Electronic Supplementary Information

Photoluminescent Supramolecular Hyperbranched Polymer without Conventional Chromophores Based on Inclusion Complexation

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Experimental and Methods

Materials. α-Cyclodextrin (α-CD, 99%, AR), N, N'-carbonyldiimidazole (CDI), and diethylenetriamine (DTA) were purchased from Aladdin (Shanghai, China). SuperDry dimethyl sulfoxide (DMSO) was obtained from J&K Chemical. Distilled water was used for preparation of aqueous solutions. Other organic solvents were all analytical reagents and used as received.

Synthesis of monomers 1. The monomers **1** were prepared by functionalized CD and DTA using CDI as cross-linker according to the previous report with some modifications.[1-3] Breiefly, a-CD (0.973g, 1 mmol) was dissolved in 20 mL dry DMSO and CDI (1.297g, 8mmol) was added to the solution. After stirring for 3 h under nitrogen atmosphere, the mixture was slowly dropwise added to large excess of DTA within 2 h. After stirring for 16 h, the product **1a** was precipitated by ether/acetone (1:9, v/v). Then the precipitate was washed with ether/acetone, dissolved in DMSO, precipitated and washed by ether/acetone repeatedly. Finally, the product was dried in vacuo at room temperature. The monomers **1**b and **1**c were synthesized in a similar manner by adjusting feed ratio of a-CD and CDI at 1:6 and 1:4, respectively.

Formation of supramolecular hyperbranched polymers: monomer **1** (0.2 g)was dissolved in 1 mL of DMSO. Then the solution was poured into 4 mL of acetone, stirred for 3 days, isolated by centrifugation, washed four times by acetone and dried in vacuo at 30℃.

Measurements

XRD and FT-IR. X-ray diffraction measurements were performed with a powder diffractometer (X'Pert PRO, PANalytical, Netherland). FT-IR spectra were recorded on a Nicolet DX Spectrometer in the range between 4000 and 400 cm^{-1}, with a resolution of 2 cm^{-1} and 64 scans.

Dynamic Light Scattering (DLS). Sizes were measured using a Zetasizer Nano (Malvern Inst. Ltd., UK) equipped with either a four-side clear cuvette. The samples were carried out in 4 serial

measurements at 25 °C (scattering angle 173º). Sample solutions were prepared by using distilled water. Before assay, the aeqeuous solutions were flitered using 0.45μm fliter.

UV-Visible and Fluoresence Spectra Spectroscopy. UV-vis absorption spectra were recorded with a Shimadzu UV-2550 spectrophotometer using a 1 cm path length quartz cuvette. Fluorescence measurements were made on a Perkin-Elmer LS55 luminesence spectrometer. The slit width of both monochromators was 7.5 nm.

Fluoresence Microscope. Fluorescence microscopy was performed on an Olympus IX70 microscope with three kinds of filter (WU: 330–385,WB: 460–490,and WG: 510–550 nm).

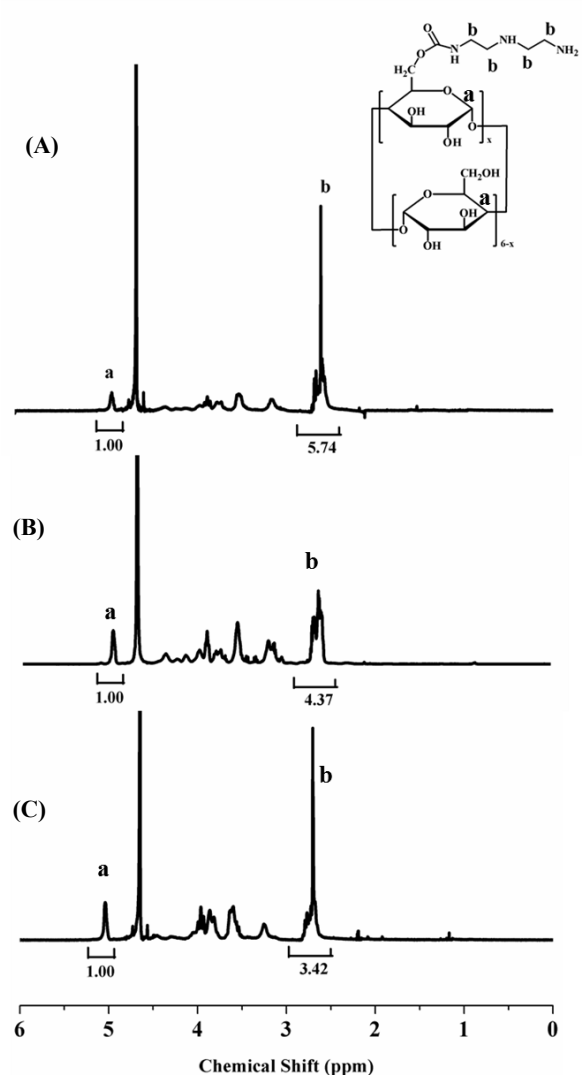

Figure S1 ^{1}H NMR spectra of monomer**s 1a**(A)**, 1b**(B), and **1c** (C).

The chemical shift associated with the unique anomeric proton (a ,O−CH−O) of glucose units of α-CD is at about 5.0 ppm. The proton peaks of DTA (-CH_2CH_2-) appeared at 2.5~2.90. These results w suggested that Az-PEG-Gal was successfully synthesized. The DTA-grafting number was calculated by the equation (1).

$$\text{DTA-grafting number} = \frac{Ib/8}{Ia/6} \quad \text{Equation (1)}$$

Herein, Ia and Ib represent integration area of peak a and b, respectively. According to equation (1), it was easy to caculate the DTA-grafting number every CD. The results indicated that every CD had 4.3 (1a), 3.3 (1b), and 2.6 (1c) DTA molecules.

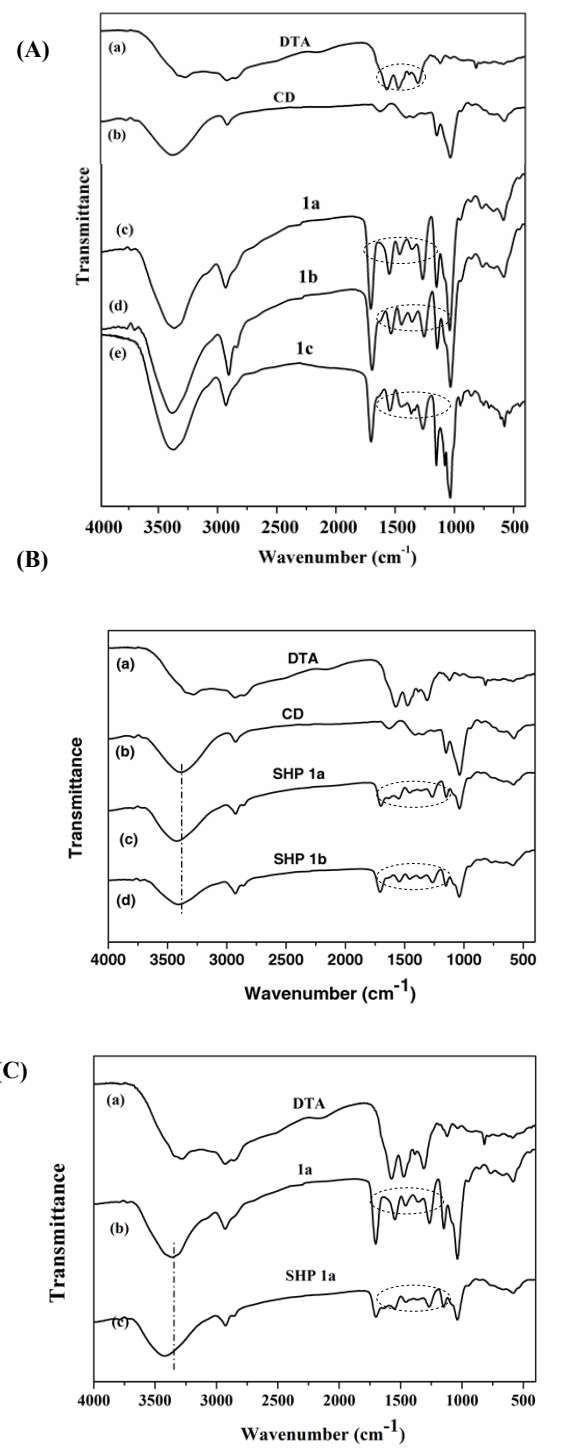

Figure S2 A) FT-IR spectra of DTA, CD, and monomers **1** with different DTA grafting levels. B) FT-IR spectra of SHP **1a** and SHP **1b**. C) FT-IR spectra of **1 a**, and SHP **1a**.

Figure S2A shows the FTIR spectra of (a) DTA, (b) α-CD, (c) **1**a, (d) **1**b, (e) **1**c. For all monomers, the typical broad peaks at 3389 cm^{-1} was normally assigned to the O-H stretching modes for CD. They also

had severl viration models during 1700-1200 cm^{-1}, which were typicl viration models for DTA. These results were consitent with ^{1}H NMR and confirmed the successful preparation of monomers **1**.

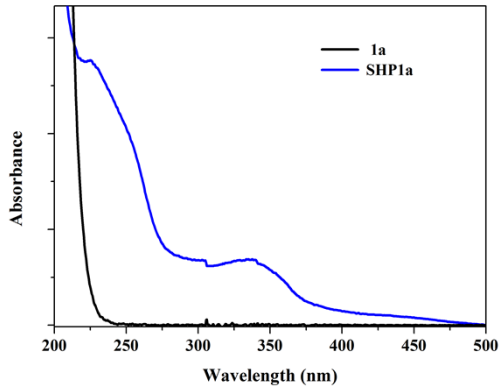

Figure S3 UV-Vis spectra of monomer **1a** and SHP **1a**. All samples were containing 0.5 mM monomer units.

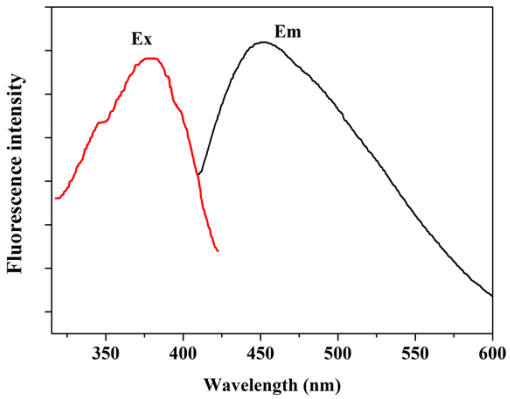

Figure S4 Emission (Em) and excitation (Ex) spectra of 0.5 mM SHP **1a** aqueous solution.

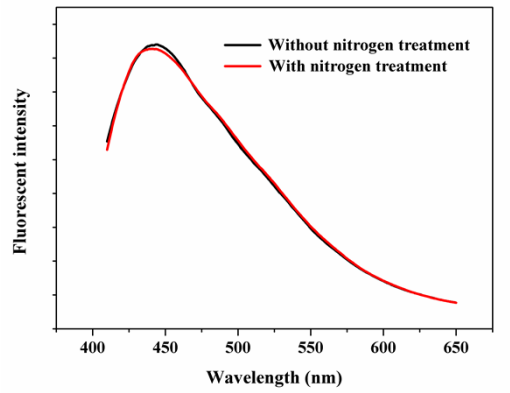

Figure S5 Emission (Em) spectra of 0.5 mM SHP **1a** aqueous solution with or without nitrogen treatment. All samples were containing 0.5 mM monomer units.

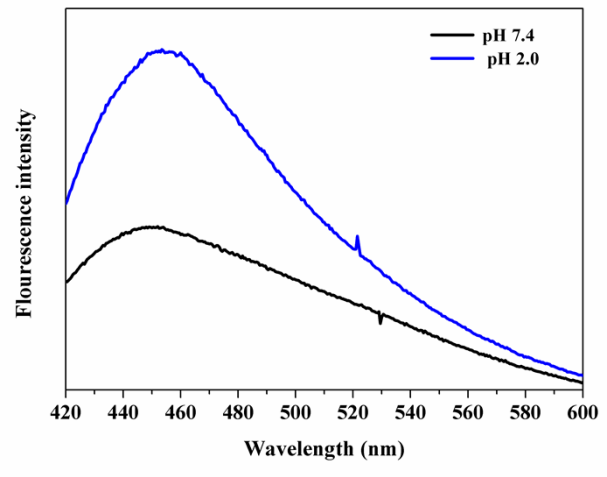

Figure S6 Fluorescence emission spectra of different SHP**1**a at different pH. All samples were containing 0.5 mM monomer units.

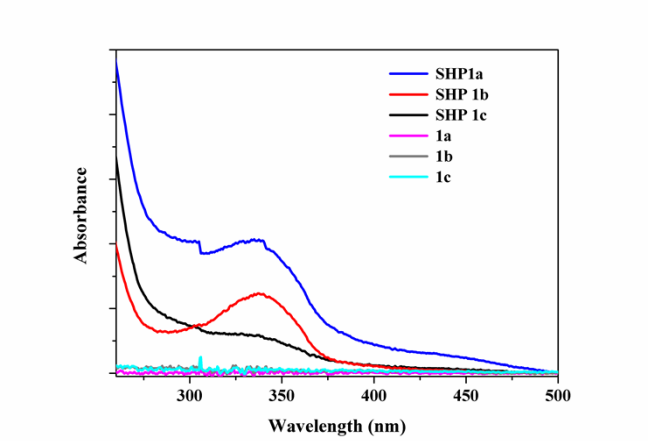

Figure S7 UV-Vis spectra of different monomers and SHPs. All samples were containing 0.5 mM monomer units.

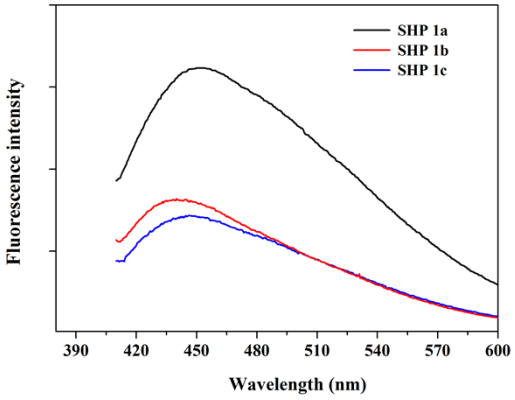

Figure S8 Fluorescence emission spectra of different SHPs. All samples were containing 0.5 mM monomer units.

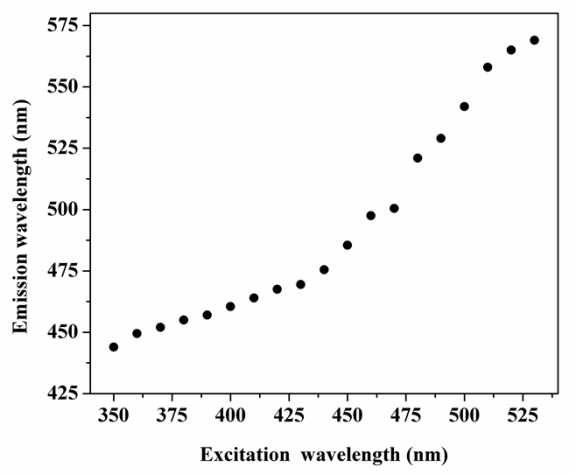

Figure S9 Fluorescence emission wavelengths with different excitation wavelengths ranging from 350 to 530 nm by 10 nm incensement.

References:

(1) Srinivasachari, S.; Fichter, K. M.; Reineke, T. M. *J Am Chem Soc* **2008**, *130*, 4618.

(2) Yang, C.; Li, H.; Goh, S. H.; Li, J. *Biomaterials* **2007**, *28*, 3245.

(3) Ooya, T.; Choi, H. S.; Yamashita, A.; Yui, N.; Sugaya, Y.; Kano, A.; Maruyama, A.; Akita, H.; Ito, R.; Kogure, K.; Harashima, H. *J Am Chem Soc* **2006**, *128*, 3852.