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Supporting Information

Covalently assembled polymer nanocapsules: a novel scaffold for light-harvesting

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1. Materials

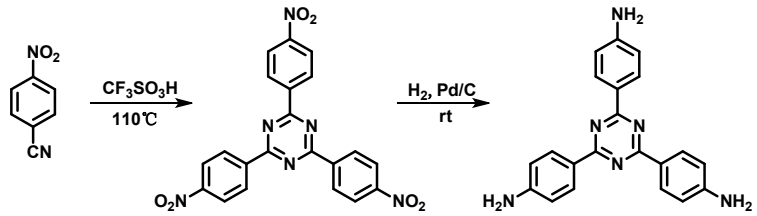
4-Nitrobenzonitrile, trifluoromethane sulfonic acid, ammonium formate, ammonium vanadate, 10% Pd/C, pyrrole, 4-nitrobenzaldehyde, acetic anhydride, propanoic acid, concentrated hydrochloric acid, stannous chloride dehydrate, and ammonium hydroxide were purchased from Energy Chemical plant and used directly. All the solvents were purchased from Beijing chemical plant.

2. Instruments and methods

SEM: SEM images were taken with a JEOL JSM 6700F apparatus. A drop of the stock solution was dripped onto a silicon wafer and air-dried.
TEM: TEM images were captured with a JEOL1011 transmission electron microscope at an acceleration voltage of 200 kV. The sample was made by dripping a drop of the stock solution on a 300-mesh, carboncoated copper grid and air-dried.
AFM: A silicon wafer was immersed into the stock solution for 8 minutes, then taken out of the solution and air-dried. The observation was performed using a Nanoscope Ⅳ.

DLS: 1mL of the sock solution was placed into the glass and the instrument was Malven Instrument zetasizer Nano ZS equipped with a He-Ne laser (633 nm, 4 mW) and an avalanche photodiode detector.
Flsorescence spectrum was obtained using fluorescence spectrophotometer 5301PC equipped with 150 W Xenon lamp, scanning from 200 nm to 900 nm.

3. Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (Tta)



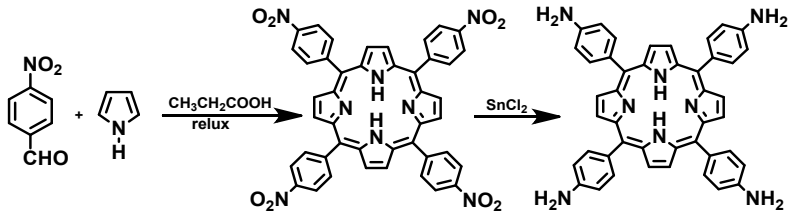
Scheme S1. The synthetic route of 4,4’,4’’-(1,3,5,-triazine-2,4,6- triyl)trianiline (Tta).

4,4’,4’’-(1,3,5,-Triazine-2,4,6- triyl)trianiline (Tta) was synthesized according to the previous procedures with little modification.[1] 4-Nitrobenzonitrile (4 g, 27.0 mmol) was heated to 110 ^{0}C for 18 hours within 5 mL trifluoromethane sulfonic acid. The reaction was monitored using TLC. After completion, the reaction mixture was poured into plenty of water. The resulting precipitate was collected and dried under vacuum in 80 ^{0}C for 24 hours to get 2,4,6-tris(4-nitrophenyl)-1,3,5-triazine as a gray solid (3.2 g, 7.2 mmol, 80%). This intermediate was directly used for the next step without any further purification.

For the reduction of 2,4,6-tris(4-nitrophenyl)-1,3,5-triazine, we employed the

method reported previously.[2] In a 100 mL flask, a catalytic amount of $HCOONH_4$ and NH_4VO_3 were added into the suspension of 2,4,6-tris(4-nitrophenyl)-1,3,5-triazin (2 g, 4.5 mmol) and 0.5 g Pd/C (10 wt%) in 60 mL dioxane/ethanol/water (v/v, 6/3/1), then stirred at room temperature for about two days. The reaction was monitored by TLC. After completion, the mixture was filtered, a large amount of water was added into the filtrate and the resulting precipitate was collected after several times washing with deionized water and dried in vacuo. The crude product was further purified using column chromatography and the final product 4, 4', 4''-(1, 3, 5-triazine-2, 4, 6-triyl)trianiline (Tta) was obtained as a yellow solid (0.66 g, 1.8 mmol, 40%). ^{1}H NMR (DMSO-d_6, 500 MHz) = 8.35 (d, 6 H), 6.69 (d, 6 H), 5.91 (s, 6 H). MS (ESI-MS) = 355.2[M + H]$^+$.

4. Synthesis of tetra(4-aminophenyl)porphyrin (Tapp)



Scheme S2. The synthetic route of Tetra(4-aminophenyl)porphyrin(Tapp).

Pyrrole (0.85 mL, 12.2 mmol) was added into the mixture of 4-nitrobenzaldehyde (1.85 g, 12.2 mmol), acetic anhydride (2 mL, 19.6 mmol) and 80 mL propanoic acid under the condition of refluxing. Then the mixture was heated to reflux for 30 minutes. After leaving the mixture in dark for one day, the dark solid was filtered off with washing by deionized water several times and dried in vacuo for 24 hours. The dark solid obtained was added into 40 mL pyridine, the mixture was heated to reflux for 1 hour. When it was cooled to room temperature, the mixture was left in 4 ^{0}C for a night. After complete precipitation, it was filtered off and washed with acetone for several times. The residue was dried in vacuo, which gived dark tetrakis(4-sulfonatophenyl)porphyrina (Tnpp) (2.1 g, 2.6 mmol, 22%) as an intermediate product. It was directly used for the next step without any further purification.

Tnpp (2.0 g, 2.5 mmol) was added into 50mL concentrated hydrochloric acid under N_2, and the mixture was stirred at room temperature for 1 hour. A 70mL concentrated hydrochloric acid solution of $SnCl_2{\cdot}2H_2O$ (4.5 g, 19.9 mmol) was dripped into Tnpp solution under N_2, the reaction was going on at 80 ^{0}C for 30 minutes. After the mixture was cooled to room temperature, ammonium hydroxide was dripped into the mixture under the condition of ice bath until pH = 8～9. The product tetra(4-aminophenyl)porphyrin (Tapp) was abstracted by chloroform for several times, the organic layer was collected and evaporated to afford purple solid, then the product was dried in vacuum (0.84 g, 1.25 mmol, 50%). ^{1}H NMR ($CDCl_3$, 500 MHz) = 8.90 (d, 8 H), 8.01 (d, 8 H), 7.07 (d, 8 H), 4.02 (s, 8 H), -2.69 (s, 2 H). MS (ESI-MS) = 675.7[M + H]$^+$.

5. Preparation of the covalently linked nanocapsules

Typically, the monomers Tta (**1**, 0.05 mg), a flat, rigid core carrying three aminos at the periphery and linkers glutaraldehyde (**3**, 1.4 μL) were mixed together in 2 mL ethanol at a weak acid condition. After leaving in room temperature for 24 h, DLS, SEM, TEM, AFM were employed to examine the assemblies. The method of preparing the covalently assembled nanocapsules in acetonitrile, the acetonitrile/ethanol mixed solvent and ethanol/dichloromethane mixed solvent was the same as that in ethanol.

6. Covalently assembled nanocapsules with different sizes obtained in various solvents.

In order to control the size of the nanocapsules, we performed the covalent assembly in various solvents. We found that the solvent in which we carried out the covalent assembly played an important role on the size of the fabricated nanocapsules. DLS analysis (Figure S1) conformed this phenomena, SEM and TEM were utilized to conform the architecture of nanocapsules (Figure S2).

When the reaction medium was acetonitrile, smaller nanocapsules with the size of about 80 nm were obtained, the size of the nanocapsules could increase to 132 nm when we performed the covalent assembly in the ethanol/acetonitrile mixed solvent (3:2, v/v). The size of the obtained nanocapsules could reach about 290 nm when the reaction medium was ethanol/dichloromethane (7:3, v/v) mixed solvent, greatly larger than that of the nanocapsules made from ethanol (180 nm).

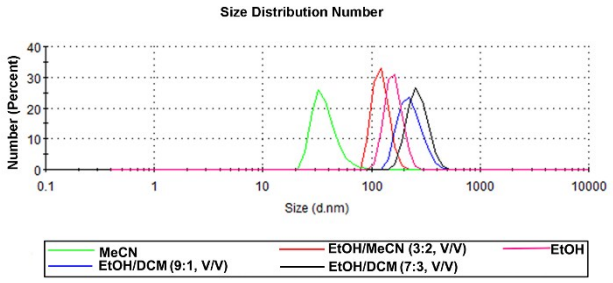


Fig. S1 DLS analysis of the assemblies carried out in various reaction media.

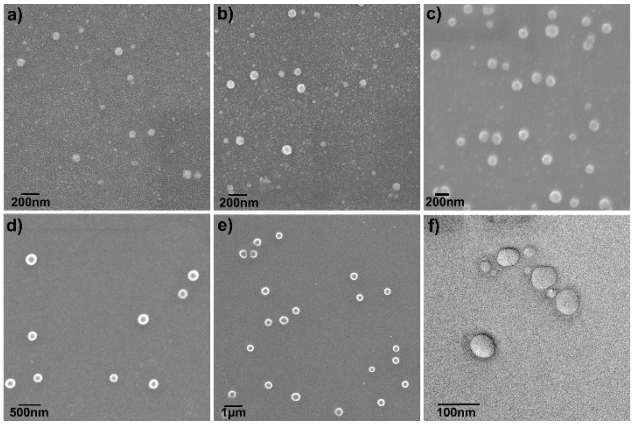


Fig. S2 SEM images of the covalent assemblies made in (a) MeCN, (b) EtOH/MeCN mixed

solvent (3:2, v/v), (c) EtOH, (d) EtOH/CH_2Cl_2 mixed solvent (9:1, v/v), (e) EtOH/CH_2Cl_2 mixed solvent (7:3, v/v). (f) TEM image of the covalent assemblies made in MeCN.

7. Monitoring the nanocapsule forming process using DLS in ethanol

Aggregates with an average diameter of 15 nm were observed using DLS after about 10 minutes, then gradually increased to 180 nm within 55 minutes, and finally maintained the same size.

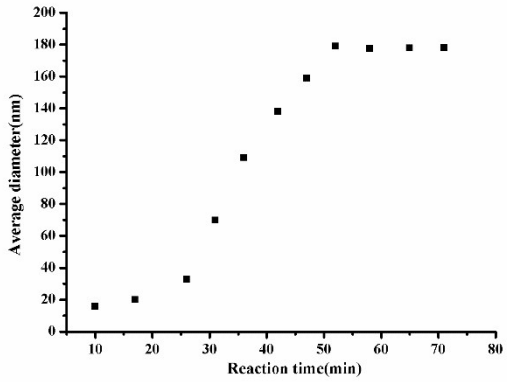


Fig. S3 The change of the average size in the formation process of polymer nanocapsules covalently assembled using Tta and glutaraldehyde.

8. Monitoring the nanocapsule forming process using TEM

TEM was utilized to investigate the polymerization process in ethanol. when the reaction was carried out for 20 minutes, we could detect nanosheets with a size of about 100 nm. After 40 minutes, larger nanosheets emerged and began to roll up. Imperfect nanocapsules with the diameter of 180 nm were observed after about 1.5 hours. After 5 or 7 hours, semi-nanocapsules were observed, when the reaction time was 15 hours, nanocapsules of about 180 nm were completely formed.

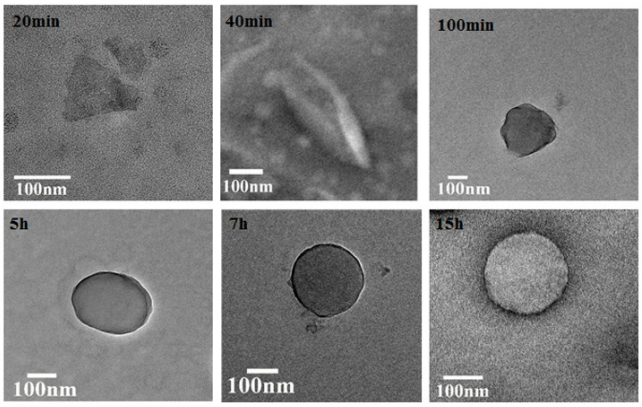


Fig. S4 The formation process of polymer nanocapsules covalently assembled using Tta and glutaraldehyde.

9. The influence of pH on the nanocapsules

Because the nanocapsules were formed through schiff base bond, which was sensitive to pH, when excess concentrated hydrochloric acid was added into the stock solution, the architecture of nanocapsules was completely destroyed, and monomers were disorderly stacked together.

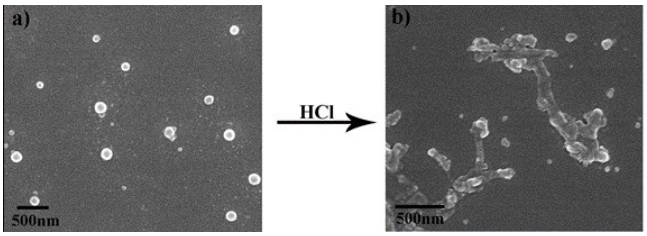


Fig. S5 (a) Tta-based nanocapsules. (b) Nanocapsules are destroyed after adding HCl.

10. Proposed forming process of covalently linked nanocapsules

According to DLS and the TEM observation, we propose the nanocapsules formation mechanism as follows:[3] firstly, the building blocks were linked by glutaraldehyde to form oligomers. Then, the oligomers reacted with each other to form 2D nanosheets, the nanosheets rolled up to reduce their energy, and the curved nanosheet continued to react with each other to generate the final nanocapsules.

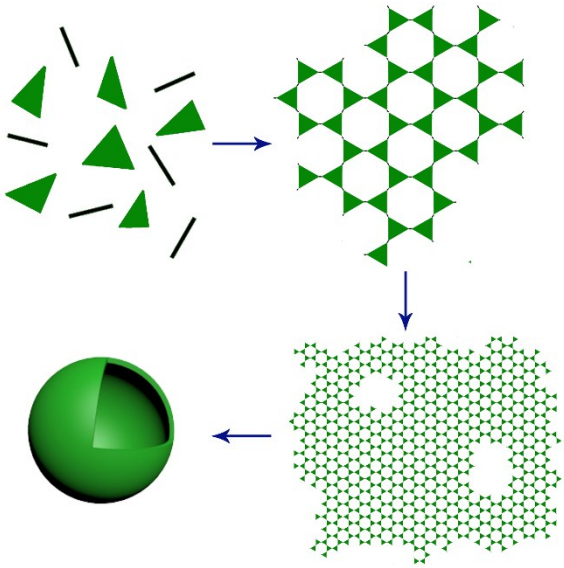


Fig. S6 Proposed forming process of covalently linked nanocapsules.

11. The influence of Tapp amount on the morphology of nanocapsules

In order to know whether the nanocapsule morphology should be influenced when Tapp with four polymerizable groups at the periphery was introduced into the assemblies as one of the building blocks, SEM was used as tool for checking

the capsules. From the SEM images, we could see that the added amount of Tapp in the coassembly system did not affect the architecture and dispersion of nanocapsules.

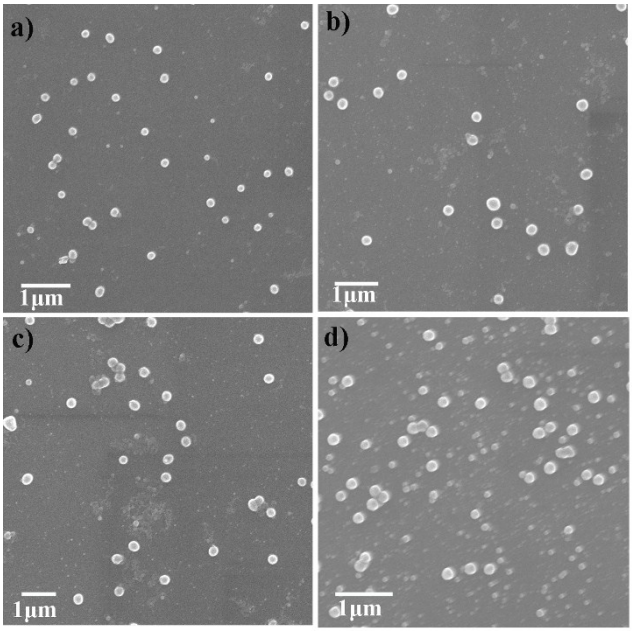


Fig. S7 Nanocapsules with different Tta: Tapp ratios: (a) 200: 1, (b) 100: 1, (c) 50: 1, and (d) Tapp as building blocks.

12. UV-vis absorption spectra of the coassembled nanocapsules

UV-vis spectra of the coassembled nanocapsules were recorded using Shimadzu UV-3600 Recording Spectrophotometer. Increasing Tapp concentration and maintaining the concentration of Tapp at the same time in this coassembly system, resulted in the improvement of the absorption spectra of Tapp monomers from 420 nm to 450 nm, and the absorption of Tta monomers between 300 nm and 400 nm was almost unchanged.

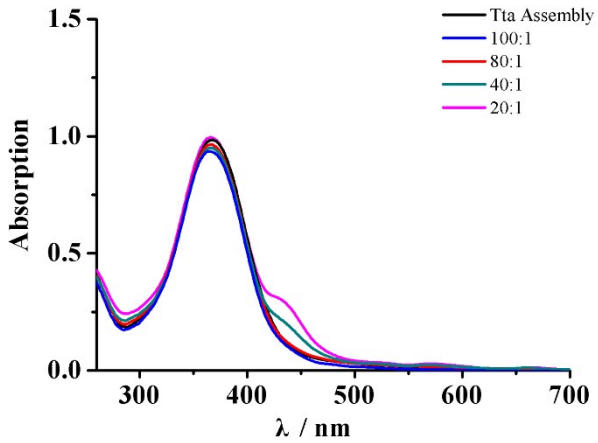


Fig. S8 UV-Vis absorption spectra of the coassembled nanocapsules with different Tta: Tapp ratios ([Tta] = 20 μM).

13. Preparation of the light-harvesting system on the covalently assembled nanocapsule

The method of preparing the covalently coassembled nanocapsule was the same as that of preparing the Tta nanocapsule in ethanol. The possible energy transfer on the light-harvesting system was as shown below.

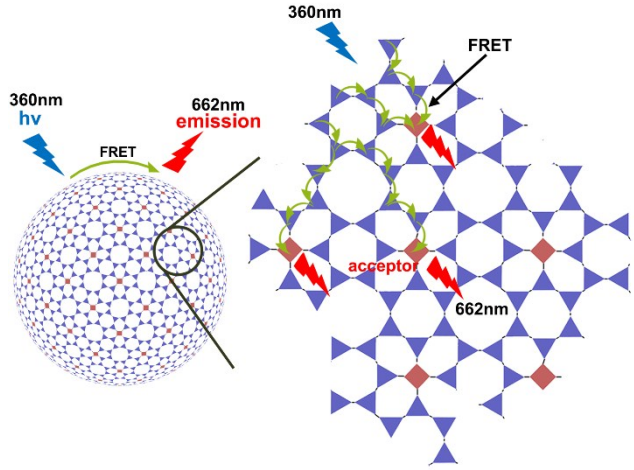


Fig. S9 Representation of the light-harvesting system on the coassembled nanocapsule.

14. Calculation of Energy transfer efficiency

The energy transfer efficiency was estimated based on Tta fluorescence quenching in this coassembly system: [4-7]

$$E=1-I_{DA}/I_D$$

where I_{DA} and I_D is the emission intensity of Tta donors in the presence and absence of Tapp acceptors.

I_{DA}/I_D	Energy transfer efficiency
200:1	23.1%
100:1	39.2%
60:1	47.3%
30:1	58.8%

Table S1. Energy transfer efficiency in this light-harvesting system.

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