**).

observed owing to the cascade intra- and intermolecular ET from dendritic gelators to the guest molecules.

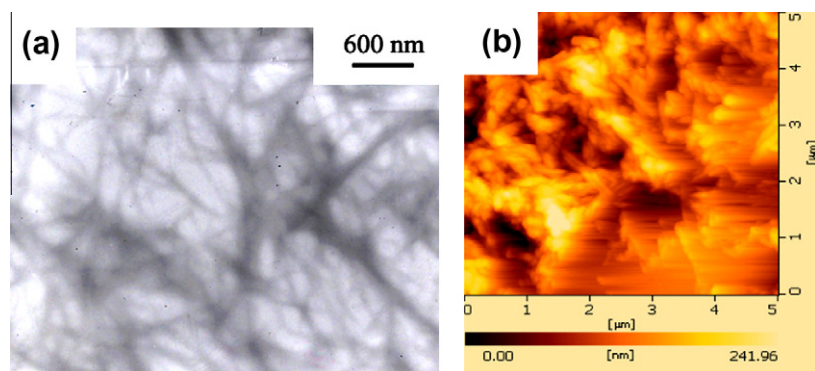
The structures of dendritic molecules referred to in the study are shown in Scheme 1. The second generation dendrons (**AB<sub>4</sub>**) with glycine and glutamic acid as building blocks were synthesized using standard DCC coupling reaction. **AB<sub>4</sub>** was further deprotected by CF<sub>3</sub>COOH to remove the Boc group in focal point and further modified with **Tyr** and **Trp** by DCC coupling to produce **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>**, respectively. These dendrons acted as efficient organogelators and formed stable gels in ethanol (EtOH), iso-propanol (<sup>i</sup>PrOH), butanol (*n*-BuOH), and ethyl acetate (AcOEt). The minimum gel concentrations (MGC) of **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** are lower than that of **AB<sub>4</sub>** in the same solvents (Supplementary data Table S1) in the order of **AB<sub>4</sub>** > **Tyr-AB<sub>4</sub>** > **Trp-AB<sub>4</sub>**, indicating that **Tyr** and **Trp** units, especially the latter fragment, enhanced the gelation ability possibly due to the stronger molecular interactions.<sup>14</sup>

Notably, **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** could co-assemble to afford transparent gels (co-gel) in EtOH, <sup>i</sup>PrOH, and *n*-BuOH when mixed together, suggesting that the two dendrons with similar structures generated fibrous networks. This is understandable because molecules prefer to assemble with structurally and geometrically

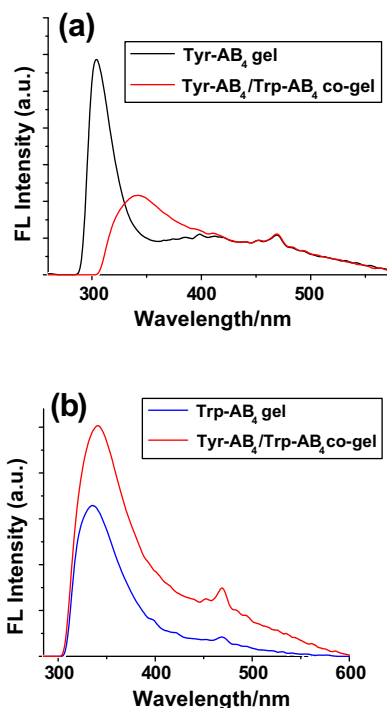
matched counterparts to build up supramolecular assembly, which is described as self-sorting or self-recognition by Lehn and Severin et al.<sup>15</sup> It is observed that the co-gels could form by **Tyr-AB<sub>4</sub>**/**Trp-AB<sub>4</sub>** with different ratios (w/w), such as 1:1 and 1.5:1, and the MGC of the co-gels depended on the selected solvents. Similarly, the mixtures of **AB<sub>4</sub>** and **Tyr-AB<sub>4</sub>** and **AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** could also form stable co-gels.

To obtain visual images of the gel-phase assemblies from **Tyr-AB<sub>4</sub>**, **Trp-AB<sub>4</sub>**, and the co-gel, transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements were performed. As shown in Figure 1, well-defined entangled 3D structures were developed. The diameter of the fibrils ranged from 50 to 100 nm and the morphology of the fibrils depended on the selected solvents. AFM images recorded in tapping mode revealed that the bundles of fibers were formed in the co-gel.

The absorption and emission properties of **AB<sub>4</sub>**, **Tyr-AB<sub>4</sub>**, and **Trp-AB<sub>4</sub>** were firstly investigated in solution. The maximal absorption wavelength of **AB<sub>4</sub>**, **Tyr-AB<sub>4</sub>**, and **Trp-AB<sub>4</sub>** in ethanol could be assigned to the characteristics of **phenyl** (257 nm), **Tyr** (275 nm), and **Trp** (282 nm) groups, respectively (Fig. S2a). It was seen that when exciting the ethanol solution of **AB<sub>4</sub>** with the wavelength



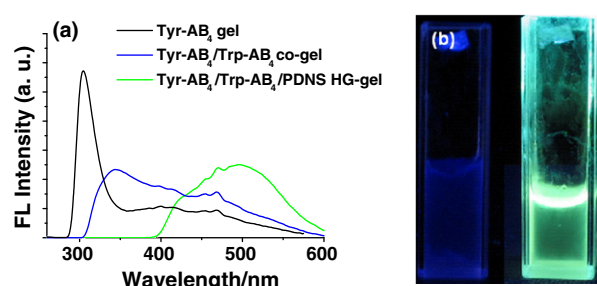
**Figure 1.** (a) TEM image and (b) AFM image of co-xerogels from **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** in ethanol.



**Figure 2.** (a) Emission spectra of **Tyr-AB<sub>4</sub>** gel ( $9.6 \times 10^{-3}$  M) and **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** co-gel ( $9.6 \times 10^{-3}$  M/ $6.4 \times 10^{-3}$  M) formed in ethanol.  $\lambda_{\text{ex}} = 257$  nm. (b) Emission spectra of **Trp-AB<sub>4</sub>** gel ( $6.4 \times 10^{-3}$  M,  $\lambda_{\text{ex}} = 282$  nm) and **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** co-gel ( $9.6 \times 10^{-3}$  M/ $6.4 \times 10^{-3}$  M,  $\lambda_{\text{ex}} = 275$  nm) formed in ethanol.

of 257 nm, the emission band appeared at 282 nm corresponding to the phenyl groups (Fig. S2b). Instead, the emission band at 303 and 340 nm assigned to **Tyr** and **Trp** groups appeared after **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** were excited separately at the same wavelength of 257 nm, indicating an efficient ET from peripheral phenyl groups to the focal amino acid unit. The gels either from **Tyr-AB<sub>4</sub>** or from **Trp-AB<sub>4</sub>** showed similar ET behavior with the dendrons in the solution (Fig. S3).

It is worthy to note that the co-gel composed of **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** showed unique ET property. As reported previously, it remains a challenge to enhance the ET efficiency in gels for most of the ET processes take place only through an intermolecular way.<sup>8</sup> For our co-gel system, high energy transfer efficiency was achieved because both intra- and intermolecular ET processes occurred. It was found that (Fig. S4) only emission band at 340 nm assigned to **Trp** unit appeared when exciting the co-gel at 275 nm (the emission above 400 nm was ascribed to the scattered light). The result proved the existence of intermolecular ET from **Tyr** to **Trp** units in the co-gel. Additionally, when the gel sample was excited at 257 nm, only the emission at 340 nm was observed again (Fig. 2a). Such a result indicated that a cascade ET took place sequentially from phenyl groups to **Tyr** by an intramolecular way, and from **Tyr** to **Trp** via an intermolecular way. Although it was not easy to obtain exact results due to the overlap of **Tyr-AB<sub>4</sub>** (donor) and **Trp-AB<sub>4</sub>** emission spectra, the fluorescence intensity of the **Tyr-AB<sub>4</sub>** was quenched completely in the presence of the **Trp-AB<sub>4</sub>**, indicating a high efficiency energy transfer from **Tyr-AB<sub>4</sub>** to **Trp-AB<sub>4</sub>**. In contrast, the physically mixed sample of **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** in the solution displayed quite different behavior (Fig. S5). When exciting the mixed sample at 275 nm, the emission bands of both **Tyr** (303 nm) and **Trp** units (340 nm) were observed. Such a result further revealed that the gel-phase assembly facilitated the occurrence of the ET process. MacPhee et al. have reported that the average distance between donors and acceptors can be tuned by adjusting their molar ratios so as



**Figure 3.** (a) Emission spectra of **Tyr-AB<sub>4</sub>** gel ( $9.6 \times 10^{-3}$  M, black line), **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** co-gel ( $9.6 \times 10^{-3}$  M/ $9.6 \times 10^{-3}$  M, blue line), and **PDNS** ( $5.7 \times 10^{-3}$  M) doped **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** HG-gel ( $9.6 \times 10^{-3}$  M/ $9.6 \times 10^{-3}$  M, green line) formed in ethanol.  $\lambda_{\text{ex}} = 254$  nm. (b) Photographs of **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** co-gel ( $9.6 \times 10^{-3}$  M, left); and **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>/PDNS** HG-gel ( $9.6 \times 10^{-3}$  M/ $1.5 \times 10^{-2}$  M, right) upon irradiated with 254 nm UV light.

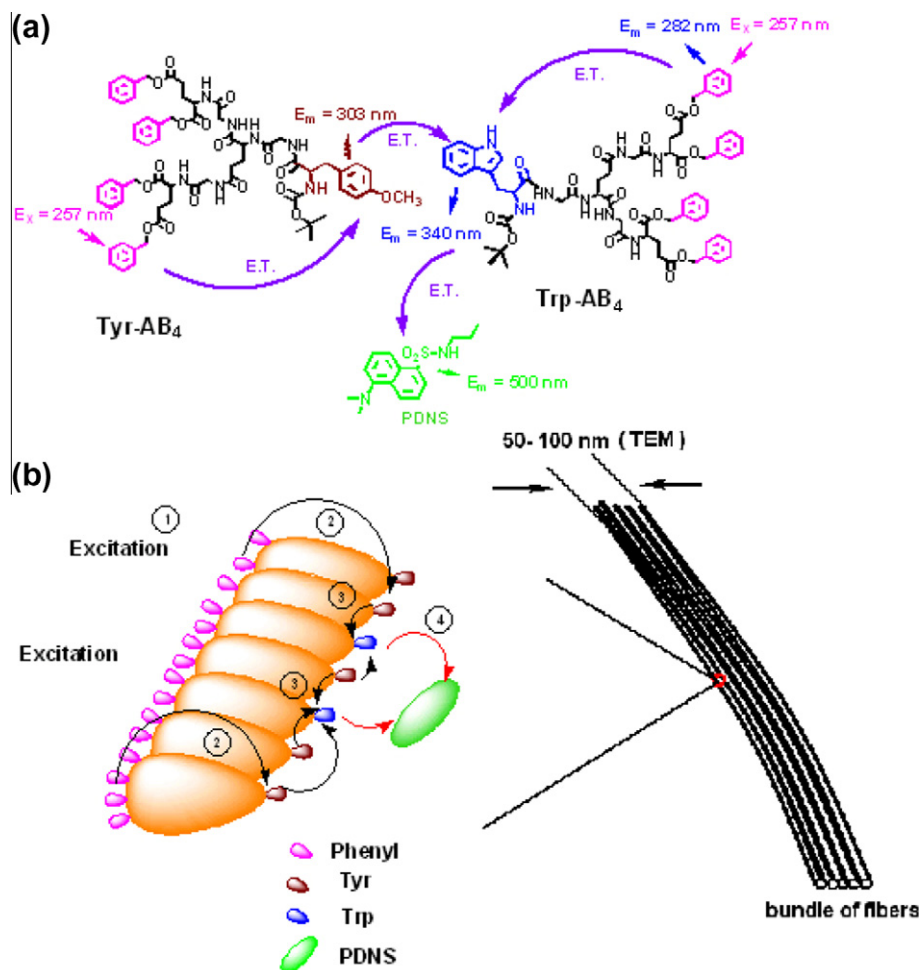
to change the energy transfer efficiency.<sup>11a,16</sup> In the co-gels from dendritic molecules, the ratio of donor to acceptor could be adjusted conveniently. In addition, considering the similar structures of **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>** that tended to co-assemble together orderly,<sup>8</sup> it is likely that the strong interaction of dendritic scaffolds shortens the distance of donor and acceptor, which facilitates the ET process and results in high ET efficiency.

The emission spectra of **Trp-AB<sub>4</sub>** gel and the co-gel are shown in Figure 2b. It displayed that the fluorescence intensity of **Trp** in the co-gel was higher than that in free **Trp-AB<sub>4</sub>** gel, indicating the light-harvesting character of the co-gel with a molar ratio of **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** 1.5:1, a feature of multi-donors per acceptor. The situation was quite similar to the natural light-harvesting system, in which the fluorescence of acceptor was enhanced due to the ET from multiple donors to one acceptor.<sup>17</sup>

To further investigate the ET process of the co-gel system, we selected propyldansylamide (**PDNS**), a dansyl derivative as the guest acceptor whose absorption ( $\lambda_{\text{abs}} = 339$  nm)<sup>18</sup> matched with the emission of the **Tyr-AB<sub>4</sub>** fibers ( $\lambda_{\text{em}} = 340$  nm). **PDNS** was added into the **Tyr-AB<sub>4</sub>/Trp-AB<sub>4</sub>** co-gel to constitute a host–guest gel ET system (HG-gel). As shown in Figure 3a, the co-gel displayed the fluorescence of **Trp** unit before doping with **PDNS**, whereas the HG-gel emitted green light ( $\lambda_{\text{em}} = 497$  nm) of **PDNS** when excited with the wavelength of 254 nm. The photographs of the gels with different colors are given in Figure 3b. It was clearly shown that the co-gel emitted blue light; but turned green after **PDNS** was doped upon irradiating with common UV light. The results suggested that a cascade ET process occurred from periphery phenyl groups to **Tyr** unit, then continually transferred to **Trp** unit, and finally to **PDNS** in the host–guest gel system.

According to the report of Ajayaghosh et al.,<sup>8f,h</sup> guest molecules were trapped in the fibrous networks and distributed around the host gelators. In such a way, they were excited by the neighboring host species. From this point of view, it could be deduced that **PDNS** was likely to be fixed in the networks of fibers and dispersed around the host gelators of **Tyr-AB<sub>4</sub>** and **Trp-AB<sub>4</sub>**, therefore leading to the efficient ET process when the host species were excited (Fig. 4).

In conclusion, ET in the gels from dendrons based on natural amino acids is firstly reported. We have demonstrated that a high efficient ET process and light-harvesting property in the co-gel system were achieved. With **PDNS** as the guest molecules, the host–guest gel system with tunable emission ranging from blue to green was obtained through cascade intra- and intermolecular ET, which mimicked the natural light-harvesting systems. Such a system based on polypeptide might be a promising candidate in the field of bionanomaterials.



**Figure 4.** (a) Anticipated energy transfer within and between dendrons based on natural amino acids glycine, glutamic acid, tyrosine, tryptophan, and guest molecule PDNS. (b) Cartoon of light-harvesting process in self-assembled fibers includes: (1) absorption of photons by the peripheral phenyl groups, (2) ET from phenyl groups to Tyr groups, (3) ET from Tyr groups to Trp groups, and (4) ET from Trp groups to guest molecules PDNS.

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## Supplementary data

Supplementary data (synthetic details and characterization for all the compounds, gelation property, TEM Images of the gels, UV and fluorescence spectra of the gels) associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2010.08.012](https://doi.org/10.1016/j.tetlet.2010.08.012).

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