Electronic Supplementary Information

# Artificial Light-harvesting Supramolecular Polymeric Nanoparticles Formed by Pillar[5]arene-based Host-guest Interaction

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#### 1. Materials and methods

Unless otherwise mentioned, materials were obtained from commercial suppliers and were used without further purification. BisP5A was synthesized according reported method.<sup>1</sup> In order to obtain anhydrous solvents, dichloromethane ( $CH_2Cl_2$ ) was distilled from  $CaH_2$ ; tetrahydrofuran (THF) was distilled from sodium and benzophenone. Column chromatography was performed over silica gel (200-300 mesh). NMR spectra were conducted on a Bruker Avance 400 spectrophotometer (400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR) or a Bruker Avance 600 spectrophotometer (2D DOSY). High-resolution mass spectrometry experiments were recorded by a Bruker Daltonics Apex IV spectrometer. Viscosity measurements were performed with a micro-Ubbelohde dilution viscometer at 25 °C in chloroform (CHCl<sub>3</sub>). Absorption and fluorescence spectra were determined on a Shimadzu UV-1601PC UV-Visible spectrophotometer and a Hitachi 4500 spectrophotometer, respectively at room temperature. Scanning electron microscopic (SEM) images were obtained using a Hitachi S-4800 instrument. Dynamic light scattering (DLS) investigations were carried out with a Dynapro nanostar dynamic light scattering detector. Fluorescence quantum yields of aqueous dispersions of nanoparticles were carried out on a FLS920 Edinburgh spectrometer equipped with an integrating sphere and a xenon lamp excitation source (Xe900). The photostability was conducted under the irradiation of Xenon lamp without filter and monitored by Hitachi 4500 spectrophotometer. Fluorescence decay profiles and time resolved fluorescence spectra were determined by single photon counting technique using a Deltaflex UltraFast lifetime Spectrofluorometer.

#### 2. Synthesis of building blocks



Scheme S1 Synthetic route of GD.

#### Synthesis of S1

5-Bromovaleronitrile (1.4 mL, 12 mmol) and NaN<sub>3</sub> (1.170 g, 18 mmol) were dissolved in N,N-dimethylformamide (5 mL) and the resulting mixture was heated at 80 °C overnight. The solution was cooled to room temperature and extracted with diethyl ether three times. The combined organic phase was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed by rotary evaporation to afford 1.339 g product as colorless liquid. Yield: 90%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  3.38-3.35 (t, 2H, J =2.8 Hz), 2.41-2.39 (t, 2H, J =2.4 Hz), 1.77-1.75 (m, 4H).

#### Synthesis of S2

S2 was synthesized via a classical Pd-catalyzed Suzuki coupling reaction. A toluene (25 mL) and ethanol (8 mL) solution of 9,10-dibromoanthracene (672 mg, 2.0 mmol), 4-methoxyphenylboronic acid (930 mg, 6.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (117 mg, 0.1 mmol), aqueous Na<sub>2</sub>CO<sub>3</sub> (2 M, 12 mL) was heated to reflux under N<sub>2</sub> atmosphere for 24 h. The solution was cooled to room temperature and extracted with dichloromethane twice. The combined organic phase was washed by brine twice and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent, the residue was purified by column chromatography (petroleum ether/ CH<sub>2</sub>Cl<sub>2</sub> = 4 / 1) to obtain 590 mg pure product as light-yellow powder. Yield: 76%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.75-7.73 (m, 4 H), 7.40-7.38 (d, 4 H, J = 8.0 Hz), 7.34-7.31 (m, 4 H), 7.15-7.13 (d, 4 H, J = 8.0 Hz), 3.96 (s, 6 H).

#### Synthesis of S3

To a solution of **S2** (391 mg, 1.0 mmol) in anhydrous  $CH_2Cl_2$  (20 mL), boron tribromide (in dichloromethane, 8 mL, 8.0 mmol) was added at 0 °C. After 12 h stirring at room temperature, the reaction was quenched by water. The resulting precipitation was collected, washed by water and dried by vacuum to afford 320 mg product as light-yellow powder, which was sufficiently pure for subsequent steps. Yield: 88%. <sup>1</sup>H NMR (Acetone-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  7.62-7.60 (m, 4 H), 7.26-7.24 (m, 4 H), 7.17-7.15 (d, 4 H, J = 8.0 Hz), 7.02-7.00 (d, 4 H, J = 8.0 Hz).

#### Synthesis of S4

A solution of **S3** (290 mg, 0.8 mmol), propargyl bromide (180  $\mu$ L, 2.4 mmol), and K<sub>2</sub>CO<sub>3</sub> (552 mg, 4.00 mmol) in 30 mL acetonitrile was refluxed under N<sub>2</sub> atmosphere overnight. After the reaction was completed, the mixture was concentrated by rotary evaporation. 100 mL water was added to dissolve K<sub>2</sub>CO<sub>3</sub> and organic phase was precipitated. The precipitate was washed by water and acetone sequentially and dried by vacuum to afford 313 mg product as light-yellow powder. Yield: 89%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  7.64-7.61 (m, 4 H), 7.44-7.40 (m, 4 H), 7.40-7.39 (d, 4 H, J = 8.8 Hz), 7.28-7.26 (d, 4 H, J = 8.8 Hz), 4.97-4.96 (d, 4 H, J = 2.0 Hz), 3.68-3.67 (t, 2 H, J = 2.0 Hz).

Synthesis of GD

**GD** was synthesized by using copper(I)-catalyzed alkyne–azide click reaction. **S4** (220 mg, 0.5 mmol), **S1** (186 mg, 1.5 mmol) and CuI (5 mg, 0.026 mmol) were added into 50 mL THF. The resulting mixture was heated at 60 °C for 15 h. After the reaction was completed, the mixture was concentrated by rotary evaporation. 100 mL CH<sub>2</sub>Cl<sub>2</sub> was added, washed by brine twice and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH= 50 / 1) to afford 299 mg pure product as light-yellow powder. Yield: 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.75 (s, 2H) 7.75-7.71 (m, 4 H), 7.42-7.40 (d, 4 H, J = 8.8 Hz), 7.34-7.32 (m, 4 H), 7.25-7.22 (d, 4 H, J = 8.8 Hz), 5.38(s, 4 H), 4.52-4.49 (t, 4 H, J = 6.8 Hz), 2.47-2.43 (t, 4 H, J = 6.8 Hz), 2.21-2.13 (m, 4 H), 1.79-1.74 (m, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  158.0, 144.9, 136.8, 132. 7, 132.1, 130.4, 127.1, 125.1, 122.8, 118.9, 115.0, 62.5, 49.5, 29.2, 22.6, 16.9. HR-ESI-MS: m/z calcd for [M + H]<sup>+</sup> C<sub>42</sub>H<sub>39</sub>N<sub>8</sub>O<sub>2</sub>: 687.3191; found: 687.3191, error: -0.1 ppm. m/z calcd for [M + NH<sub>4</sub>]<sup>+</sup> C<sub>42</sub>H<sub>42</sub>N<sub>9</sub>O<sub>2</sub>: 704.3466; found: 704.3456, error: -0.1 ppm.



Scheme S2 Synthetic route of GA.

Synthesis of S5

S5 was synthesized via a classical Pd-catalyzed Sonagoshira coupling reaction. An anhydrous THF (10 mL) and Et<sub>3</sub>N (5 mL) solution of 9,10-dibromoanthracene (336 mg, 1.0 mmol), 2-(4-ethynylphenoxy)tetrahydro-2H-pyran (606 mg, 3.0 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (35 mg,

0.05 mmol), CuI (9 mg, 0.05 mmol) was heated at 80 °C under N<sub>2</sub> atmosphere for 24 h. After the reaction was completed, solution was cooled to room temperature and concentrated by rotary evaporation. 100 mL CH<sub>2</sub>Cl<sub>2</sub> was added, washed with brine twice and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography (petroleum ether/ CH<sub>2</sub>Cl<sub>2</sub> = 2 / 1) to afford 353 mg pure product as orange powder. Yield: 61%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.69-8.67 (m, 4 H), 7.71-7.69 (d, 4H, J = 8.4 Hz), 7.64-7.61 (m, 4 H), 7.15-7.14 (d, 4H, J = 8.4 Hz), 5.52-5.11 (t, 2H, J = 2.8 Hz), 3.96-3.90 (m, 2H), 3.68-3.64 (m, 2H), 1.99-1.92 (m, 2H), 1.85-1.81 (m, 4H), 1.67-1.61 (m, 6H).

#### Synthesis of S6

A  $CH_3CH_2OH$  (20 mL) solution of **S6** (289 g, 0.5 mmol) and pyridinium toluene-4sulphonate (5 mg, 0.02 mmol) was refluxed for 1 h. After the reaction was completed, solution was cooled to room temperature and concentrated by rotary evaporation. 100 mL  $CH_2Cl_2$  was added, washed with brine twice and dried over anhydrous  $Na_2SO_4$ . Solvent was removed by rotary evaporation to afford 187 mg product as orange powder, which was sufficiently pure for subsequent steps. Yield: 91%.

#### Synthesis of S7

The synthesis of **S7** was similar with **S4**. A solution of **S6** (164 g, 0.4 mmol), propargyl bromide (90  $\mu$ L, 1.2 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.55 g, 4.00 mmol) in 30 mL acetonitrile was refluxed under N<sub>2</sub> atmosphere overnight. After the reaction was completed, the mixture was concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub> = 2 / 1) to afford 171 mg pure product as orange powder. Yield: 88% <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.69-8.67 (m, 4 H), 7.74-7.72 (d, 4H, J = 8.8 Hz), 7.64-7.62 (m, 4 H), 7.08-7.06 (d, 4H, J = 8.8 Hz), 4.78-4.77 (d, 4H, J = 2.4 Hz), 2.58-2.57 (t, 2H, J = 2.4 Hz).

#### Synthesis of GA

GA was synthesized by using copper(I)-catalyzed alkyne–azide click reaction like GD. S7 (150 mg, 0.3 mmol), S1 (112 mg, 0.9 mmol) and CuI (5 mg, 0.026 mmol) were added into 20 mL THF. After the resulting mixture was heated at 60 °C for 15 h, reaction was cooled to room temperature and followed by the removal of solvent. 120 mL CH<sub>2</sub>Cl<sub>2</sub> was added, washed by brine twice and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/ CH<sub>3</sub>OH= 50 / 1) to afford 207 mg pure product as orange powder. Yield: 85 %. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  8.69-8.67 (m, 4 H), 8.30 (s, 2H), 7.86-7.84 (d, 4H, J = 8.4 Hz), 7.80-7.77 (m, 4 H), 7.23-7.21 (d, 4H, J = 8.4 Hz), 5.27 (s, 2H), 4.46-4.43 (t, 4H, J = 7.2 Hz), 2.58-2.55 (t, 2H, J = 7.2 Hz), 1.97-1.90 (m, 2H), 1.60-1.51 (m, 4H). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz, ppm):  $\delta$  159.4, 142.9, 133.9, 131.7, 128.1, 127.4, 125.2, 121.0, 118.1, 115.9, 115.1, 103.5, 85.4, 61.9, 49.1, 29.3, 22.5, 16.2. HR-ESI-MS: m/z calcd for [M + H]<sup>+</sup> C<sub>46</sub>H<sub>39</sub>N<sub>8</sub>O<sub>2</sub>: 735.3172; found: 735.3190, error: 2.5 ppm. m/z calcd for [M + NH<sub>4</sub>]<sup>+</sup> C<sub>46</sub>H<sub>42</sub>N<sub>9</sub>O<sub>2</sub>: 752.3455; found: 752.3456, error: 0.1 ppm.

#### 3. Preparation of nanoparticles

Supramolecular polymeric nanoparticles (**SPNPs**) composed of **bisP5A** and **GD**: A solution of **bisP5A** (6.4 mg) and **GD** (2.7 mg) in CHCl<sub>3</sub> (200  $\mu$ L) was quickly added into deionized water with cetyl trimethyl ammonium bromide (CTAB) as surfactant (10 mL, 0.9 mM). The resulting mixture was sonicated for 25 min. After centrifuge-washing with deionized water three times, the water-dispersible nanoparticles were obtained.

Light-harvesting supramolecular polymeric nanoparticles (LHSPNPs) were prepared with various GA/GD ratios. 5.9 mg GA was dissolved in 2 mL CHCl<sub>3</sub> to prepare stock solution. 27 mg GD was dissolved in 10 mL CHCl<sub>3</sub> to prepare stock solution. A certain fraction of stock solution of GA was mixed with a certain fraction of stock solution of GD (Table S1) and the solvent was removed followed by the addition of 6.4 mg bisP5A and 200  $\mu$ L CHCl<sub>3</sub>. The resulting solution was quickly ejected into deionized water with cetyl trimethyl ammonium bromide (CTAB) as surfactant (10 mL, 0.9 mM). The resulting mixture was sonicated for 25 min. After centrifuge-washing with deionized water three times, the water-dispersible nanoparticles were obtained.

Table S1 The volume of stock solutions of GA and GD for preparation of LHSPNPs.

GA/GD (in mole)	0.5:99.5	1.0:99.0	1.5:98.5	2.0:98.0	2.5:97.5	3.0:97.0
$V_{GA}\left(\mu L\right)$	5	10	15	20	25	30
$V_{\text{GD}}\left(\mu L\right)$	498	495	493	390	488	485

#### 4. Absorption and fluorescence spectra of GD and GA



Fig. S1 Absorption spectra (a) and normalized absorption and fluorescence spectra (b) of **GD** and **GA** in CHCl<sub>3</sub> solution. The molar extinction coefficients ( $\varepsilon$ ) were obtained by Beer-Lambert Law: Abs =  $\varepsilon$ bc (b: pathlength, 1 cm; c: concentration, 5 × 10<sup>-6</sup> M).



Fig. S2 Spectral overlap of GD emission with GA absorption in CHCl<sub>3</sub> solution.

5. Characterization of the host-guest interaction between bisP5A and GD and the formation of supramolecular polymers



Fig. S3 <sup>1</sup>H NMR spectra (4 mM, CDCl<sub>3</sub>, 400 MHz, 298 K) of **GD** (a), **bisP5A** (c), and their equimolar mixture (b).



Fig. S4 <sup>1</sup>H–<sup>1</sup>H COSY spectrum of equimolar mixture of **GD** and **bisP5A** (40 mM, CDCl<sub>3</sub>, 600 MHz, 298 K).



Fig. S5 ROESY spectrum of equimolar mixture of **GD** and **bisP5A** (40 mM, CDCl<sub>3</sub>, 600 MHz, 298 K).



Fig. S6 Spectroscopic and physical characterization of equimolar mixture of **bisP5A** and **GD** at various concentrations. (a) Concentration dependence of diffusion coefficient D (600 MHz, CDCl<sub>3</sub>, 298 K), (b) Specific viscosity (298 K), values by the lines indicate the slopes.

#### 6. The chemical structure of building block for quadruple-hydrogen-bond based SPNPs



Scheme S3 Chemical structure of building block for quadruple-hydrogen-bond based SPNPs.

#### 7. The calculated structural parameters of pillar[5]arene



Fig. S7 The chemical structure (a) and minimized energy structure (b, side view; c, top view; d, top view with van der Waals radius) of dimethoxypillar[5]arene. D: the diameter of the circumcircle of the regular pentagon, 13.5 Å; d: the diameter of the inscribed circle of the regular pentagon, 4.1 Å.

#### 8. The comparison <sup>1</sup>H NMR spectra of GA and bisP5A



Fig. S8 <sup>1</sup>H NMR spectra (4 mM, CDCl<sub>3</sub>, 400 MHz, 298 K) of GA (a), bisP5A (c), and their equimolar mixture (b).





Fig. S9 The SEM images and distribution of the hydrodynamic diameter of **LHSPNPs** from DLS. The scale bars in SEM images were 500 nm, and the molar ratios of **GA/GD** were 0.5:99.5 in a, a'; 1.0:99.0 in b, b'; 1.5:98.5 in c, c'; 2.0:98.0 in d, d'; 2.5:97.5 in e, e'; 3.0:97.0 in f, f'.

10. The comparison of normalized excitation spectrum of LHSPNPs and absorption spectrum of SPNPs



Fig. S10 Normalized excitation spectrum of aqueous dispersion of LHSPNPs (GA: GD = 2.0:98.0,  $\lambda_{em} = 494$  nm) and absorption spectrum of aqueous dispersion of SPNPs of GD and bisP5A.

#### 11. The photostability of aqueous dispersion of LHSPNPs.

We tested the photostability of of aqueous dispersion of **LHSPNPs**. The fresh prepared **LHSPNPs** (**GA**: **GD** = 2.0.98.0) without removing surfactant was irradiated by Xenon lamp without filter in air. The emission spectra of **LHSPNPs** was detected every 20 min. The emissive intensities at both 430 nm and 494 nm showed minor decrease after irradiation for 2 h, suggesting good photostability of these **LHSPNPs**.



Fig. S11. Time dependence of relative emissive intensity of LHSPNPs (GA: GD = 2.0:98.0) at (a) 430 nm and (b) 494 nm.

#### 12. Time-resolved fluorescence measurements of LHSPNPs.



Fig. S12 (a) Fluorescence decay profiles of aqueous dispersion of **LHSPNPs** (**GA**: **GD** = 2.0:98.0,  $\lambda_{exc} = 375$  nm). The monitor wavelengths were 429 nm and 489 nm, which was assigned to the emission of **GD** and **GA**, respectively. (b) 3D time-resolved fluorescence spectra of aqueous dispersion of **LHSPNPs** after excitation (**GA**: **GD** = 1.0:99.0,  $\lambda_{exc} = 375$  nm). The moment when **GD** begun to be excited was set as 0 ns.



#### 13. Light-harvesting properties of LHSPNPs with various GA/GD ratios

Fig. S13 Fluorescence spectra of **LHSPNPs** excited by 378 nm and 450 nm (molar ratios of **GA**/ **GD** were shown in the spectra.

Table S2 Energy transfer efficiencies ( $\varphi_{ET}$ ) and antenna effects of LHSPNPs.

GA/GD (in mole)	0.5:99.5	1.0:99.0	1.5:98.5	2.0:98.0	2.5:97.5	3.0:97.0
$\phi_{\text{ET}}{}^a$	51%	63%	67%	69%	78%	85%
antenna effect <sup>b</sup>	22	18	16	15	10	9

a:  $\phi_{ET} = 1 - I_{430 \text{ nm (in LHSPNPs)}} / I_{430 \text{ nm (in SPNPs)}}$ 

b: antenna effect =I  $_{494 \text{ nm} (\lambda \text{ exc} = 378 \text{ nm})} / I _{494 \text{ nm} (\lambda \text{ exc} = 450 \text{ nm})}$ 

LH scaffolds	Energy donor	Energy acceptor	$\phi \text{ et}^{a}$
<b>LHSPNPs</b> in this work	DPA derivative	DPEA derivative	85%
Organic nanoparticles <sup>2</sup>	Rhodamine B	Cy5	80%
Lipid membrane <sup>3</sup>	PPE-CO2-7	DiI	30%
Organic Nanocrystals <sup>4</sup>	BF2bcz	BF2cna or BF2dan	95%
Polymeric nanoparticles <sup>5</sup>	poly(9-vinylcarbazole), Coumarin 153	Nile red	91%
Protein-assembled nanoparticles <sup>6</sup>	Porphyrin derivative	Phycocyanin	80%
Protein-assembled nanowires <sup>7</sup>	DPA derivative	Eosin Y	59%
Macrocyclic Amphiphiles <sup>8</sup>	1,8-ANS	DBT	97%
DNA-templated chromophore arrays9	JOE, TAMRA	Texas Red	77%
Polymeric vesicles <sup>10</sup>	NBD-Cl	Rhodamine B	80%
Macrocyclic assemblies <sup>11</sup>	OPV-I	Nile red	72%
DNA assemblies <sup>12</sup>	FAM, Cy3	Cy5	68%
Hyperbranched polymers <sup>13</sup>	Coumarin 2	Coumarin 343	98%
Polymeric nanoparticles <sup>14</sup>	Rhodamine B octadecyl ester	Cy5 derivative	75%
Protein-assembled nanoarrays <sup>15</sup>	CdTe QDs1	CdTe QDs2	56%

Table S3 Energy transfer efficiencies of our LHSPNPs and some reported scaffolds.

a: if the authors reported a series of energy efficiencies of similar light-harvesting systems, then we only listed the highest one.



Fig. S14 Fluorescence decay profiles of aqueous dispersion of **SPNPs** of **GD** and **bisP5A** and **LHSPNPs** with various **GA**/ **GD** molar ratios, ,  $\lambda_{exc} = 375 \text{ nm}$ ,  $\lambda_{monitor} = 430 \text{ nm}$ , RIF = instrument response function).

### 14. Copies of <sup>1</sup>H NMR, <sup>13</sup>C NMR and HR-ESI-MS



Fig. S15 <sup>1</sup>H NMR spectrum of **bisP5A** in CDCl<sub>3</sub>.



Fig. S16 <sup>13</sup>C NMR spectrum of **bisP5A** in CDCl<sub>3</sub>.



Fig. S17 HR-ESI spectrum of **bisP5A**.



Fig. S18 <sup>1</sup>H NMR spectrum of **GD** in CDCl<sub>3</sub>.



Fig. S19 <sup>13</sup>C NMR spectrum of **GD** in CDCl<sub>3</sub>.



Fig. S20 HR-ESI spectrum of GD.



Fig. S22 <sup>13</sup>C NMR spectrum of GA in DMSO-d<sub>6</sub>.



Fig. S23 HR-ESI spectrum of GA.

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