2013 ISEF

Organic Light-Emitting Nano Vesicles Self-Assembled from Bis-Urea Containing Fluorescent Molecules

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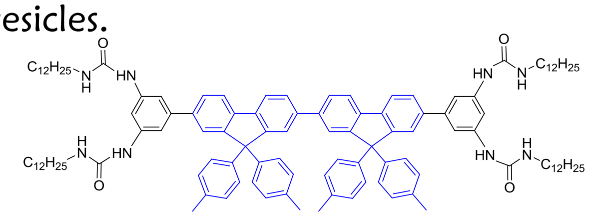
Fair ID: TWN001

Project ID: CH305

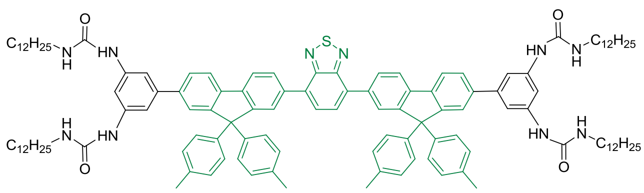
Category: Chemistry/Organic Chemistry

Abstract

Scientists learned from the natural biology systems for gathering useful information to design organic molecules capable of self-assembling into interesting nano-scale architectures. In this research, we have designed and synthesized two organic light-emitting molecules (Blue Compound and Green compound) for the characterizations of their self-assembly nano structures and study their interactions at different levels. The desired molecules were configured with rigid π-conjugated cores serving as the emissive chromophores and end-capped with bis-urea groups that can govern the self-assembly behaviors. In addition, the central chromophore structures were selected to obtain a good spectral overlap between blue molecule's emission and the absorption of green molecule. This molecular design strategy gave us the possibility for studying the energy interplay between them. We used SEM and TEM to characterize the nano structures in various media and found these two molecules can spontaneously form spherical nano structures with the averaged size around 400 nm. The interesting uniform nano-vesicles were formed by subtle intermolecular interactions such as π-π stacking from the planar rigid π cores, hydrogen bonds from the bis-urea groups, and van der Waals forces from the long alkyl side chains. The energy transfers between them were investigated in molecular level and nano scale by fluorescent spectroscopy and confocal microscopy, respectively. We will present the different energy transfer behaviors at various scales and demonstrated interesting applications of these emissive organic nano vesicles.



Blue Compound (BC)



Green Compound (GC)

Introduction

Bionics and nano technology have grown rapidly nowadays. Nature molecules such as protein and DNA can self-assemble into certain structures by virtue of the intermolecular forces, which play significant roles in the nature biology system. Recently, scientists have designed organic molecules that can self-assemble into nano structures. Therefore, we decided to synthesize two organic fluorescent compounds that can self-assemble into complete vesicles. In addition, the good spectral overlap between Blue Compound's emission and Green Compound's absorption gave us the possibility for studying the energy transfer behaviors between them, and demonstrated interesting applications of these emissive organic nano structures.

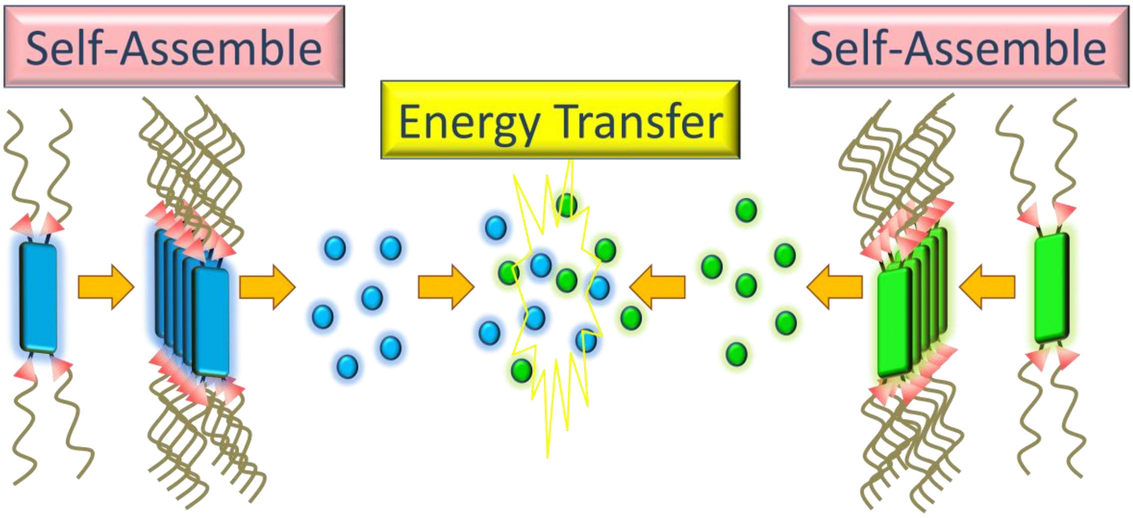


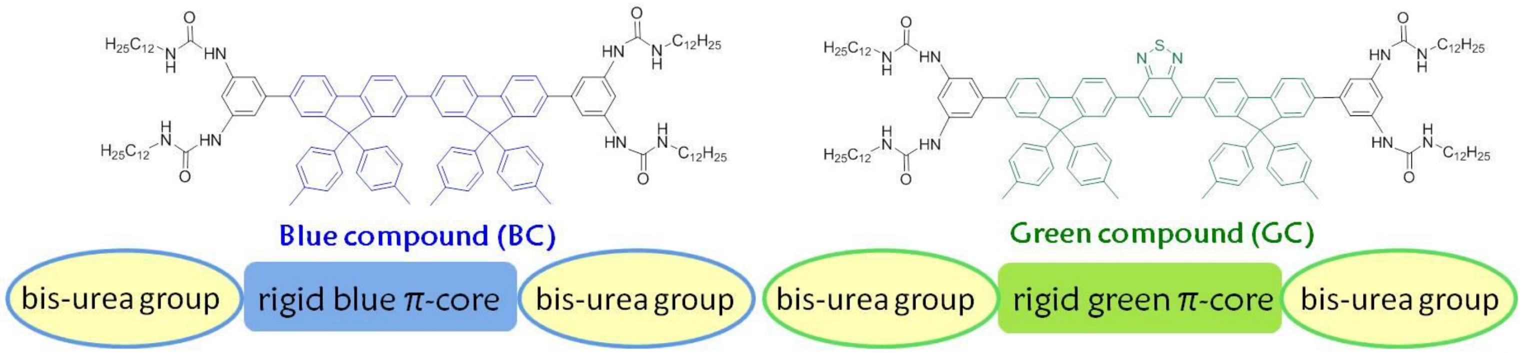
Fig. 1 Interaction of BC and GC

Objectives

1. To synthesize two organic light-emitting compounds with the capability to self-assemble.
2. To study the energy transfer behavior between the two self-assembled nano structures.

Experimental

1. Molecule Designing



Give intermolecular hydrogen bonds (urea) and van der Waals forces (long hydrocarbon chain) for molecular self-assembly.

Give intermolecular π-π stacking for self-assembly and light-emitting (fluorescence).

2. **Nano Microstructure Observation** : Scanning Electronic Microscope (SEM, FEI Nova NanoSEM 200), Transmission Electronic Microscope (TEM, Hitachi H-7650) and Dynamic Light Scattering (DLS), High-voltage TEM (Tecnai G2 200kv)

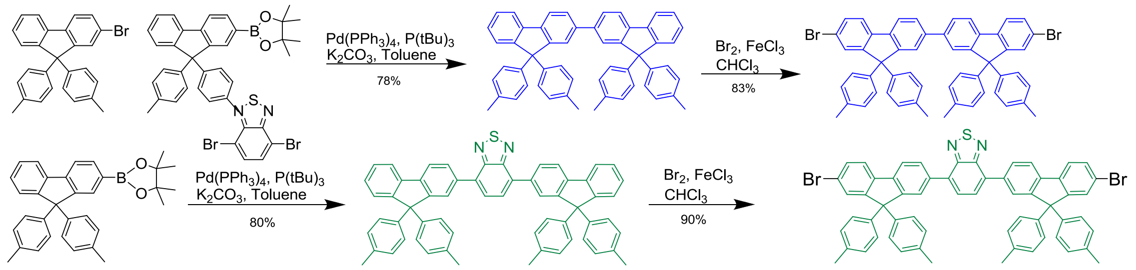
3. **Photophysical properties** : UV-Vis (Jasco V-670), Fluorescence Spectroscopy (Hitachi F4500)

4. **Energy Transfer Observation** : Laser Scanning Confocal Microscope (Leica TCS SP5)

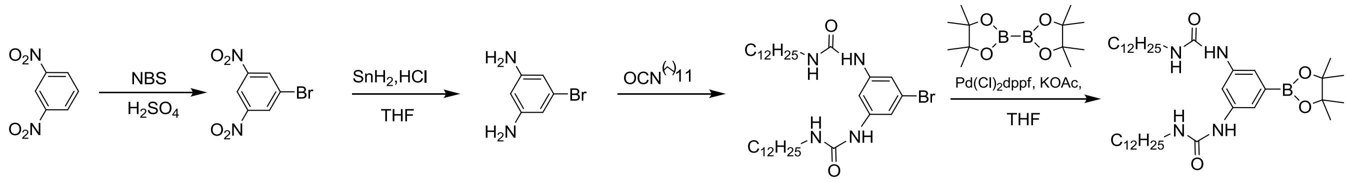
Results and Discussion

1. Synthesis of BC and GC

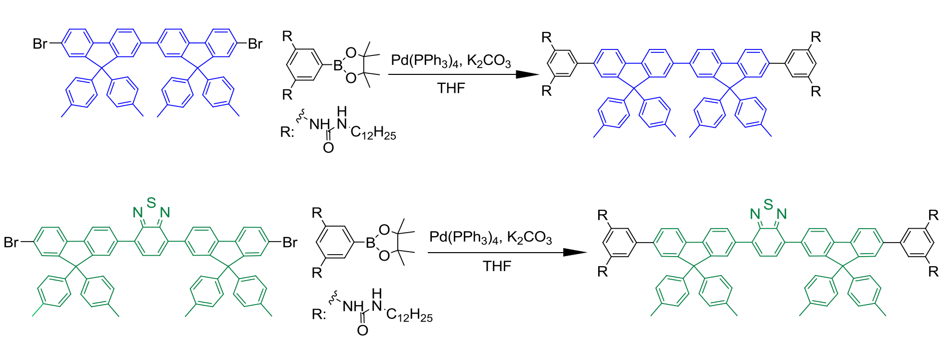
(1) Chromophores



(2) Self-assembling groups



(3) Combination of chromophores and self-assembling groups



2. Capability to Self-assemble

(2) Solvents select

A. MeOH : a polar solvent competitive to molecules' hydrogen bondings.

B. Cyclohexane : cycloalkane is competitive to van der Waals forces

C. Toluene : an aromatic hydrocarbon competitive to π- π stacking and van der Waals forces

(3) Sample preparation (10^{-4}M)

A. 1 Tetrahydrofuran (THF)

B. 1:5 THF : MeOH

C. 1:5 THF : Cyclohexane

D. 1:5 THF : Toluene

E. 1 Toluene

(4) Self-Assembly results by SEM and TEM images

A. THF

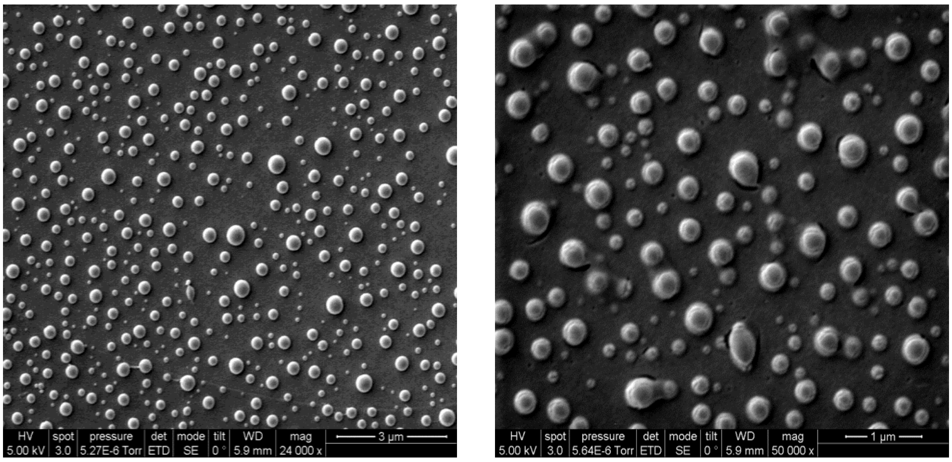


Fig. 2 BC in 10^{-4} M THF under SEM

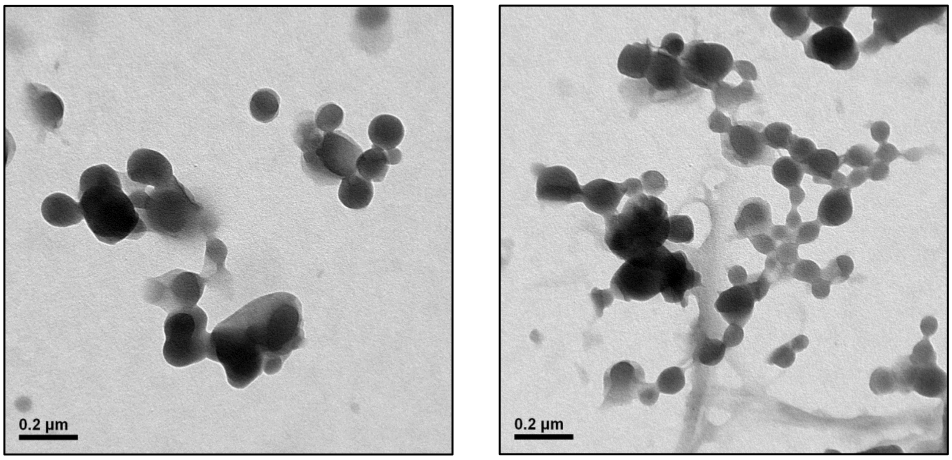


Fig. 3 BC in 10^{-4} M THF under TEM

B. THF : MeOH (1:5)

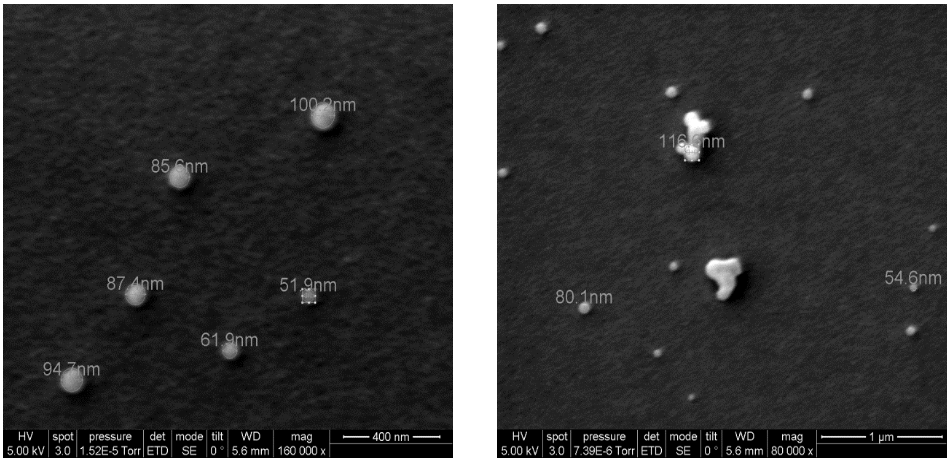


Fig. 4 BC in THF : MeOH (1:5) under SEM

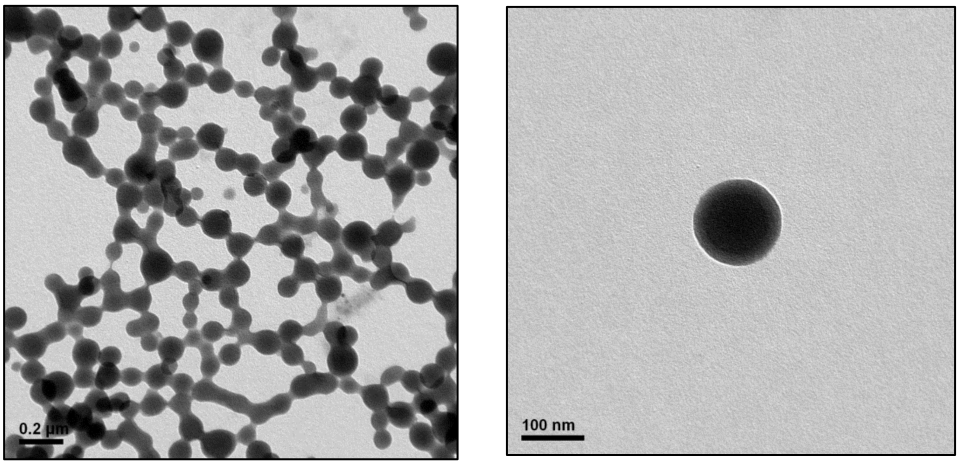


Fig. 5 BC in THF : MeOH (1:5) under TEM

C. THF : Cyclohexane (1:5)

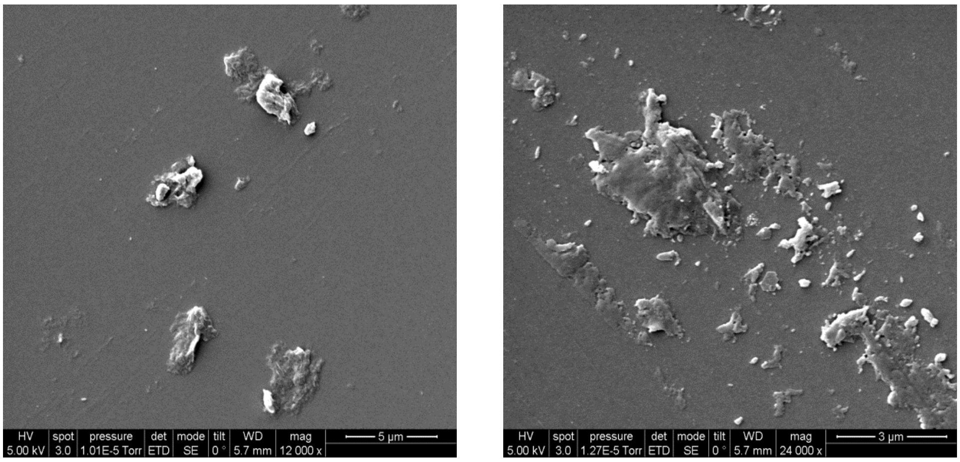


Fig. 6 BC in THF : Cyclohexane (1:5) under SEM

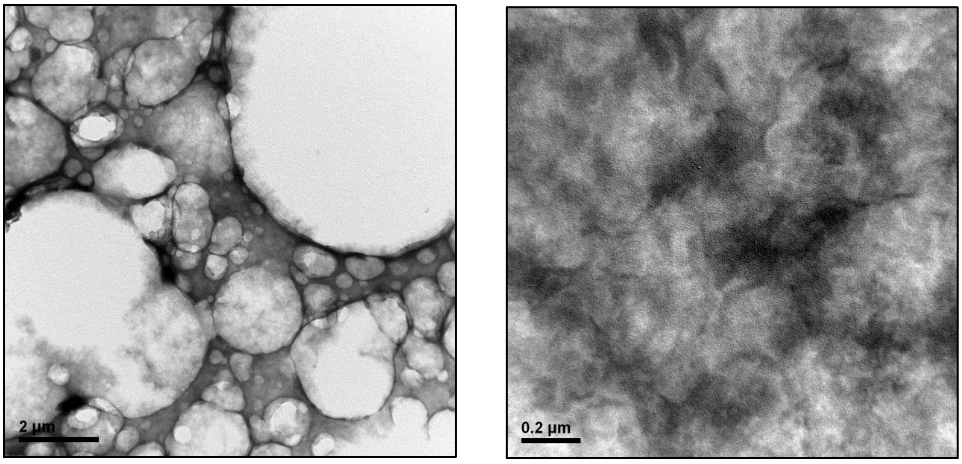


Fig. 7 BC in THF : Cyclohexane (1:5) under TEM

D. THF : Toluene (1:5)

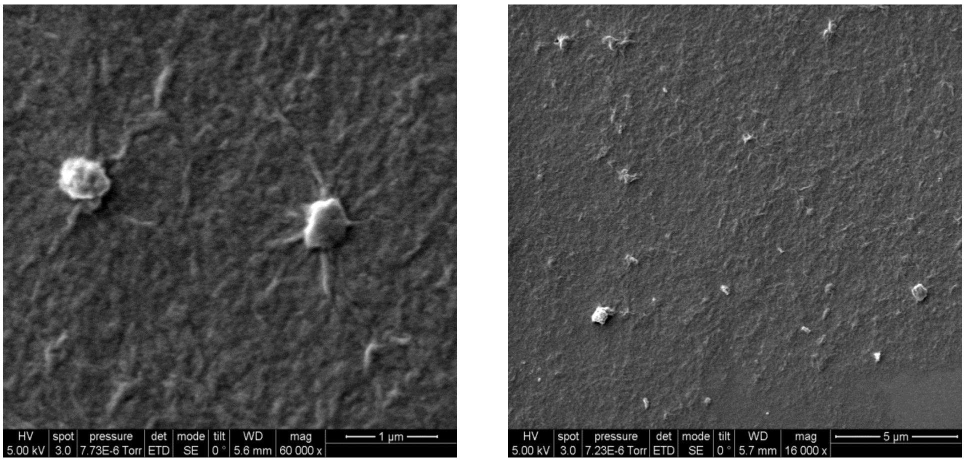


Fig. 8 BC in THF : Toluene (1:5) under SEM

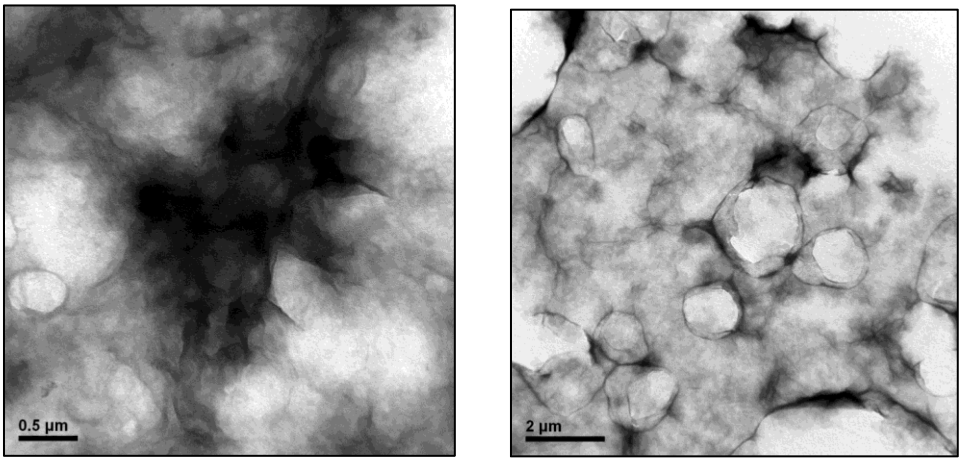


Fig. 9 BC in THF : Toluene (1:5) under TEM

E. 10^{-4} M Toluene

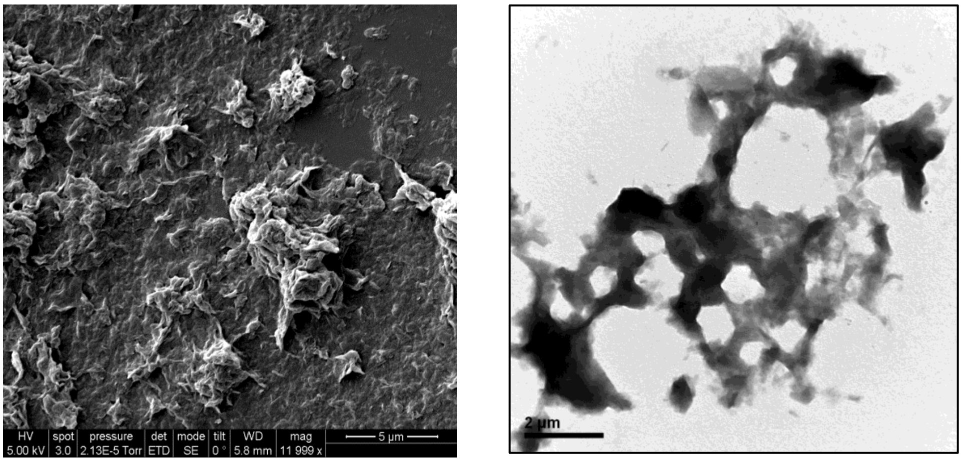


Fig. 10,11 BC in Toluene under SEM/TEM

1. SEM and TEM results show that **BC** is able to self-assemble into discrete spheres in THF and THF/MeOH mixed solutions (Fig. 2,3,4,5), while not observed in cyclohexane and toluene. Instead, aggregates without specific features were formed (Fig. 6,7,8,9,10,11).
2. Cyclohexane and toluene can reduce van der Waals interactions. In addition, toluene can weaken intermolecular π-π stacking.
3. Due to the interference of hydrogen bonding interactions, the observed spherical structures of **BC** in THF containing MeOH is not as good as in pure THF (Fig. 2,3 vs. Fig. 4,5).
4. *Similar self-assembly behaviors have also been found for GC molecule in various solvents*.

(4) Self-assembly study by high voltage TEM

The nature of nano spheres was analyzed with high resolution TEM. The result (Fig. 12) clearly shows it is *hollow*, indicating the formation of nano *vesicles* from the molecular self-assembly of **BC** in THF.

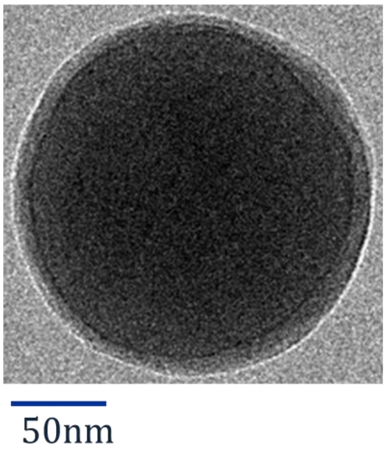


Fig.12 Nano vesicle under high voltage TEM

(5) Capability of self-assembly by DLS

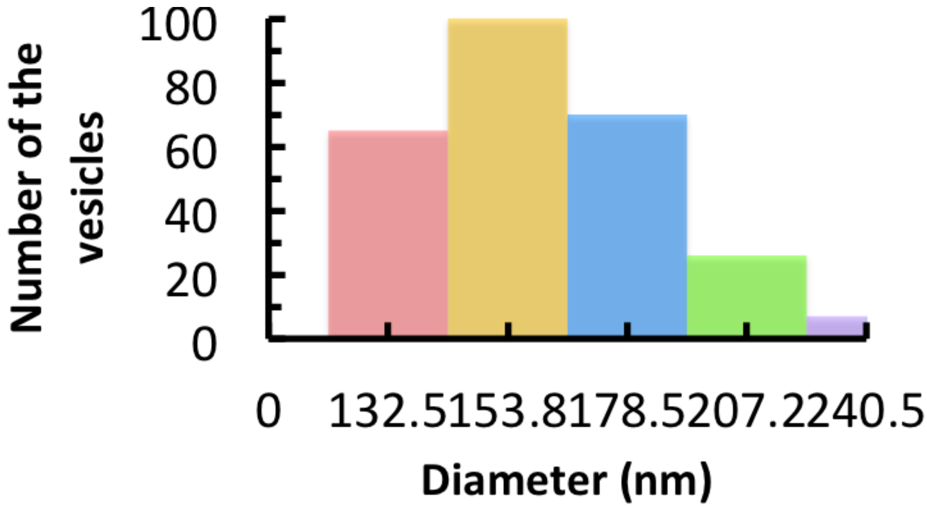


Fig.13 Analysis of the sizes of the nano vesicles

The formation of nano vesicles was spontaneously achieved in THF solution. This assumption was verified by dynamic light scattering (DLS) analysis of BC (10^{-4} M) in THF, showing an averaged particle size of ~160 nm (Fig. 13), which is consistent with TEM analysis.

3. Energy transfer results

(1) Energy transfer study by Fluorescence Spectroscope

I. The emission spectrum of BC overlaps with the absorption spectrum of GC between 400~500 nm (Fig. 14), This results shows good possibility of performing energy transfer between them.

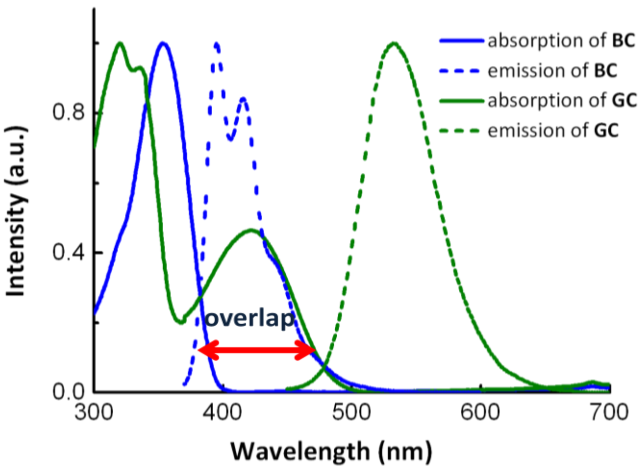


Fig. 14 Emission and absorption of BC and GC by UV-Vis and fluorescence spectroscope

II. With the addition of GC into a BC solution, the blue fluorescence (~400 nm) of BC was gradually quenched, while the intensity of GC's green fluorescence (~ 550 nm) increases (Fig. 15)

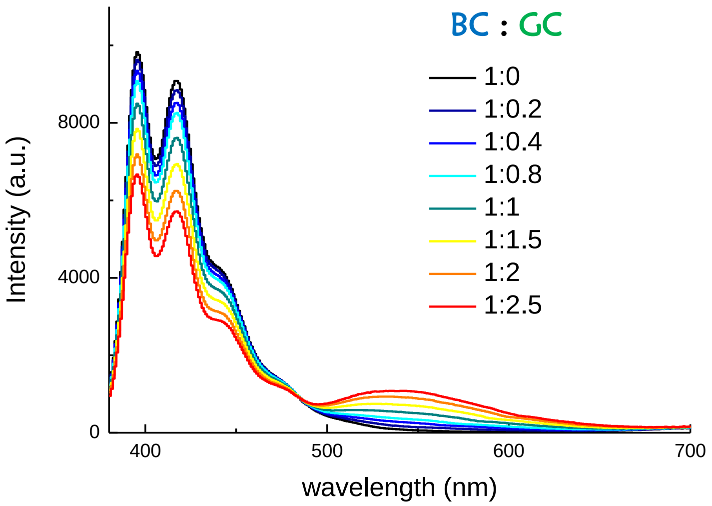


Fig. 15 Energy transfer spectrum of BC/GC in solution at various ratios

III. Stern-Volmer analysis of the quenching of BC emission by GC gave a linear plot (Fig. 16). This results indicates that the energy transfer between BC and GC vesicles is efficient.

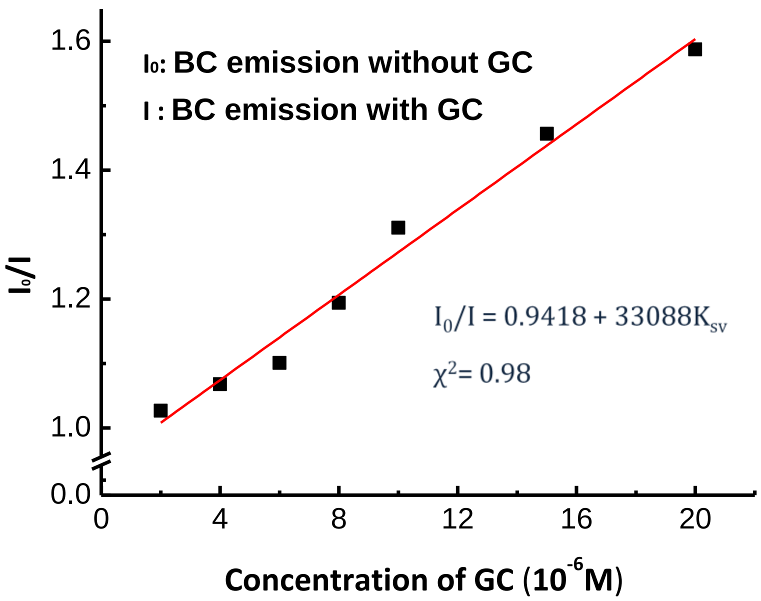


Fig.16 Stern-Volmer analysis of fluorescence quenching of BC and GC

(2) Energy transfer study by Laser Scanning Confocal Microscope

I. Preparation

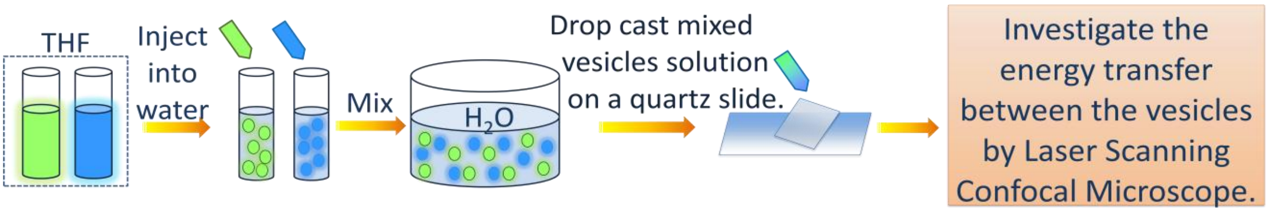


Fig.17 Production of a dilute sample for confocal microscopy images.

BC and GC cannot dissolve in water. This step can keep them from self-assembling in the same vesicle.

II. Observation with LSCM

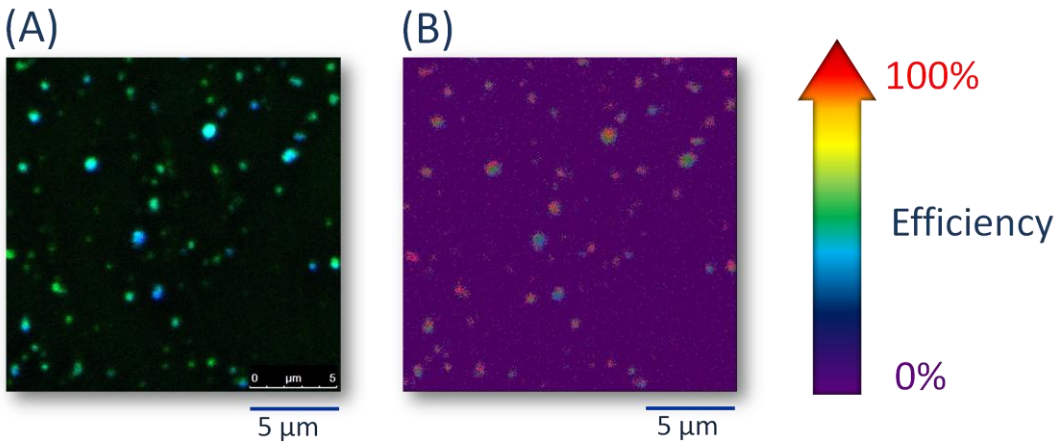


Fig.18 LSCM analysis of

(A) BC and GC mixed vesicles, (B) Energy transfer efficiency profile.

The LSCM-observed discrete BC and GC vesicles indicate no interchanges between BC and GC molecules during the vesicle formation processes (Fig. 18A). Energy transfer behaviors can be observed on the BC-GC contacted vesicles as exciting on BC vesicles (Fig. 18B).

4. Potential application of the fluorescent hollow vesicles

(1) Preparation of QDs inside the vesicles

Mix a **BC** vesicle solution (200 μL, 10^{-4} M, THF) with **CdSe** dried from a hexane solution. → Drop cast the mixed Solution on a quartz slide. → Investigate the energy transfer by LSCM.

(2) Observation with LSCM and TEM

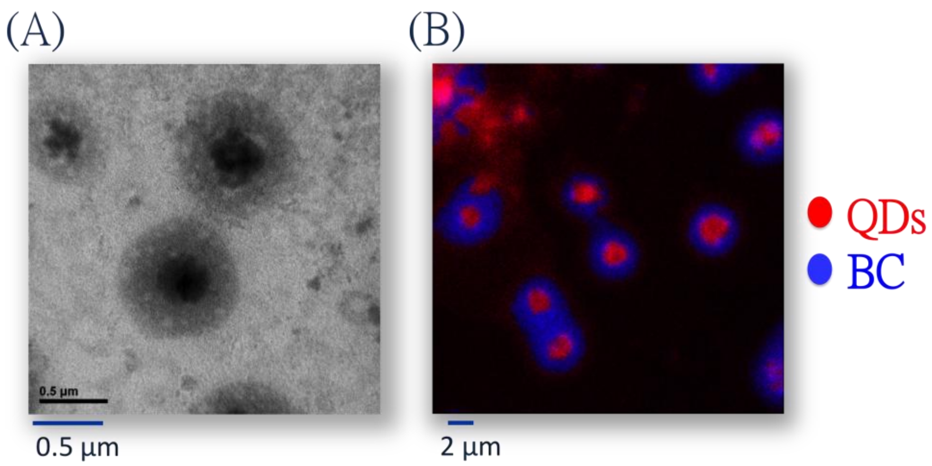


Figure 19. LSCM analysis of BC and CdSe mixed solution.

(A) TEM image of QDs-encapsulated vesicles

(B) Overlap of BC and CdSe

I. The CdSe quantum dots aggregating into a cluster was surrounded by blue light-emitting BC vesicles (Fig. 19A). The core-shell structure emits their individual fluorescence as observed by LSCM (Fig. 19B), and performs efficient energy transfer behavior due to the good spectral overlap.

II. TEM and LSCM results indicate that QDs were encapsulated inside the vesicles. Therefore, these self-assembled vesicles may have potential to serve as capsule for drug delivery with optical tracking ability.

Conclusions

1. Two organic molecules (BC and GC) which are able to have light-emitting and self-assembly functions have been successfully synthesized.
2. Intermolecular forces such as hydrogen-bonding, van der Waals forces, and p-p interactions, appeared to play important roles in self-assembly.
3. Due to their good spectral overlap, efficient energy transfer behaviors between BC and GC vesicles have been verified by fluorescence and LSCM analyses.
4. The hollow nature of our light-emitting vesicles can be potentially used as an optical-tracking for delivery purpose.

References

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