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. In order to obtain anhydrous solvents, dichloromethane (CH$_2$Cl$_2$) 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 $^1$H NMR and 100 MHz for $^{13}$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$_3$). 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 Dynapar 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 NaN₃ (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 Na₂SO₄. Solvent was removed by rotary evaporation to afford 1.339 g product as colorless liquid. Yield: 90%. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 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(PPh₃)₄ (117 mg, 0.1 mmol), aqueous Na₂CO₃ (2 M, 12 mL) was heated to reflux under N₂ 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 Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (petroleum ether/CH₂Cl₂ = 4/1) to obtain 590 mg pure product as light-yellow powder. Yield: 76%. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 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 CH₂Cl₂ (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%. ¹H NMR (Acetone-d₆, 400 MHz, ppm): δ 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 µL, 2.4 mmol), and K₂CO₃ (552 mg, 4.00 mmol) in 30 mL acetonitrile was refluxed under N₂ atmosphere overnight. After the reaction was completed, the mixture was concentrated by rotary evaporation. 100 mL water was added to dissolve K₂CO₃ 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%. ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 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 CH₂Cl₂ was added, washed by brine twice and dried over anhydrous Na₂SO₄. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography (CH₂Cl₂/ CH₃OH= 50 / 1) to afford 299 mg pure product as light-yellow powder. Yield: 87%. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 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). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ 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]⁺ C₄₂H₃₉N₈O₂: 687.3191; found: 687.3191, error: -0.1 ppm. m/z calcd for [M + NH₄]⁺ C₄₂H₄₂N₉O₂: 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 Et₃N (5 mL) solution of 9,10-dibromoanthracene (336 mg, 1.0 mmol), 2-(4-ethynylphenoxy)tetrahydro-2H-pyran (606 mg, 3.0 mmol), Pd(PPh₃)₂Cl₂ (35 mg,
0.05 mmol), CuI (9 mg, 0.05 mmol) was heated at 80 °C under N₂ atmosphere for 24 h. After the reaction was completed, solution was cooled to room temperature and concentrated by rotary evaporation. 100 mL CH₂Cl₂ was added, washed with brine twice and dried over anhydrous Na₂SO₄. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography (petroleum ether/ CH₂Cl₂ = 2 / 1) to afford 353 mg pure product as orange powder. Yield: 61%. ¹H NMR (CDCl₃, 400 MHz, ppm): δ 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 CH₃CH₂OH (20 mL) solution of S6 (289 g, 0.5 mmol) and pyridinium toluene-4-sulphonate (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 CH₂Cl₂ was added, washed with brine twice and dried over anhydrous Na₂SO₄. 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 µL, 1.2 mmol), and K₂CO₃ (0.55 g, 4.00 mmol) in 30 mL acetonitrile was refluxed under N₂ atmosphere overnight. After the reaction was completed, the mixture was concentrated by rotary evaporation. The residue was purified by column chromatography (petroleum ether/ CH₂Cl₂ = 2 / 1) to afford 171 mg pure product as orange powder. Yield: 88% ¹H NMR (CDCl₃, 400 MHz, ppm): δ 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 CH₂Cl₂ was added, washed by brine twice and dried over anhydrous Na₂SO₄. Solvent was removed by rotary evaporation and the crude product was purified by column chromatography (CH₂Cl₂/ CH₃OH= 50 / 1) to afford 207 mg pure product as orange powder. Yield: 85 %. ¹H NMR (DMSO-d₆, 400 MHz, ppm): δ 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). ¹³C NMR (DMSO-d₆, 100 MHz, ppm): δ 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]⁺ C₄₆H₃₀N₈O₂: 735.3172; found: 735.3190, error: 2.5 ppm. m/z calcd for [M + NH₄]⁺ C₄₆H₃₂N₈O₂: 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 CHCl₃ (200 μL) 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 CHCl₃ to prepare stock solution. 27 mg GD was dissolved in 10 mL CHCl₃ 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 μL CHCl₃. 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.

<table>
<thead>
<tr>
<th>GA/GD (in mole)</th>
<th>0.5:99.5</th>
<th>1.0:99.0</th>
<th>1.5:98.5</th>
<th>2.0:98.0</th>
<th>2.5:97.5</th>
<th>3.0:97.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₆₆₆₆ (μL)</td>
<td>5</td>
<td>10</td>
<td>15</td>
<td>20</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>V₆₆₆₆ (μL)</td>
<td>498</td>
<td>495</td>
<td>493</td>
<td>390</td>
<td>488</td>
<td>485</td>
</tr>
</tbody>
</table>

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 CHCl₃ solution. The molar extinction coefficients (ε) were obtained by Beer-Lambert Law: Abs = εbc (b: pathlength, 1 cm; c: concentration, 5 × 10⁻⁶ M).](image)
5. Characterization of the host–guest interaction between bisP5A and GD and the formation of supramolecular polymers

Fig. S2 Spectral overlap of GD emission with GA absorption in CHCl₃ solution.

Fig. S3 ¹H NMR spectra (4 mM, CDCl₃, 400 MHz, 298 K) of GD (a), bisP5A (c), and their equimolar mixture (b).
Fig. S4 $^1$H–$^1$H COSY spectrum of equimolar mixture of GD and bisP5A (40 mM, CDCl$_3$, 600 MHz, 298 K).

Fig. S5 ROESY spectrum of equimolar mixture of GD and bisP5A (40 mM, CDCl$_3$, 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, CDCl₃, 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**

![Chemical structure of building block for quadruple-hydrogen-bond based SPNPs](image)

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


![ Structural parameters of pillar[5]arene ](image)

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 $^1$H NMR spectra of GA and bisP5A

Fig. S8 $^1$H NMR spectra (4 mM, CDCl$_3$, 400 MHz, 298 K) of **GA** (a), **bisP5A** (c), and their equimolar mixture (b).

9. SEM images and hydrodynamic diameter distribution of LHSPNPs

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

![Normalized excitation spectrum of aqueous dispersion of LHSPNPs](image)

Fig. S10 Normalized excitation spectrum of aqueous dispersion of LHSPNPs (GA: GD = 2.0:98.0, λ\text{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 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.

![Time dependence of relative emissive intensity of LHSPNPs](image)

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, λ_{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, λ_{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 (φ_{ET}) and antenna effects of LHSPNPs.

<table>
<thead>
<tr>
<th>GA/GD (in mole)</th>
<th>0.5:99.5</th>
<th>1.0:99.0</th>
<th>1.5:98.5</th>
<th>2.0:98.0</th>
<th>2.5:97.5</th>
<th>3.0:97.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>φ_{ET}^{a}</td>
<td>51%</td>
<td>63%</td>
<td>67%</td>
<td>69%</td>
<td>78%</td>
<td>85%</td>
</tr>
<tr>
<td>antenna effect^{b}</td>
<td>22</td>
<td>18</td>
<td>16</td>
<td>15</td>
<td>10</td>
<td>9</td>
</tr>
</tbody>
</table>

a: φ_{ET} = 1 - \frac{I_{430 \text{ nm} (in \ LHSPNPs)}}{I_{430 \text{ nm} (in \ SPNPs)}}

b: antenna effect = \frac{I_{494 \text{ nm} (\lambda_{exc} = 378 \text{ nm})}}{I_{494 \text{ nm} (\lambda_{exc} = 450 \text{ nm})}}
<table>
<thead>
<tr>
<th>LH scaffolds</th>
<th>Energy donor</th>
<th>Energy acceptor</th>
<th>$\phi_{ET}^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>LHSPNPs in this work</strong></td>
<td>DPA derivative</td>
<td>DPEA derivative</td>
<td>85%</td>
</tr>
<tr>
<td>Organic nanoparticles$^2$</td>
<td>Rhodamine B</td>
<td>Cy5</td>
<td>80%</td>
</tr>
<tr>
<td>Lipid membrane$^3$</td>
<td>PPE-CO2-7</td>
<td>Dil</td>
<td>30%</td>
</tr>
<tr>
<td>Organic Nanocrystals$^4$</td>
<td>BF2bcz</td>
<td>BF2cna or BF2dan</td>
<td>95%</td>
</tr>
<tr>
<td>Polymeric nanoparticles$^5$</td>
<td>poly(9-vinylcarbazole),</td>
<td>Nile red</td>
<td>91%</td>
</tr>
<tr>
<td>Protein-assembled nanoparticles$^6$</td>
<td>Coumarin 153</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protein-assembled nanowires$^7$</td>
<td>DPA derivative</td>
<td>Eosin Y</td>
<td>59%</td>
</tr>
<tr>
<td>Macrocyclic Amphipiles$^8$</td>
<td>1,8-ANS</td>
<td>DBT</td>
<td>97%</td>
</tr>
<tr>
<td>DNA-templated chromophore arrays$^9$</td>
<td>JOE, TAMRA</td>
<td>Texas Red</td>
<td>77%</td>
</tr>
<tr>
<td>Polymeric vesicles$^{10}$</td>
<td>NBD-Cl</td>
<td>Rhodamine B</td>
<td>80%</td>
</tr>
<tr>
<td>DNA assemblies$^{11}$</td>
<td>OPV-I</td>
<td>Nile red</td>
<td>72%</td>
</tr>
<tr>
<td>Hyperbranched polymers$^{13}$</td>
<td>OPV-I</td>
<td>Nile red</td>
<td>72%</td>
</tr>
<tr>
<td>Polymeric nanoparticles$^{14}$</td>
<td>Rhodamine B octadecyl ester</td>
<td>Cy5 derivative</td>
<td>75%</td>
</tr>
<tr>
<td>Protein-assembled nanoarrays$^{15}$</td>
<td>CdTe QDs1</td>
<td>CdTe QDs2</td>
<td>56%</td>
</tr>
</tbody>
</table>

*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, $\lambda_{exc} = 375$ nm, $\lambda_{monitor} = 430$ nm, RIF = instrument response function).
14. Copies of $^1$H NMR, $^{13}$C NMR and HR-ESI-MS

Fig. S15 $^1$H NMR spectrum of bisP5A in CDCl$_3$.

Fig. S16 $^{13}$C NMR spectrum of bisP5A in CDCl$_3$. 
Fig. S17 HR-ESI spectrum of bisP5A.

Fig. S18 $^1$H NMR spectrum of GD in CDCl$_3$. 
Fig. S19 $^{13}$C NMR spectrum of GD in CDCl$_3$.

Fig. S20 HR-ESI spectrum of GD.
Fig. S21 $^1$H NMR spectrum of GA in DMSO-d$_6$.

Fig. S22 $^{13}$C NMR spectrum of GA in DMSO-d$_6$. 
Fig. S23 HR-ESI spectrum of GA.

15. References