Water-dispersible nanospheres of hydrogen-bonded supramolecular polymers and their application for mimicking light-harvesting systems

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Water-dispersible Nanospheres of Hydrogen-bonded Supramolecular Polymers and Their Application for Mimicking Light-harvesting System

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1. Materials and methods.

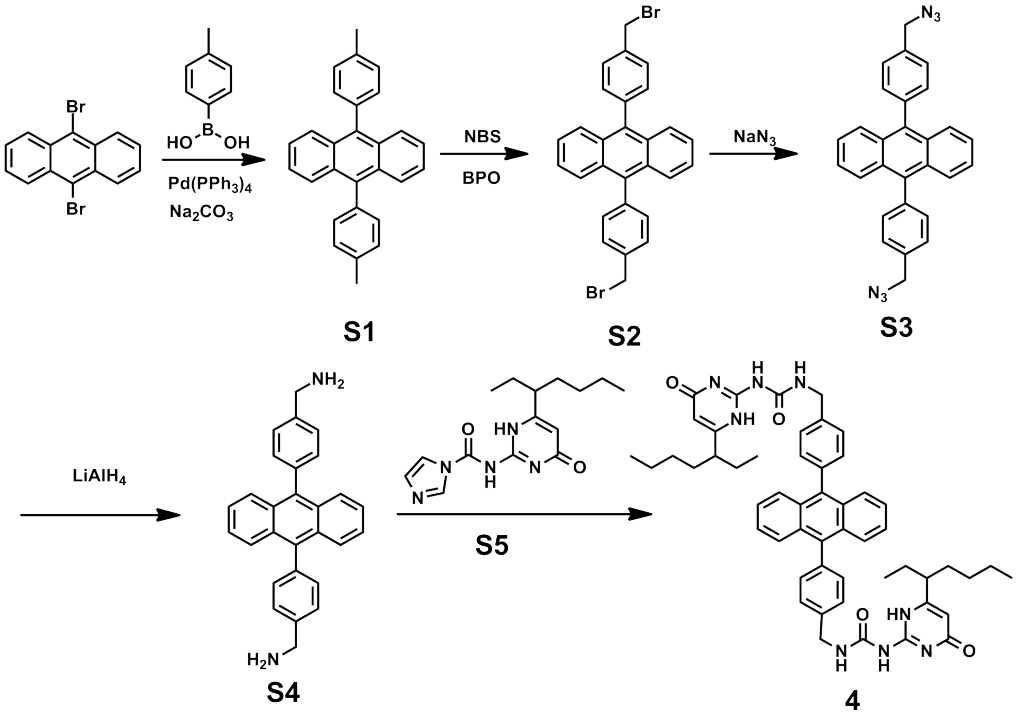
Unless otherwise noted, all chemicals were commercially available and were used without further purification. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using TMS as internal standard at room temperature. Mass spectra (EI) were obtained in the positive ion mode on a Waters GCT premier. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex IV spectromenter. Fourier-Transform Infrared (FT-IR) Spectra were recorded on a Varian Excalibur 3100 spectrometer. Transmission electron microscopic (TEM) images were obtained using a JEOL - 2100 microscope with an accelerating voltage of 200 kV and scanning electron microscopic (SEM) images were obtained using a Hitachi S - 4300 or S - 4800 instruments. The size distribution of nanospheres in TEM image was obtained by using the nano measurer, version 1.2.0. Dynamic light scattering (DLS) investigations were carried out on a Dynapro nanostar dynamic light scattering detector. Absorption spectra were determined on a Shimadzu UV-1601PC UV-Visible spectrophotometer. Fluorescence spectra were determined on a Hitachi 4500 spectrophotometer.

All the SEM samples were conducted on silica wafer and thin gold film (3~5 nm) was sputtered onto their surface to enhance conductivity. TEM samples were prepared by placing one drop of the water dispersion of the nanospheres onto a carbon-coated copper grid. 300 nanospheres in TEM image was chosen at random for size distribution analysis. DLS measurements were performed 3 times at least for each sample to get reliable results. FT-IR samples were prepared by crushing the dry state nanospheres into transparent film with KBr or dropping their water solution onto CaF plate and dried in the oven at 45 ℃. The final concentration of chromophore **4** for preparing the nanospheres was determined by extracting the composition from water to chloroform thoroughly. From the absorption spectrum and concentration，we got the molar extinction coefficient of chromophore **4** in water was 1.22×10^{4} $M^{-1}cm^{-1}$ ± 5%. The concentration of chromophore **5** doped in the nanosphere was according to the molar ratio between **4** and **5** in precursor $CHCl_3$ solution.

2. Synthesis of compound 1-5.

Synthesis of compound 4.

*We took compound **4** as an example to describe the synthetic processes in detail.*



Preparation of compound S1.

S1 was synthesized via a classical Pd - catalyzed Suzuki coupling. A toluene (60 mL) and ethanol (20 mL) solution of 9, 10 - dibromoanthracene (3.36 g, 10 mmol), *p* - tolylboronic acid (4.08 g, 30 mmol), Pd (PPh_3)$_4$ (0.58 g, 0.5 mmol), aqueous Na_2CO_3 (2 M, 30 mL) was heated to reflux under N_2 atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane. The combined organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography (petroleum ether/ CH_2Cl_2 = 4 / 1) to obtain 3.18 g of pure product as light yellow powder. Yield: 89 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.70 (m, 4 H), 7.42-7.35(m, 8 H), 7.32 - 7.29(m, 4 H), 2.54(s, 6 H).

Preparation of compound S2.

N-Bromosuccinimide (NBS, 2.12 g, 12 mmol) and benzoyl peroxide (BPO, 40.0 mg, 0.16 mmol) were added to a solution of **S1** (2.15 g, 6 mmol) in CCl_4 (30 mL). The mixture was heated to reflux under N_2 atomosphere overnight. Then the mixture was cooled to room temperature, filtered, and concentrated in *vacuo* to give a yellow solid. The product was used directly for the subsequent step without purification.

Preparation of compound S3.

NaN_3 (0.98 mg, 15 mmol) was added into a solution of crude compound **S2** in 15 mL DMF, then the mixture was stirred at 50 ℃ for 5 h. After the reaction was completed, dichloromethane (75 mL) was added and the resulting mixture was washed with water (50 mL) for several times. After the organic phase was dried over Na_2SO_4, the solvent was removed with reduced pressure. The residue was purified by column chromatography using petroleum ether/ CH_2Cl_2 (3: 1, v / v) to afford 1.66 g of product. Yield: 63 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 - 7.65(m, 4 H), 7.58(d, 4 H, *J* = 7.6 Hz), 7.51(d, 4 H, *J* = 8 Hz), 7.36 - 7.33(m, 4 H), 4.56(s, 4 H).

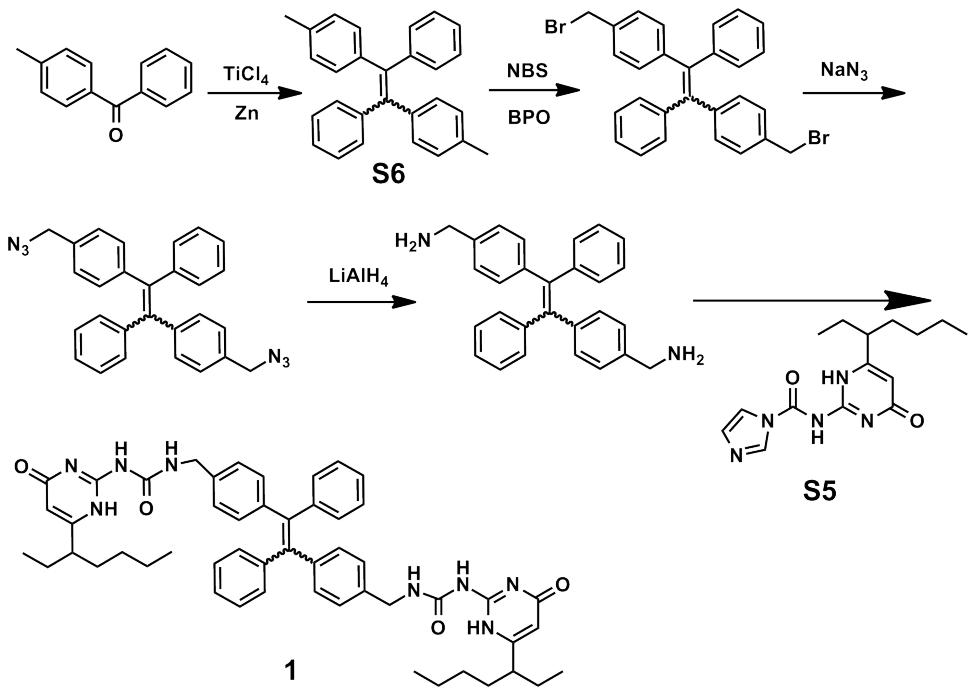
Preparation of compound S4.

To a solution of compound **S3** (1.66 g, 3.77 mmol) in 50 mL of dry THF was added $LiAlH_4$ (0.71 g, 18.8 mmol) cautiously. The reaction was completed after stirring at 66 ℃ overnight and then quenched with methanol. The solid was removed by filtration and filtrate was concentrated by rotary evaporation. $CHCl_3$ was added and the resulted solution was washed with 10 % NaOH, 2 M HCl, and water sequentially and dried over Na_2SO_4. The solvent was removed under reduced pressure to afford 1.1 g of product. Yield: 76 %.^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.74-7.71 (m, 4 H), 7.58 (d, 4 H, *J* = 8.0 Hz), 7.48 (d, 4 H, *J* = 8.0 Hz), 7.36-7.32 (d, 4 H, *J* = 8.0 Hz), 4.09 (s, 4 H).

Preparation of compound 4.

To a solution of **S4** (1.1 g, 2.87 mmol) in 50 mL of dry CH_2Cl_2 was added **S5** [1] (2.17 g, 7.17 mmol) and stirred at room temperature for 5 h. The solution was washed with 2 M HCl, saturated aqueous $NaHCO_3$, brine and dried over Na_2SO_4. After the solvent was removed by rotary evaporation, further purification was carried out by column chromatography using CH_2Cl_2 / CH_3OH (100: 1, v / v) as eluent to afford 1.97 g of product. Yield: 80 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.25 (s, 2 H), 12.22 (s, 2 H), 11.03 (s, 2 H), 7.73 (d, 4 H, *J* = 8.4 Hz), 7.63(d, 4 H, *J* = 7.6 Hz), 7.45(d,4 H,*J* = 7.2 Hz), 7.31 (d, 4 H,*J* = 6.8Hz), 5.90 (s, 2 H), 4.69 (d, 4 H, *J* = 3.6 Hz), 2.35 (m, 2 H), 1.66 (m, 8 H), 1.28 (m, 8 H), 0.89 (m, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.37, 157.21, 155.81, 155.00, 138.08, 137.82, 137.04, 131.57, 130.01, 127.44, 124.97, 106.44, 45.49, 43.42, 32.97, 29.42, 26.74, 22.59, 13.97, 11.81. HR-ESI-MS: m / z calcd for $[M+H]^+$ $C_{52}H_{59}N_8O_4$: 859.46538; found: 859.46656, error: -1.4 ppm.

Synthesis of compound 1.

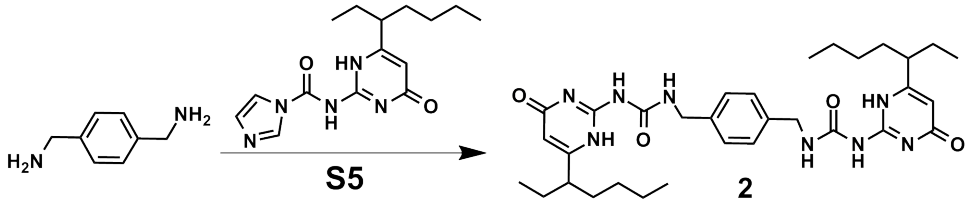


Preparation of compound S6.

S6 was synthesized via McMury coupling. $TiCl_4$ (4.6 mL, 8.0 g, 42 mmol) was added into a stirred suspension of zinc powder (6.5 g, 100 mmol) dropwise at 0 ℃, then the slurry was refluxed for 3 h. After pyridine (1.7 mL, 1.7 g, 21 mmol) was added, a THF solution (50 mL) of 4-methylbenzophenone (0.88 g, 4.5 mmol) was added over a 5 h period by syringe pump to the refluxing reaction mixture. The reflux was continued for half an hour after the addition was completed. After cooling to room temperature, the reaction mixture was poured into saturated aqueous K_2CO_3 (100 mL) and stirred until the organic phase was separated. The organic phase was collected and solvent was removed by rotary evaporation. CH_2Cl_2 (100 mL) was added to the residue and the resulting mixture was washed with water. The organic phase was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ CH_2Cl_2 = 5 / 1) to obtain 0.68 g pure product. Yield: 84 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-6.99 (m, 10 H), 6.91(d, 8 H, J = 9.6 Hz), 2.26(d, 6 H, J = 7.2 Hz).

The rest synthesis procedure of compound **1** was similar to that of compound **4**.Total yield from S6 to **1**: 41 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.15 (d, 2 H, J = 9.6 Hz), 12.02 (d, 2 H, J = 16.4 Hz), 10.74 (br, 2 H), 7.09 (m, 18 H), 5.78 (s, 2 H), 4.38 (d, 4 H, J = 4.4 Hz), 2.30 (m, 2 H), 1.67 (m, 8 H), 1.30 (m, 8 H), 0.90 (m, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.16, 156.97, 155.61, 154.87, 143.91, 142.54, 140.62, 136.80, 131.47, 127.70, 126.62, 106.30, 45.42, 43.16, 32.92, 29.38, 26.69, 22.56, 13.96, 11.77. HR-ESI-MS: m / z calcd for $[M+H]^+$ $C_{52}H_{61}N_8O_4$: 861.48103; found: 861.47964, error: 1.6 ppm.

Synthesis of compound 2.

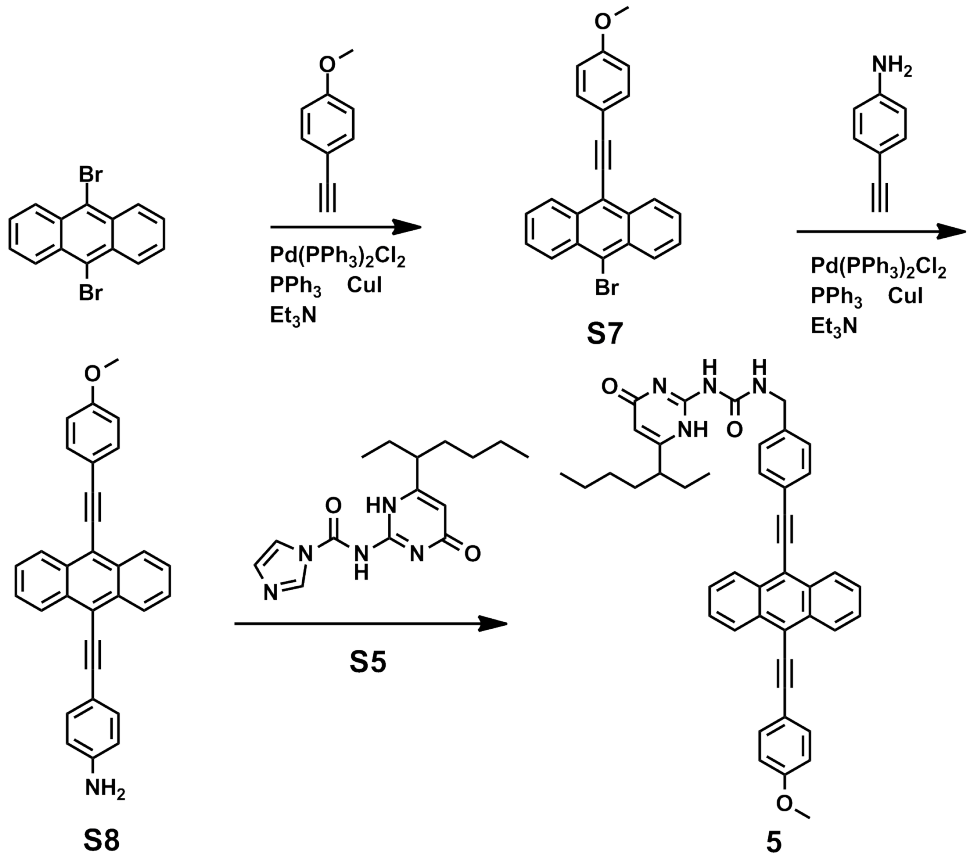


Compound **2** was synthesized following the procedure similar to the last step of compound **4**. Yield: 77.4 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 13.13 (s, 2 H), 11.94 (s, 2 H), 10.90 (t, 2 H), 7.37 (s, 4 H), 5.78 (s, 2 H), 4.43 (br, 4 H), 2.27 (m, 2 H), 1.67 (m, 8 H), 1.26 (m, 8 H), 0.86 (m, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 173.21, 156.84, 155.49, 154.83, 137.80, 127.81, 106.32, 45.40, 43.05, 32.91, 29.36, 26.66, 22.52, 13.94, 11.75. HR-ESI-MS: m / z calcd for $[M+H]^+$ $C_{32}H_{47}N_8O_4$: 607.37148; found: 607.37046, error: 1.7 ppm.

Synthesis of compound 3. [2]

*The synthesis of compound **3** has been reported by our group in literature [2].*

Synthesis of compound 5.



Preparation of compound S7.

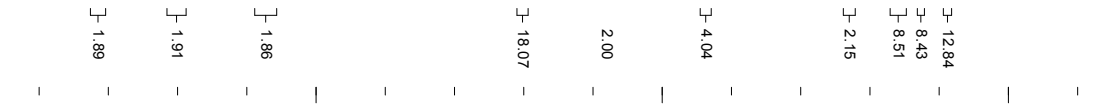
S7 was synthesized via a classical Pd-catalyzed Sonogashira coupling. To a solution of 9, 10 - bibromoanthracene (672 mg, 2 mmol) in 50 mL CH_3CN was added 1-ethynyl-4- methoxybenzene (264 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (1.4 g,0.2 mmol), CuI (760 mg, 0.4 mmol), PPh_3 (1.05 g, 0.4 mmol), and 5 mL Et_3N, then the mixture was stirred at room temperature for 12 h under N_2 atmosphere. After the reaction completed, the solvent was removed under reduced pressure. The further purification was carried out by column chromatography using petroleum ether/ CH_2Cl_2 (10 / 1, v / v) to afford 390 mg of product. Yield: 50.4 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (m, 2 H), 8.57 (m, 2 H), 7.72(d, 2 H, *J* = 8.4 Hz), 7.64 (m, 4 H), 6.99 (d, 2 H, *J* = 8.8 Hz), 3.89 (s, 3 H).

Preparation of compound S8.

To a solution of compound **S7** (390 mg, 1 mmol) in 50 mL CH_3CN was added 4-ethynylaniline (234 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (702 mg,0.1 mmol), CuI (380 mg, 0.2 mmol), PPh_3 (524 mg, 0.2 mmol), and 3 mL Et_3N, then the mixture was stirred at room temperature for 12 h under N_2 atmosphere. After the mixture was completed, the solvent was removed und reduced pressure. The further purification was carried out by column chromatography using petroleum ether / ethyl acetate (3 / 1, v / v) to afford 282 mg of product. Yield: 66 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (m, 4 H), 7.72 (m, 8 H), 6.99 (d, 2 H, *J* = 8.4 Hz), 6.75 (d, 2 H, *J* = 8 Hz), 3.88 (s, 3 H).

Preparation of compound 5.

A solution of **S8** (282 mg, 0.66 mmol) in 30 mL dry CH_2Cl_2 was added **S5** (300 mg, 0.99 mmol) and stirred at room temperature for 5 h. The solution was washed with 2 M HCl, saturated aqueous $NaHCO_3$, brine and dried over Na_2SO_4. After the solvent was removed by rotary evaporation, the further purification was carried out by column chromatography using CH_2Cl_2 / CH_3OH (100: 1, v / v) as eluent to afford 315 mg of product. Yield: 47 %. ^{1}H NMR ($CDCl_3$ +5 μL TFA, 400 MHz): δ 8.70 (m, 4 H), 7.78 (d, 2 H, *J* = 8.4Hz), 7.73 (d, 2 H, *J* = 8.4 Hz), 7.64 (m, 4 H), 7.56 (d, 2 H, *J* = 8.4 Hz), 7.01 (d, 2 H, *J* = 8.4 Hz), 6.17 (br, 1 H), 3.90 (s, 3 H), 2.53 (m, 1 H), 1.65 (m, 4 H), 1.19 (m, 4 H), 0.89 (m, 6 H). HR-ESI-MS: m / z calcd for $[M+H]^+$ $C_{43}H_{39}N_4O_3$: 659.30167; found: 659.30044, error: 1.9 ppm. Despite many attempts have made, we still failed to get satisfied ^{13}C NMR of this compound due to its limited solubility.


12.84
8.43
8.51
2.15
4.04
2.00
18.07
1.86
1.91
1.89


12.70
8.98
8.51
2.12
4.00
2.00
3.97
1.93
1.99
1.97

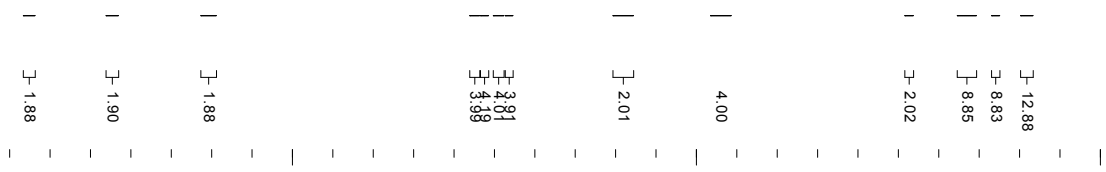
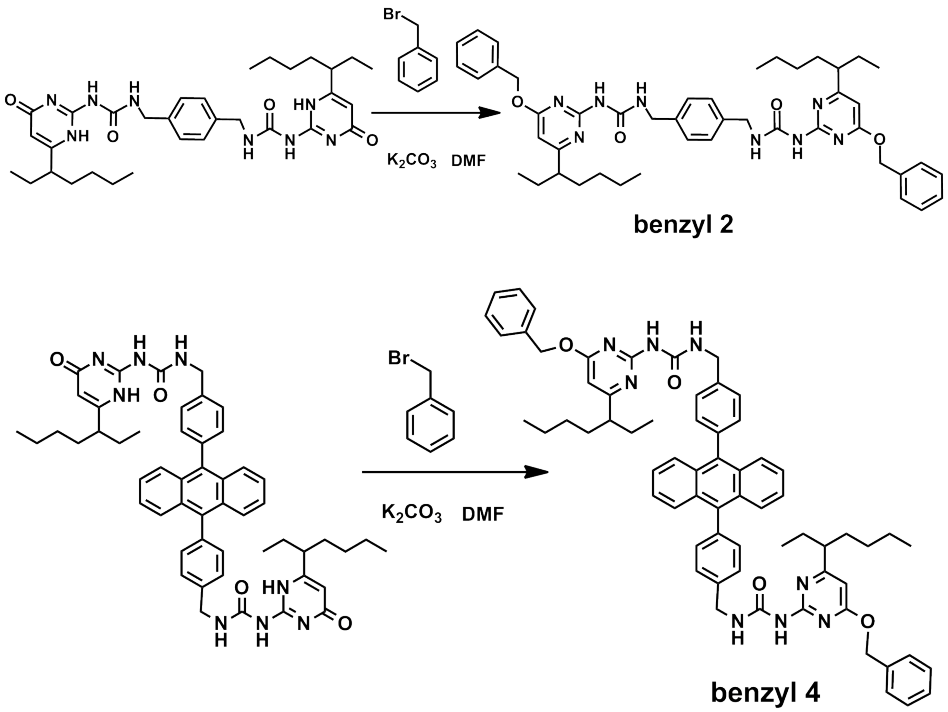


Fig. S1. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of compound **1**, **2** and **4**.

3. Synthesis of compound benzyl 2 and benzyl 4.

Synthesis of compound benzyl 2.



Scheme S1. Synthesis of compounds **benzyl 2** and **benzyl 4**.

To a mixture of compound **2** (121 mg, 0.2 mmol) and benzyl bromide (102 mg, 0.75 mmol) in 3 mL DMF, K_2CO_3 (110 mg, 0.8 mmol) was added and the reaction heated to 70 ℃for 12 h under N_2 atmosphere. Then the resulting mixture was cold to room temperature and diluted by 50 mL ethyl acetate, washed with 1 M HCl, saturated aqueous $NaHCO_3$, brine and dried over Na_2SO_4. After the solvent was removed by rotary evaporation, further purification was carried out by column chromatography using CH_2Cl_2 / CH_3OH (100: 1, v / v) as eluent to afford 102 mg of product. Yield: 65.1%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.71 (s, 2 H), 7.50 (s, 2 H), 7.38 (m, 12 H), 6.14 (s, 2 H), 5.25 (s, 4 H), 4.53 (d, 4 H, J = 5.2 Hz), 2.32 (m, 2 H), 1.48 (m, 8 H), 1.19 (m, 8 H), 0.81 (m, 6 H), 0.72(m, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.31, 170.01, 157.56, 154.56, 137.94, 136.00, 128.66, 128.34, 128.14, 100.74, 68.27, 48.81, 43.93, 34.07, 29.58, 27.63, 22.73, 14.00, 11.97. HR-ESI-MS: m / z calcd for $[M+H]^+$ $C_{46}H_{59}N_8O_4$:787.46538; found: 787.46525, error: 0.2 ppm.

Compound **benzyl 4** was synthesized by using similar procedure with compound **benzyl 2**.Yield: 43 %. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.92 (s, 2 H), 7.70 - 7.67 (m, 4 H), 7.61 (d, 4 H, J = 7.6Hz), 7.48 - 7.29 (m, 9 H), 6.19 (s, 2 H), 5.35 (s, 4 H), 4.75 (d, 4 H, J = 3.2 Hz), 2.39 (m, 2 H), 1.55 (m, 8 H), 1.12 (m, 8 H), 0.79 (m, 12 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.17, 170.20, 157.66, 154.72, 138.27, 137.98, 136.95, 136.10, 131.75, 130.05, 128.77, 128.47, 128.39, 127.98, 127.07, 125.13, 101.17, 68.41, 48.96, 44.31, 34.38, 29.71, 27.94, 22.86, 14.09, 12.14. HR-ESI-MS: m / z calcd for $[M+H]^+$ $C_{66}H_{71}N_8O_4$: 1039.55928; found: 1039.55673, error: 2.5 ppm.

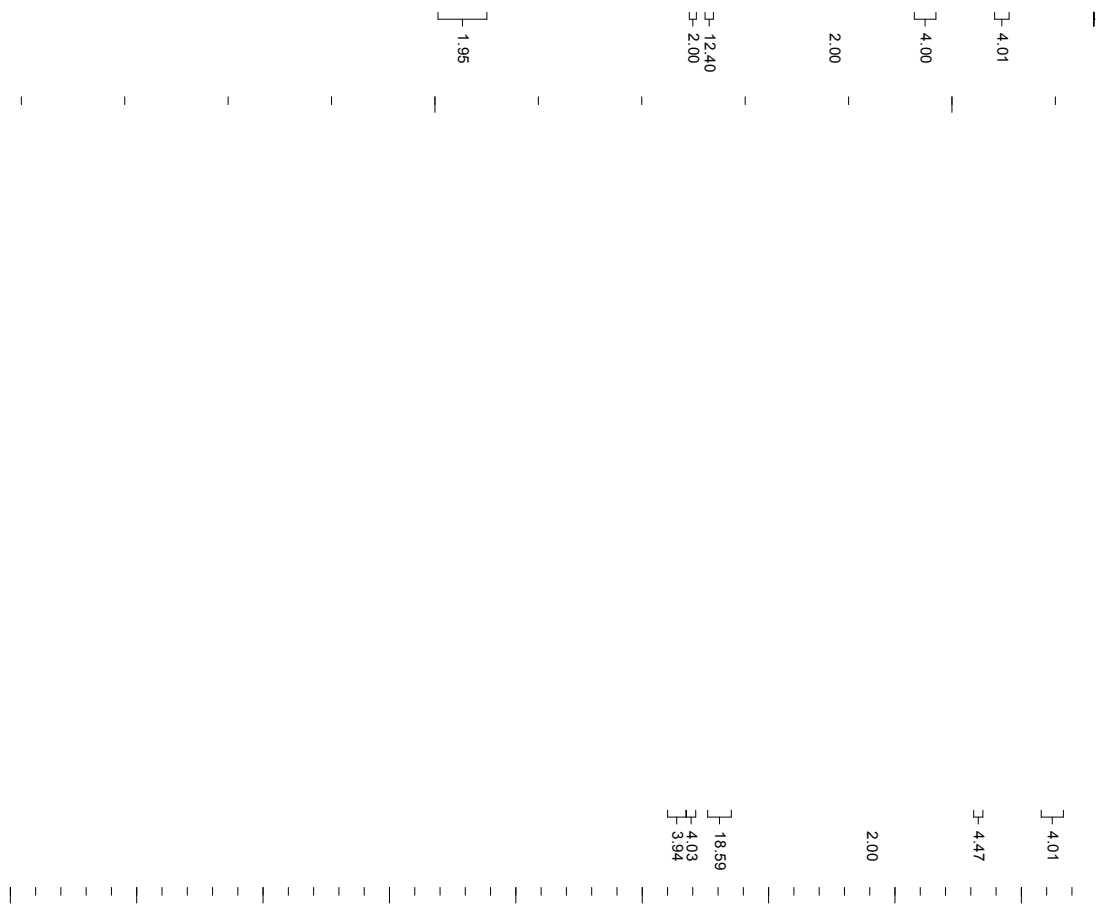


Fig. S2. Partial ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **benzyl 2** and **benzyl 4**.

4. Specific viscosity of compound 1-4.

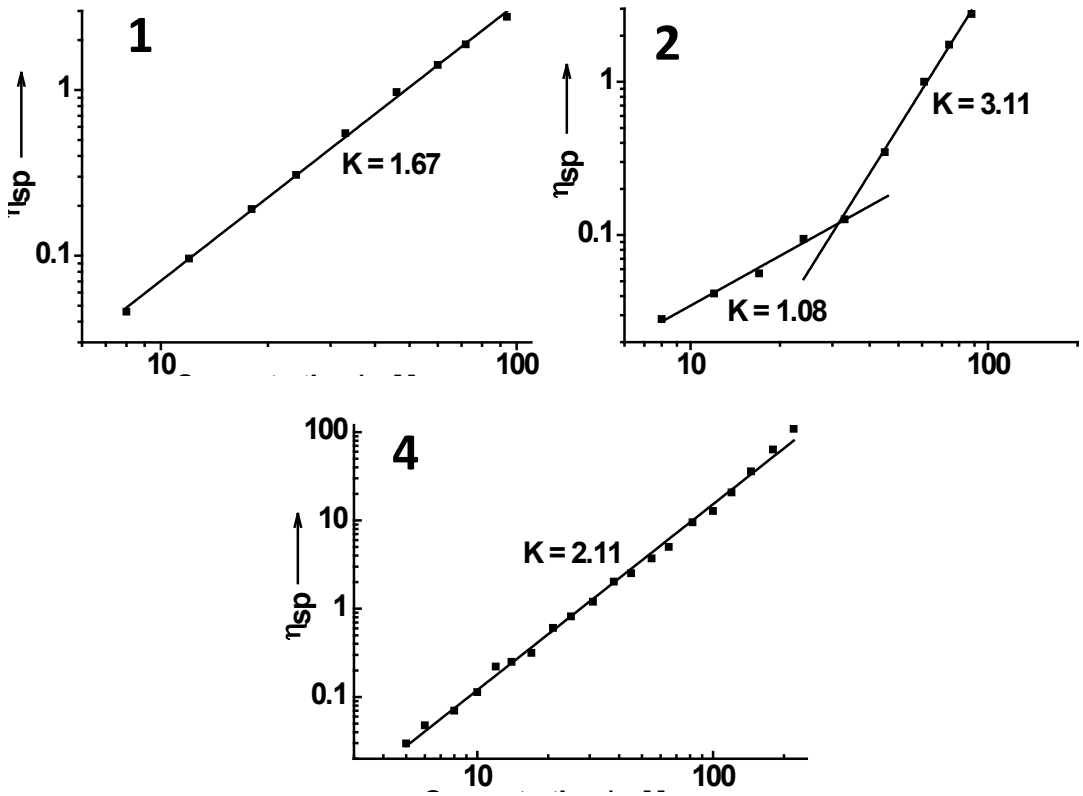


Fig. S3. Specific viscosity of compound **1**, **2** and **4** in $CHCl_3$ solutions versus the concentration (303K). K values by the lines indicate the slopes. Specific viscosity of compound **3** see reference [2].

5. Detailed procedure for the preparation of nanosperes

The detailed procedure for the preparation of nanosperes: 200 μL stock solution of supramolecular polymers in chloroform (25 mg/ mL) was quickly added to 10 mL aqueous solution of surfactants (above the critical micelle concentration). The resulting mixture was sonicated for 25 minutes, followed by three cycles of centrifuge-wash with water to afford water-dispersible nanospheres.

6. SEM, TEM and DLS images of nanospheres.

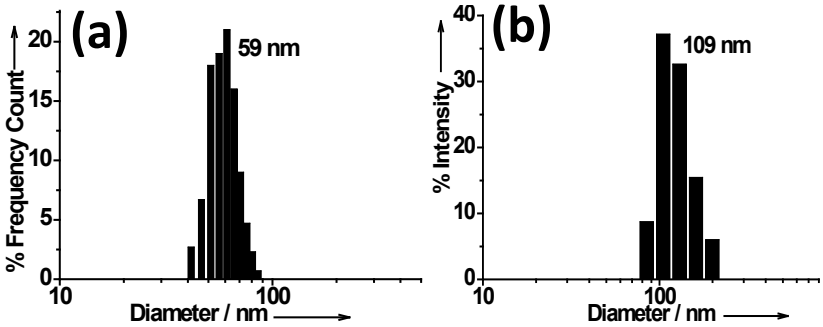


Fig. S4. (a) Size distribution of nanospheres in TEM image of Fig.1b. (b) Distribution of the hydrodynamic diameter of nanospheres prepared from supramolecular polymers of **1** in water at 298 K. The diameters estimated from DLS were reasonably bigger than those observed by TEM and SEM, because DLS measured hydrodynamic diameter of fully hydrated nanospheres in water. In contrast, TEM and SEM measured the diameter of collapsed nanospheres in dry state. [3-4]

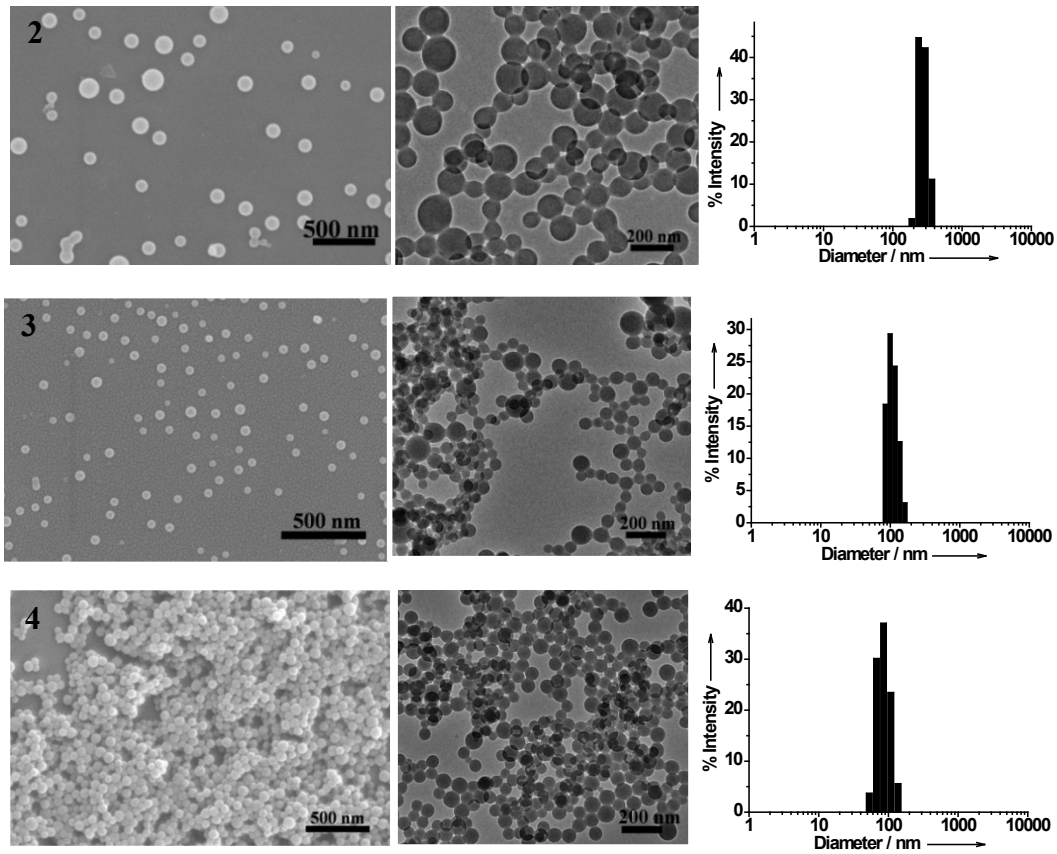


Fig. S5. SEM, TEM and DLS images of nanospheres prepared from supramolecular polymers of **2**, **3** and **4** at the same mass concentration (25 mg/mL). The slightly higher size of nanospheres prepared from supramolecular **2** may due to its higher molar concentration at the identical mass concentration compared with others. The higher molar concentration increased the polymerization degree which may influence on the size of nanospheres.

	TEM/SEM / nm	DLS / nm
1	~60 nm	~109 nm
2	~119 nm	~260 nm
3	~49 nm	~103 nm
4	~52 nm	~94 nm

Table S1. The TEM/SEM and DLS sizes of nanospheres prepared from supramolecular polymers **1**, **2**, **3** and **4**.

7. FT-IR spectra of 1-4 based nanospheres.

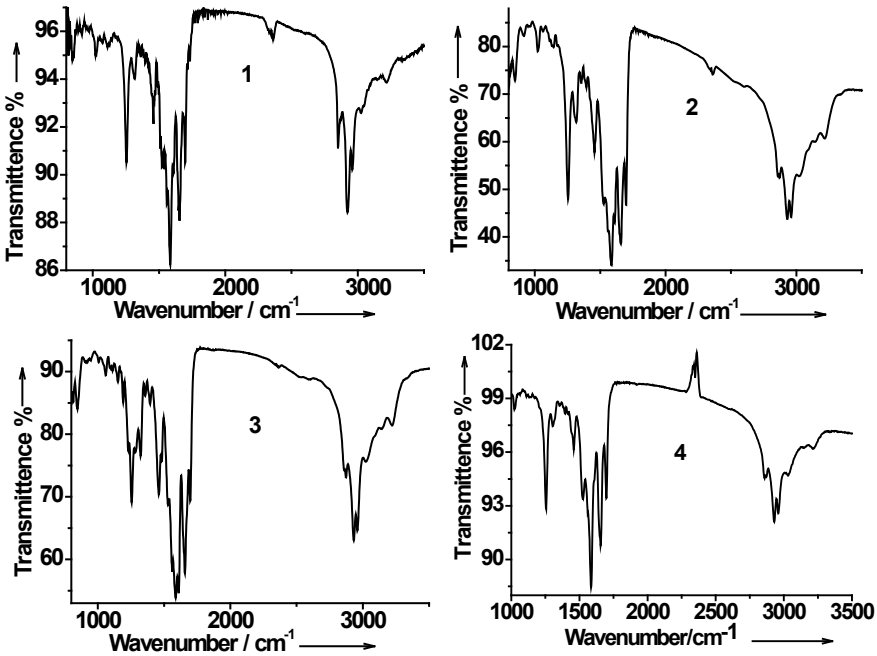


Fig. S6. FT-IR spectra of nanospheres prepared from supramolecular polymers of **1**-**4**.

8. SEM spectra of benzyl 2 and benzyl 4 based aggregates.

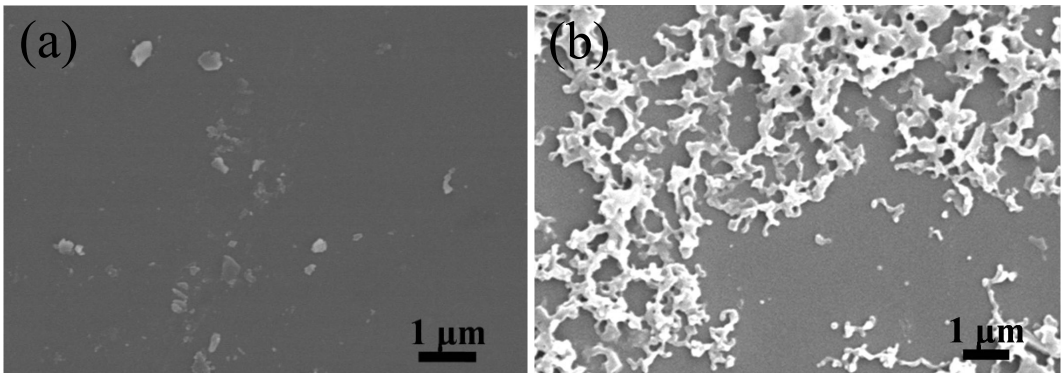


Fig. S7. The SEM spectra of a) **benzyl 2** and b) **benzyl 4** based aggregates. Both **benzyl 2** and **benzyl 4** were 25 mg/mLin $CHCl_3$ for preparing the aggregates by miniemulsion.

9. Nanospheres prepared from supramolecular polymers of 4 by using SDS and pluronic F-127 as surfactants.

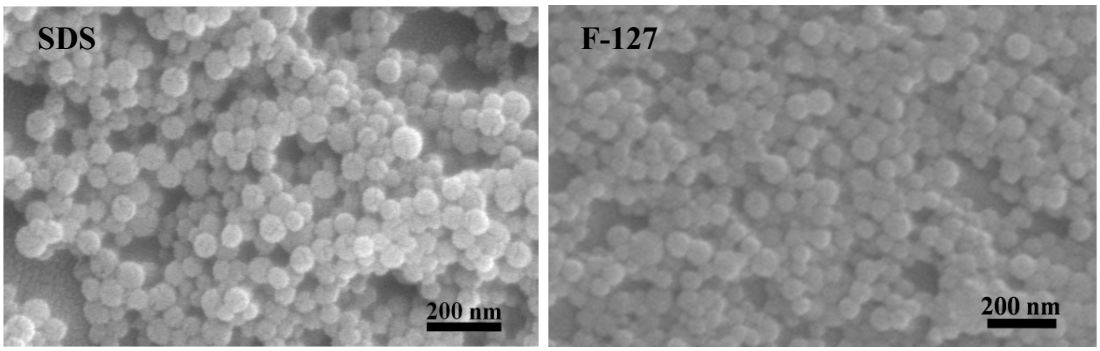


Fig. S8. The defined nanospheres prepared from supramolecular polymers of **4** by using surfactants SDS (sodium dodecyl sulfate, 2.6 mg/mL in water) and pluronic F-127 (Ethylene Oxide/Propylene Oxide Block Copolymer, 1.6 mg/mL).

10. Nanospheres prepared from supramolecular polymers of 4 in precursor solutions with different concentration.

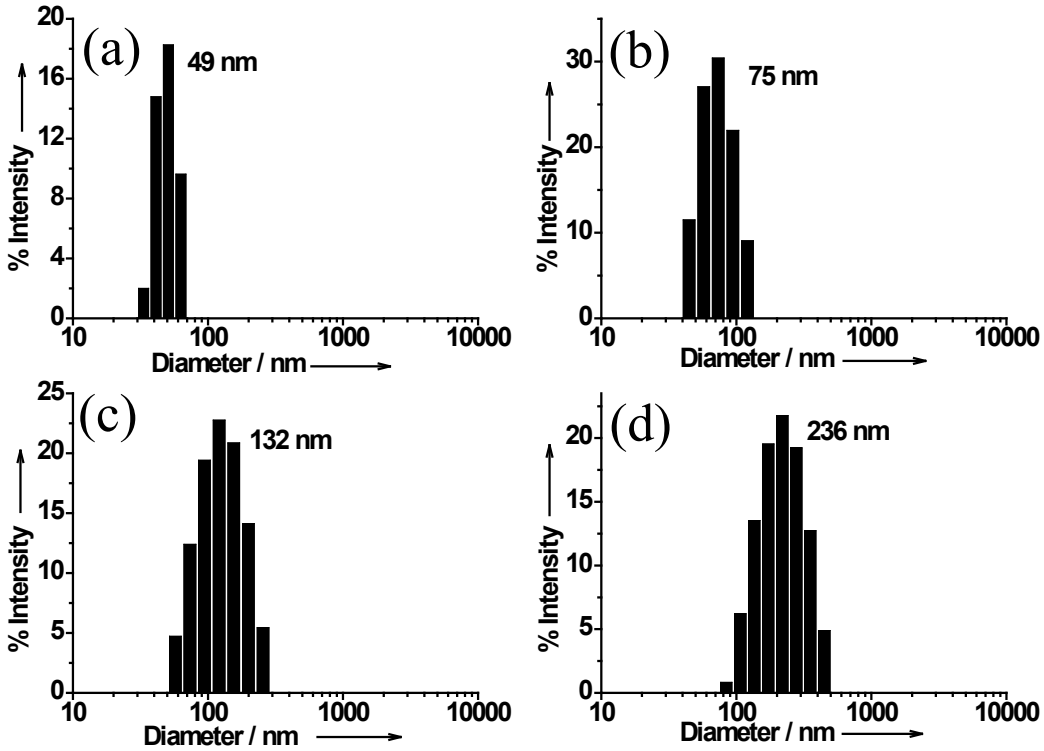


Fig. S9. DLS measurements of nanospheres prepared from supramolecular polymers of **4** wih different mass concentration (5 mg/mL, 15 mg/mL, 50 mg/mL and 100 mg/mL in $CHCl_3$ for a, b, c and d, respectively).

11. Overlap between the emission of 4 and absorption of 5.

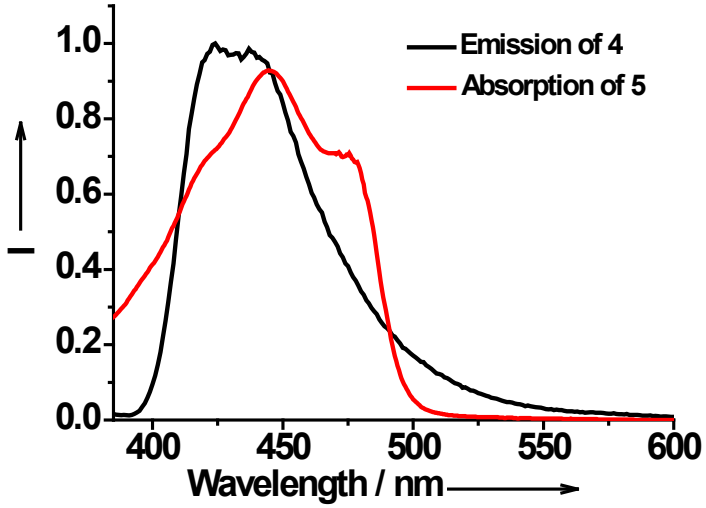


Fig. S10. The overlap between the emission of **4** and absorption of **5** in $CHCl_3$ solutions. The concentrations are 49.7 μM and 3.3 μM, respectively.

12. Normalized excitation spectrum and absorption spectrum.

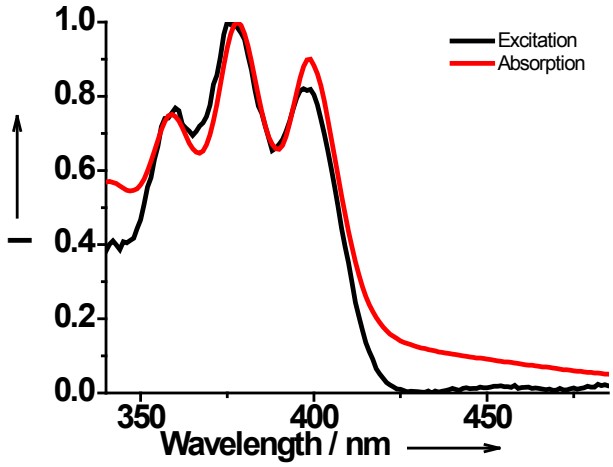


Fig. S11. Normalized excitation spectrum of nanospheres prepared from supramolecular polymers of 176:1 of **4** to **5** and absorption spectrum of nanospheres prepared from supramolecular polymers of **4**.

13. Time-resolved fluorescence measurements.

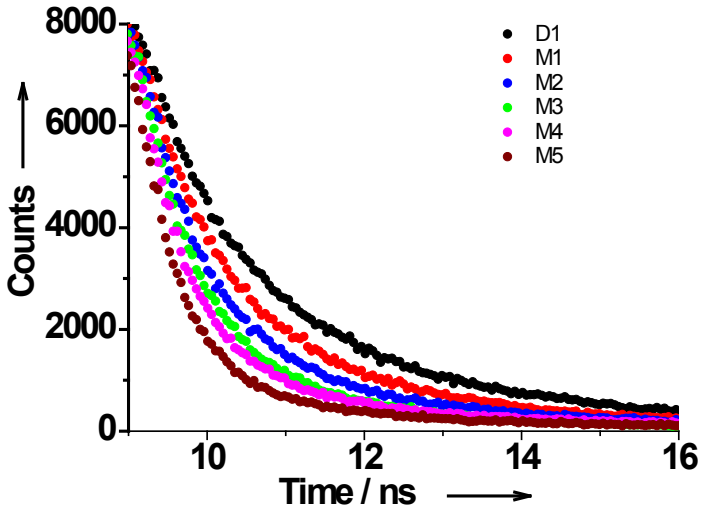


Fig. S12. Time-resolved fluorescence measurements for nanospheres prepared from supramolecular polymers of **4** or **4** with different concentrations of **5**. The spectra were measured with excitation wavelength at 375 nm and detection at 440 nm. D1 and M1-M5 were fluorescence decay profiles of **4** based nanospheres in water (65 μM), and nanospheres based on **4** with different concentration of **5** (molar ratio of **4** to **5**: 352/1, 176/1, 88/1, 58/1 and 44/1, respectively).

14. Antenna effect.

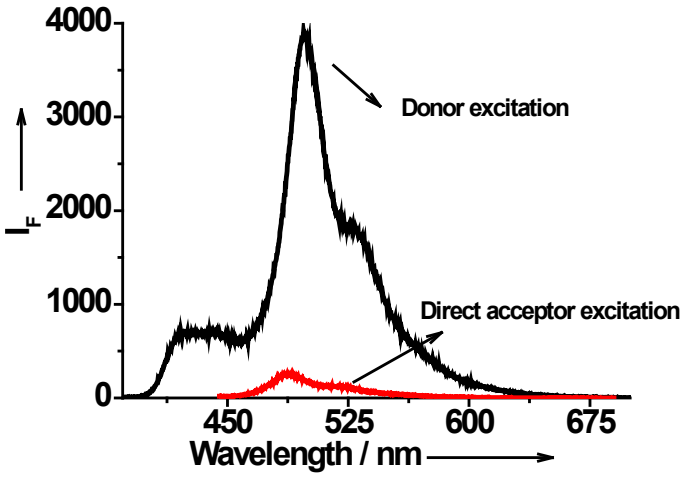


Fig. S13. The antenna effect for nanospheres with 88:1 molar ratio of donor to acceptor. The black and red lines are the spectra excited by 375 nm and 445 nm, respectively.

D:A ratio	44:1	58:1	88:1	176:1	352:1
Antenna effect	11	13	20	29	35

Table S2. The antenna effect for each sample (Solid line, λ_{ex} = 375 nm) is shown relative to the acceptor emission by direct excitation (Dash line, λ_{ex} = 445 nm).

15. Absorption and emission spectra of 4 in chloroform.

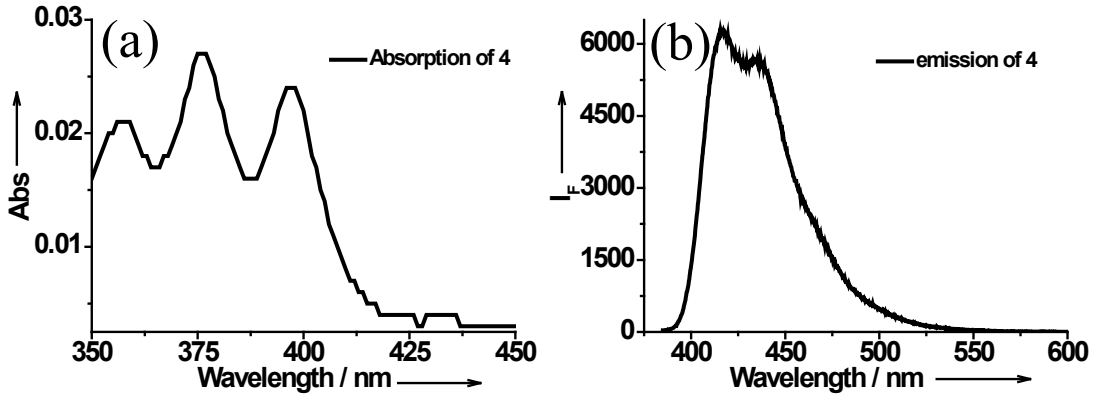


Fig. S14. The absorption (a) and emission (b, λ_{ex} = 375 nm) spectra of monomer **4** in chloroform. The concentration of **4** is 2.1μM. The quantum yield is 0.87 in chloroform (standard sample: 9, 10-Diphenylanthracene in cyclohexane, η = 0.9). Due to the relative high critical polymerization concentration of monomer **4**, the optical properties especially the absorption spectrum of supramolecular polymers is out of the measurement range.

Reference.

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