# Formation and Fluorescent Properties of Supramolecular Hyper-branched Polymer (SHP) based on Host–guest Interactions

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## Introduction

It has been interestingly found that primary amine-terminated hyperbranched poly(amino ester) and hyperbranched poly(amido amine) (PAMAM) can emit fluorescence, although they do not contain any fluorescent functional groups. This fluorescent properties have great potential application as biological probe. These hyperbranched polymers (HP) are usually prepared from covalent polymerization of ABm (m≥2) monomers. Supramolecular chemistry has spawned the emergence of supramolecular hyperbranched polymers (SHPs). To date few researches explored to develop fluorescent HPs *via* noncovalent interactions from monomers without any fluorescent functional groups. Here, we report the formation of SHPs from self-organization of ABm monomers 1 containing recognition site α-cyclodextrin (CD) and diethylenetriamine (DTA) moieties in dimethyl sulfoxide (DMSO)/acetone (Fig. 1). It was unexpectedly found that these SHPs displayed strong fluorescence emission and could emit bright wide-band fluorescence depending upon the excitation wavelength.

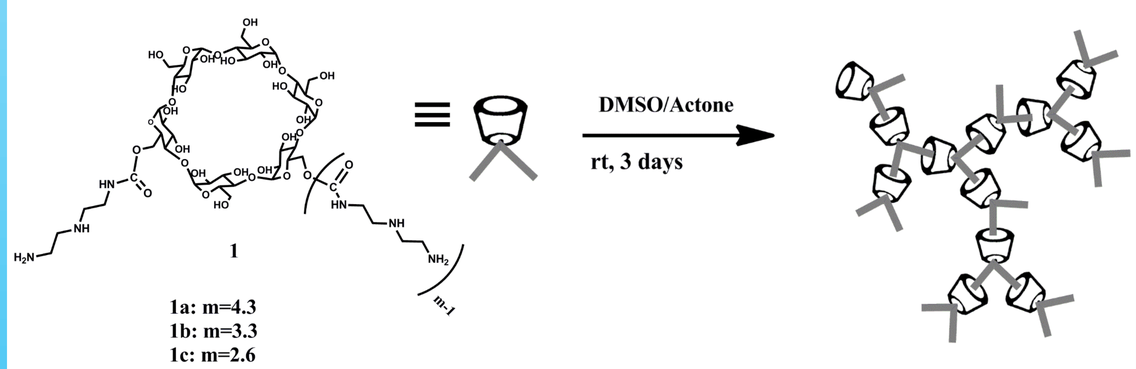


Fig. 1 Structures of monomers and schematic illustration of the formation of the SHPs based on the host-guest interaction between α-CD and aliphatic amines.

## Results & Discussion

### Characterization of SHPs

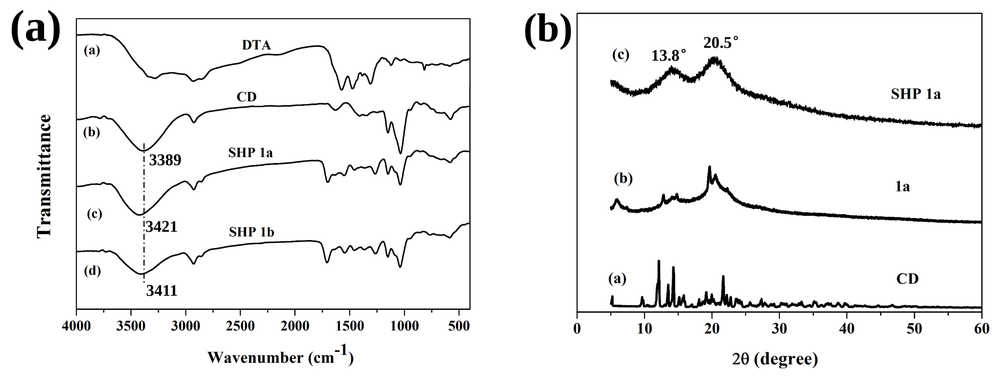


Fig. 2 FT-IR spectra (a) and X-ray diffraction patterns of α-CD, DTA, monomer 1a, and SHP 1a.

➢ The shifted peaks of FT-IR and two intense 2θ-peaks of XRD (typical crystalline peaks of the inclusion complexes with α-CD) confirmed the formation of SHPs.

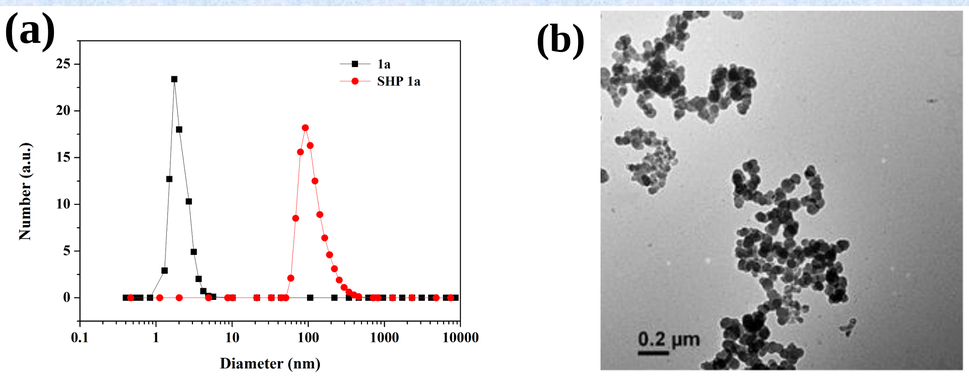


Fig. 3 DLS plots (a) and typical image (b) of 0.5 mM SHP 1a aqueous solution (in distilled water).

➢ The formed SHP 1a had size-peak at 118.6 ± 52.9 nm, and TEM indicated that SHP 1a formed spherical aggregates with diameters around 60 nm. These results further confirmed the formation of SHPs.

### UV-vis and fluorescent properties of SHPs

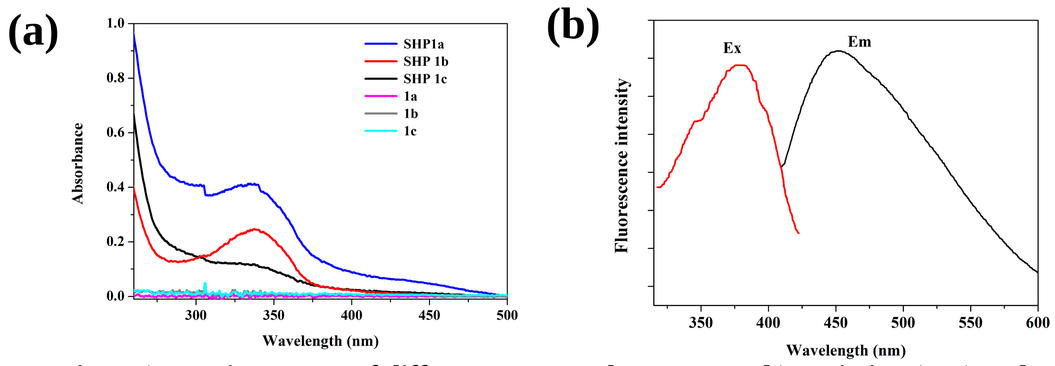


Fig. 4 a) UV-vis spectra of different SHPs and monomers. b) Emission (Em) and excitation (Ex) spectra of 0.5 mM SHP 1a aqueous solution.

➢ The SHP had a new UV absorption band at around 340 nm and presented emission band at 450 nm with excitation band at 380 nm, which can be attributed to the formation of SHPs and the enhancement of the chain rigidity caused by big α-CD molecules.

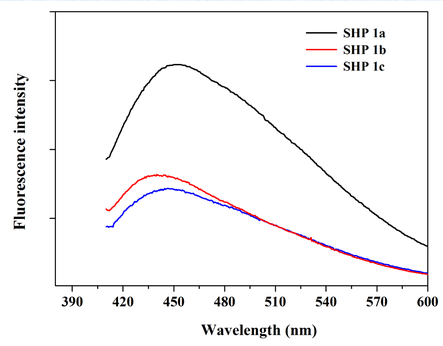


Fig. 5 Fluorescence emission spectra of formed SHPs based on host-guest interaction.

➢ The emission intensity at 450 nm increased with the grafting-level (m) increasing, which may be owing to the higher degree of branching in SHPs and relatively tighter structures of SHPs caused by grafting-level increasing.

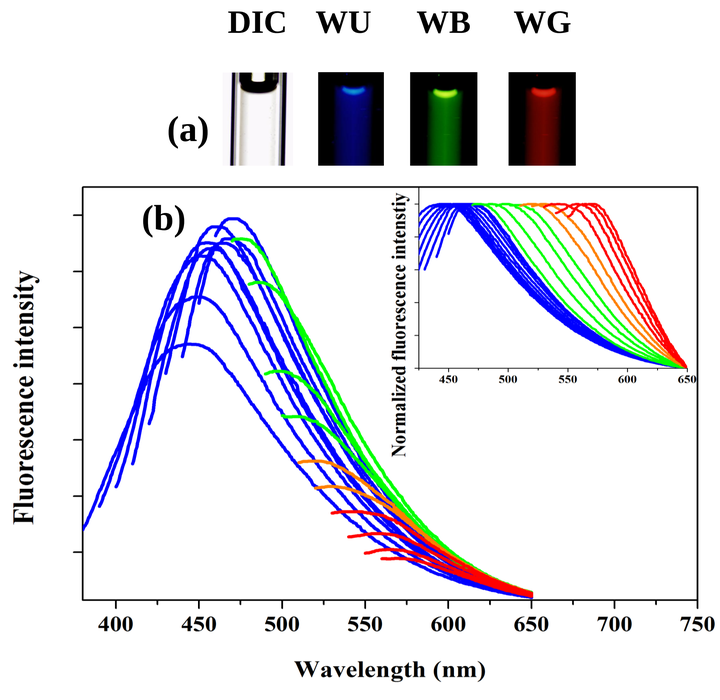


Fig. 6 a) Fluorescence microscope images of 0.5 mM SHP 1a in 1 mm glass capillary with wall thickness of 0.1mm. b) Fluorescence emission spectra of 0.5 mM SHP 1a with different excitation wavelengths from 350 nm on the left to 530 nm on the right in 10 nm increment. The inset image indicated the normalized emission spectra.

➢ The formed SHP *via* host-guest interaction can emit bright wide-band fluorescence depending upon the excitation wavelength, which may be attributed to the high structural heterogeneity and the broad size distribution.

## Conclusion

Novel supramolecular hyperbranched polymer (SHP) was prepared simply based on the host-guest interactions between cyclodextrin and aliphatic amines. Interestingly, the SHPs can emit bright wide-band fluorescence depending upon the excitation wavelength, although the monomer did not contain any fluorescent functional groups. These fluorescent SHPs may have a potential application as a novel fluorescent probe for imaging and diagnosis.

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