Electronic Supplementary Material (ESI) for ChemComm.

Effect of Scaffold Structures on the Artificial Light-Harvesting Systems: A Case Study with an AIEE-active Pillar[5]arene Dimer

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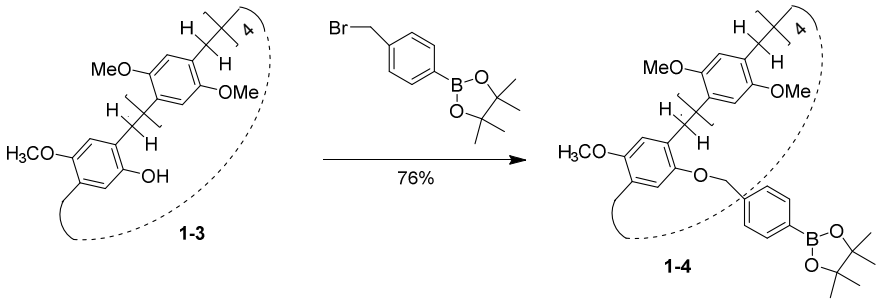
1. Experimental Procedures

1.1 Chemicals and instruments

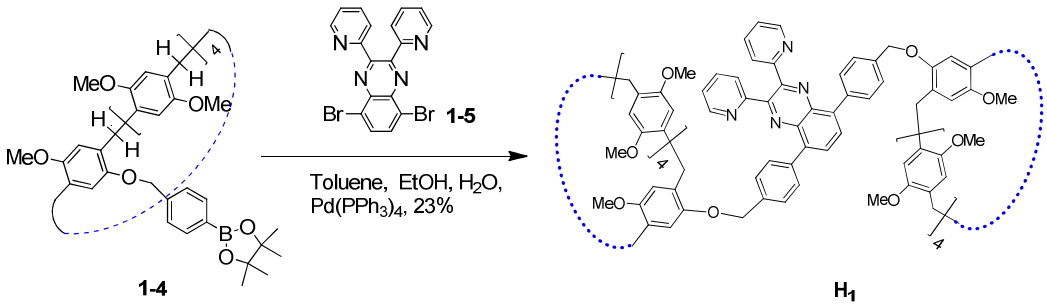
All solvents were obtained from commercial resources or dried according to the standard procedure. Other materials were purchased from Aladdin, Adamas and J&K and were used for synthesis without further purification. The molecules **G1**[1] and **G2**[2] were synthesized according to the previous procedures. NMR spectra were recorded on Bruker advance III 400 MHz and chemical shifts were expressed in ppm using TMS as an internal standard. The UV-vis absorption spectra were recorded using a Helios Alpha UV-vis scanning spectraphotometer. Fluorescence spectra were obtained with a Hitachi F-4500 FL spectrophotometer with quartz cuvette.

*1.2 Synthesis of **1-4***



1-4 was synthesized with a Williamson reaction. A mixture of **1-3** (1.2 g, 1.6 mmol), 2-(4-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.4 g, 4.8 mmol) and NaH (0.38 g, 16 mmol) were dissolved in 30 mL DMF. The resulting solution was heated to 80 ºC overnight under N_2 atmosphere. The solution was concentrated by rotary evaporation and the crude product was purified by column chromatography (PE/DCM/EA, 10/1/1 as eluent) to afford 1.2 g pure product as white powder. Yield: 76%

*1.3 Synthesis of **H1***



H1 was synthesized with a suzuki reaction. **1-4** (1.9 g, 2 mmol), **1-5** (443 mg, 1 mmol), Na_2CO_3 (2.12 g, 20 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) were dissolved in a mixed solvent of 30 mL toluene, 6 mL ethanol and 6 mL H_2O. The solution was refluxed for 20 hours under N_2 atmosphere. After the reaction was completed, the mixture was concentrated by the rotary evaporation and the crude product was purified by column chromatography (PE/DCM/EA, 10/5/3 as eluent) to afford 0.89 g pure product as yellow powder. Yield: 23%. Melting point: 193-195 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): 8.25(2H, d, Py-H), 8.17(d, 2H, Py-H), 7.97(s, 2H, Ar-H), 7.87(d, 4H, Ar-H), 7.78(t, 76-7.8, 2H), 7.63(7.62-7.64, d, 4H, Ar-H), 7.18(m, 7.2-7.16, 2H), 6.9(s, 2H), 6.87(s, 2H), 6.7(m, 6.80-6.72, 16H, Ar-H), 4.99(s, 4H, OCH_2), 3.9(s, 4H), 3.79(t, 16H), 3.7(s, 6H), 3.65(3.63-3.67, m, 42H), 3.34(s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 157.4, 157.4, 151.0, 151.0, 150.6, 149.9, 149.9, 147.8, 147.8, 139.3, 139.3, 138.4, 138.4, 137.4, 137.4, 136.7, 136.7, 130.0, 130.0, 128.3, 128.3, 128.3, 128.3, 127.8, 127.8, 126.7, 126.7, 126.7, 126.7, 123.8, 122.7, 113.9, 70.4, 70.4, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.6, 55.2, 55.2, 29.3, 29.3, 29.3, 29.3, 29.3, 29.3, 29.3, 29.3, 29.3, 29.3. HRMS: m/z calcd. for $[M+H]^+$ $C_{120}H_{117}N_4O_{20}$: 1933.8064; found 1933.8256.

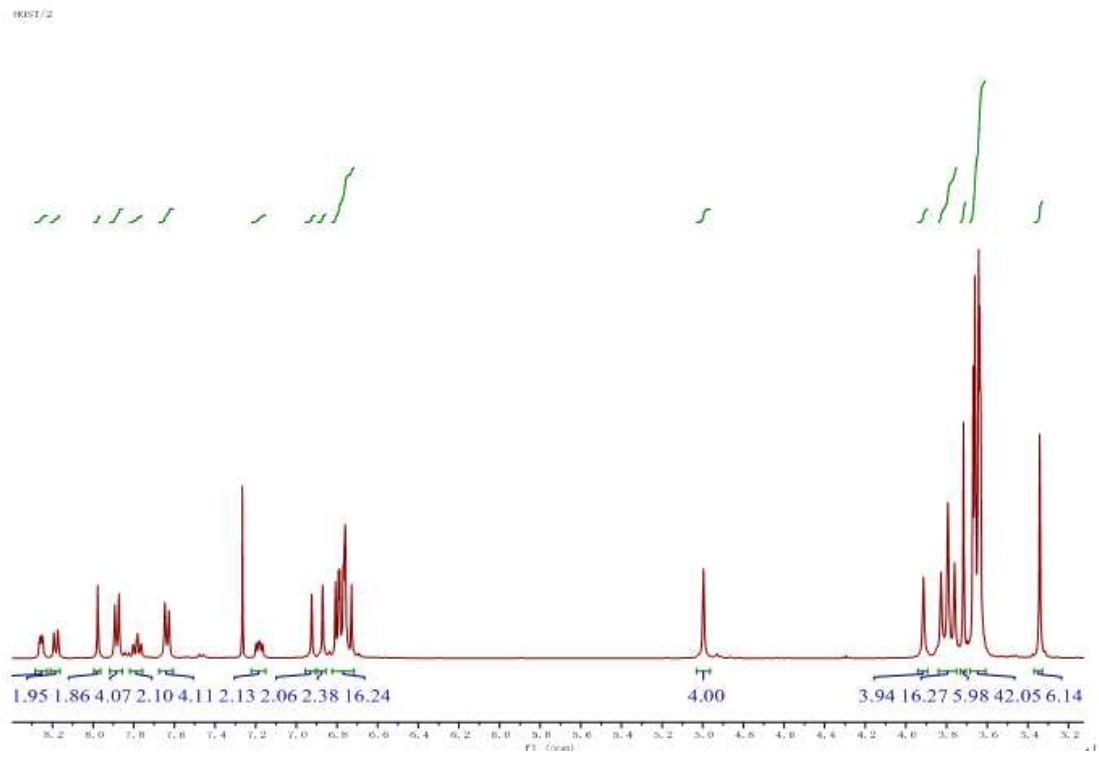


Figure S1. ^{1}H NMR spectrum of **H1** (400 MHz, $CDCl_3$, 298 K)

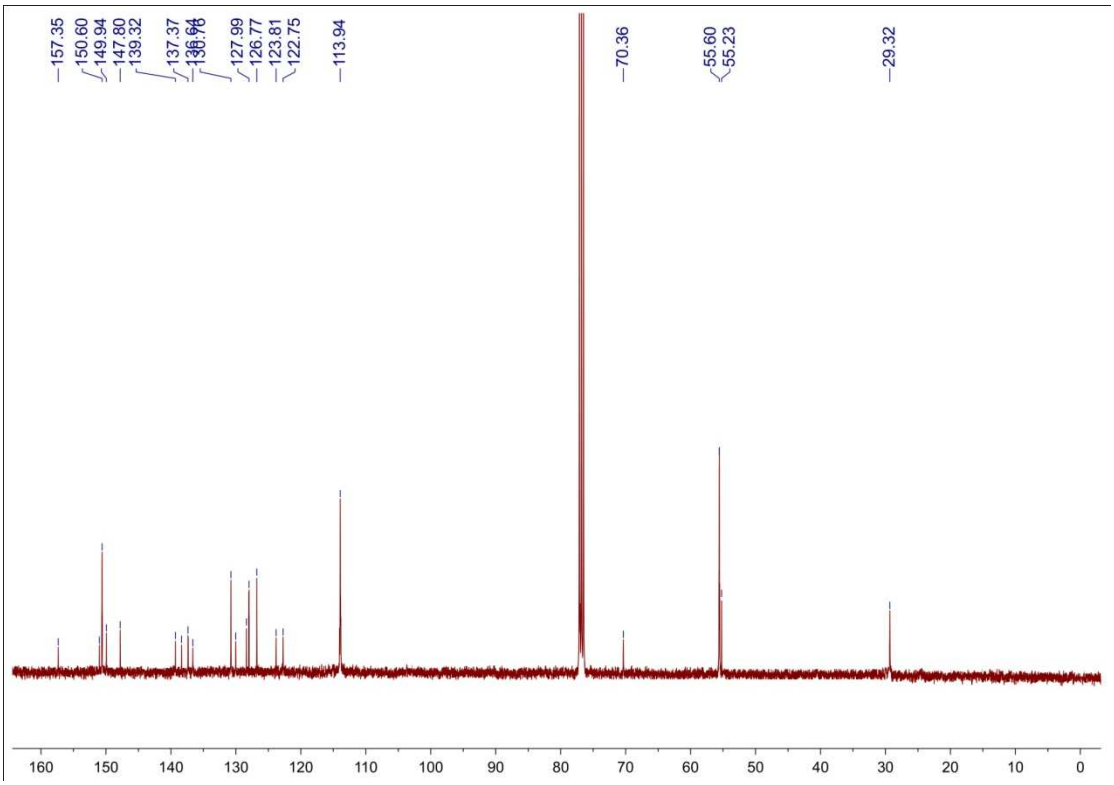


Figure S2. ^{13}C NMR spectrum of **H1** (100 MHz, $CDCl_3$, 298 K)

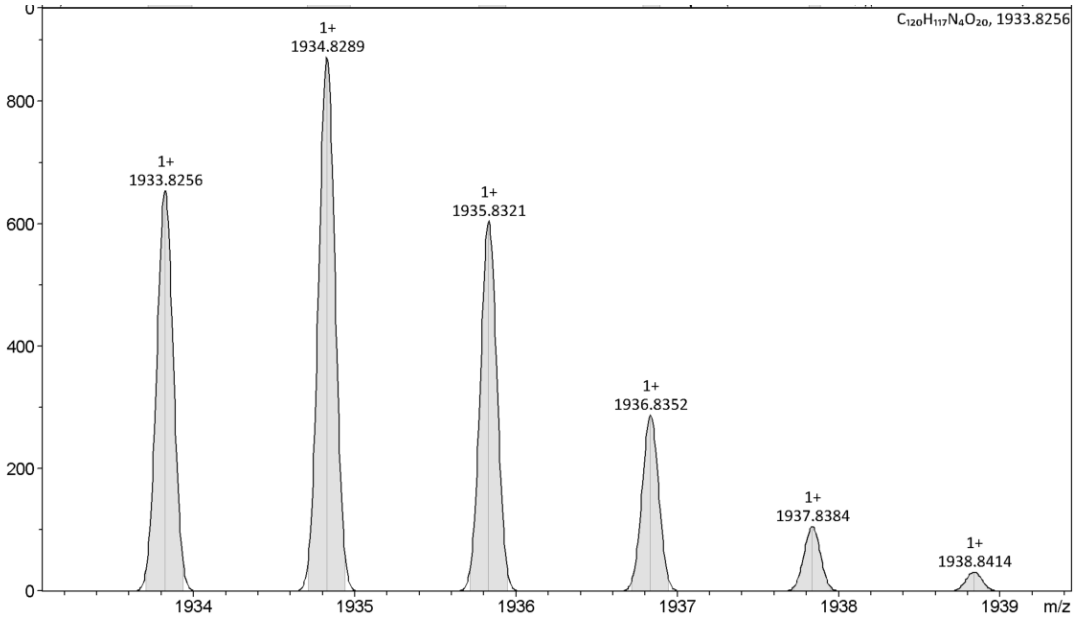
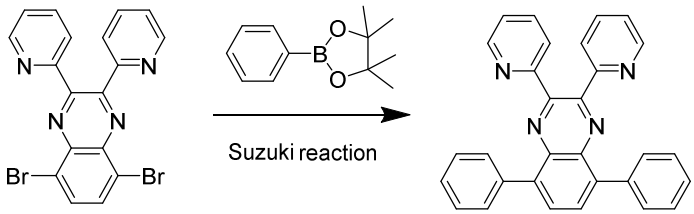


Figure S3. ^{1}H RMS (ESI) spectrum of compound **H1**+1.

*1.4 Synthesis of **C1**.*



1-5 (0.5 g, 1.1 mmol), 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (0.67 g, 3.3 mmol), Na_2CO_3 (0.58 g, 5.5 mmol) and $Pd(PPh_3)_4$ (0.12 g, 0.11 mmol) were dissolved in a mixed solution of 30 mL THF and 5 mL H_2O. The mixture was fluxed under N_2 atmosphere for 20 hours. The mixture was concentrated by the rotary evaporation and the crude product was purified by column chromatography (PE/DCM/EA, 10/5/2 as eluent) to afford 0.36 g pure product as yellow powder. Yield: 80%. Melting point: 160-162 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): 8.23(2H, d, Py-H), 8.19(d, 2H, Py-H), 7.95(s, 2H, Ar-H), 7.87(7.90-7.79, m, 6H), 7.54(7.58-7.50, t, 4H), 7.45(7.49-7.40, d, 2H), 7.18(t, 7.2-7.16, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298

K), δ (ppm):157.7, 157.7, 151.0, 151.0, 148.0, 148.0, 148.0, 148.0, 139.7, 139.7, 138.5, 138.5, 138.1, 138.1, 136.8, 136.8, 131.0, 131.0, 131.0, 131.0, 130.3, 130.3, 128.0, 128.0, 128.0, 128.0, 127.7, 127.7, 124.0, 122.9. HRMS: m/z calcd. for $[M+H]^+$ $C_{30}H_{21}N_4$: 437.169; found 437.1761.

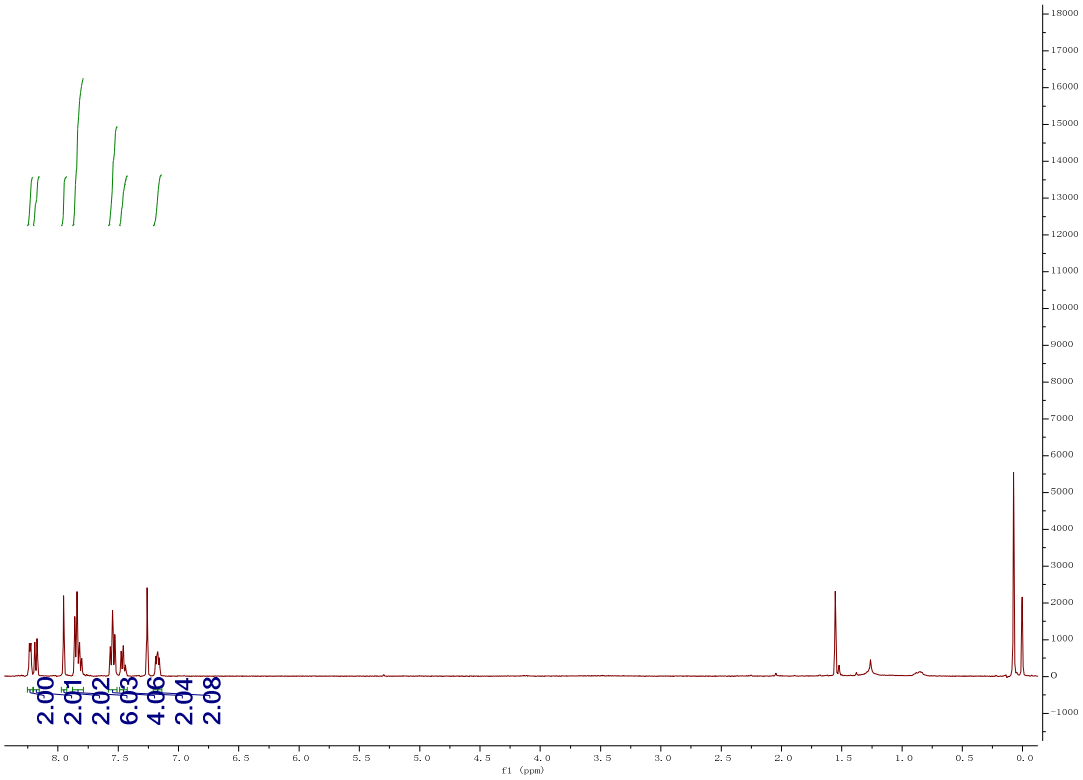


Figure S4. ^{1}H NMR spectrum of **C1** (400 MHz, $CDCl_3$, 298 K)

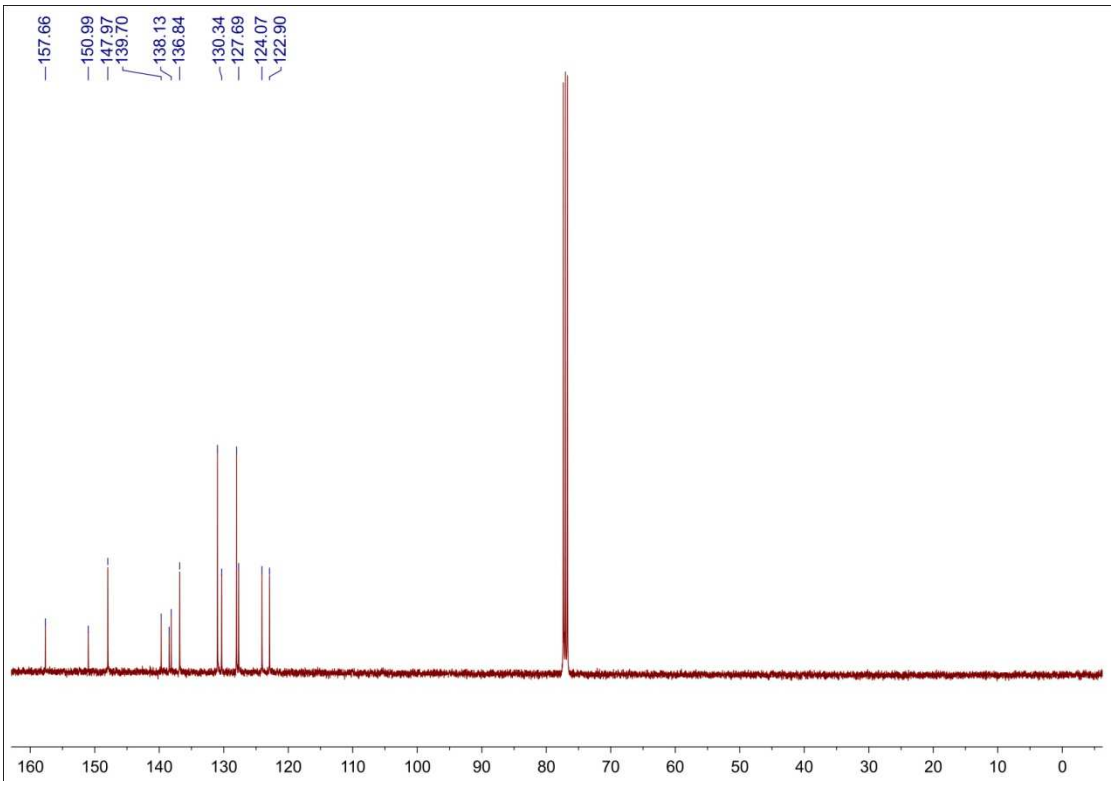


Figure S5. ^{13}C NMR spectrum of **C1** (100 MHz, $CDCl_3$, 298 K)

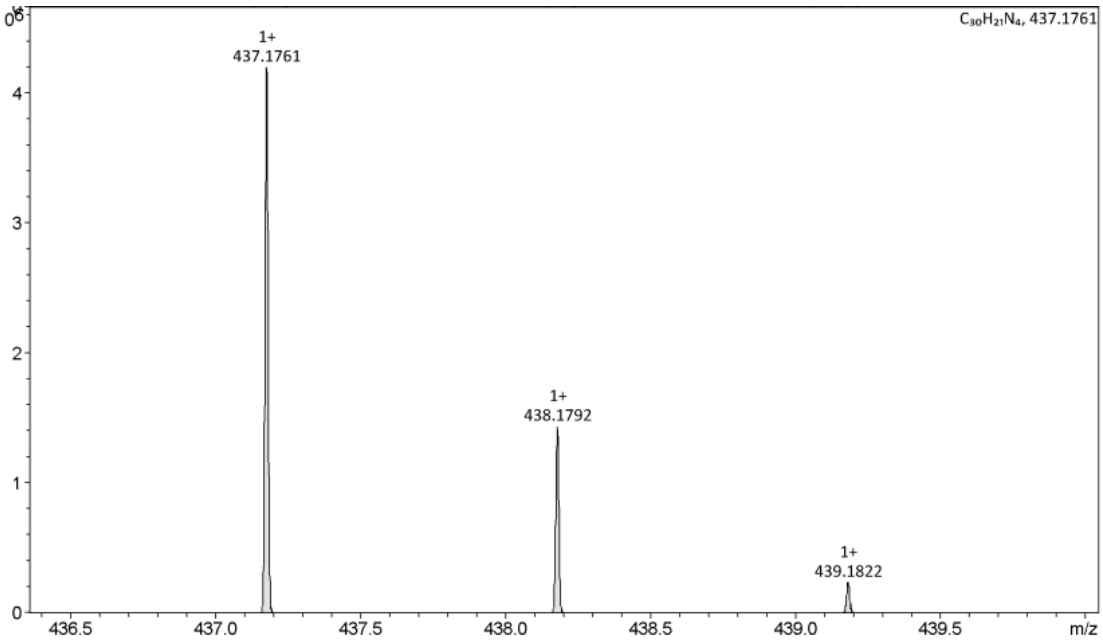
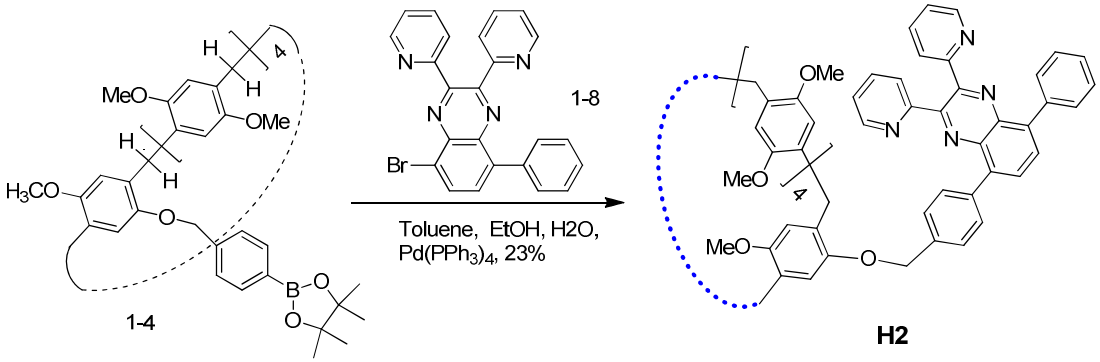


Figure S6. ^{1}H RMS (ESI) spectrum of compound **C1**+1

*1.5 Synthesis of **H2**.*



H2 was synthesized by the Suzuki reaction. **1-4** (0.95 g, 1 mmol), **1-8** (443 mg, 1 mmol), Na_2CO_3 (1 g, 10 mmol) and $Pd(PPh_3)_4$ (0.12g, 0.1 mmol) were dissolved in the mixed solvents of 30 ml toluene, 6 ml ethanol and 6 ml H_2O. The solution was refluxed for 20 hours under N_2 atmosphere. After the reaction was completed, the mixture was concentrated by the rotary evaporation and the crude product was purified by column chromatography (PE/Toluene/EA=10/8/3 as eluent) to afford 0.35 g pure product as yellow powder. Yield: 30%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): 8.24(2H, s, Py-H), 8.178(t, 2H, Py-H), 7.97(m, 2H), 7.87(d, 3H, Ar-H), 7.78(m, 76-7.8, 2H), 7.58(7.63-7.53, d, 4H, Ar-H), 7.18(m, 7.2-7.15, 2H), 6.9(d, 2H), 6.86(d, 2H), 6.75(m, 6.80-6.70, 10H, Ar-H), 4.99(s, 2H, OCH_2), 3.79(t, 10H), 3.7(s, 3H), 3.63(3.66-3.57, m, 24H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K), δ (ppm): 157.6, 157.6, 150.9, 150.9, 150.9, 150.9, 150.9, 150.9, 150.9, 150.9, 150.9, 150.9, 150.9, 150.2, 150.2, 148.0, 148.0, 139.8, 139.4, 138.5, 138.5, 138.1, 137.6, 137.6, 136.9, 136.9, 131.0, 131.0, 131.0, 131.0, 131.0, 131.0, 131.0, 131.0, 131.0, 131.0, 130.4, 130.4, 128.2, 128.2, 128.1, 128.1, 127.8, 127.8, 127.0, 127.0, 127.0, 127.0, 127.0, 124.1, 122.9, 115.3, 114.2, 114.2, 114.2, 114.2, 114.2, 114.2, 114.2, 114.2, 114.2, 114.2, 70.6, 55.8, 55.8, 55.8, 55.8, 55.8, 55.8, 55.8, 55.8, 55.5, 29.8, 29.8, 29.8, 29.8,

29.8. HRMS: m/z calcd. for $[M+H]^+$ $C_{75}H_{69}N_4O_{10}$: 1185.5; found 1185.5008.

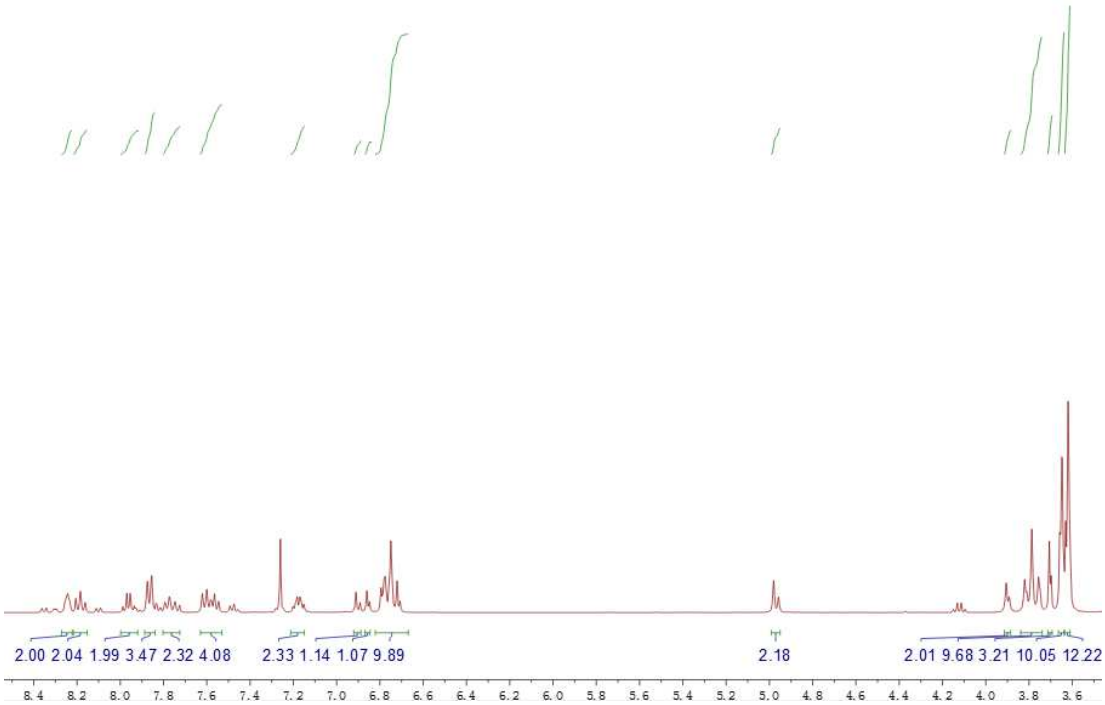


Figure S7. ^{1}H NMR spectrum of **H2** (400 MHz, $CDCl_3$, 298 K)

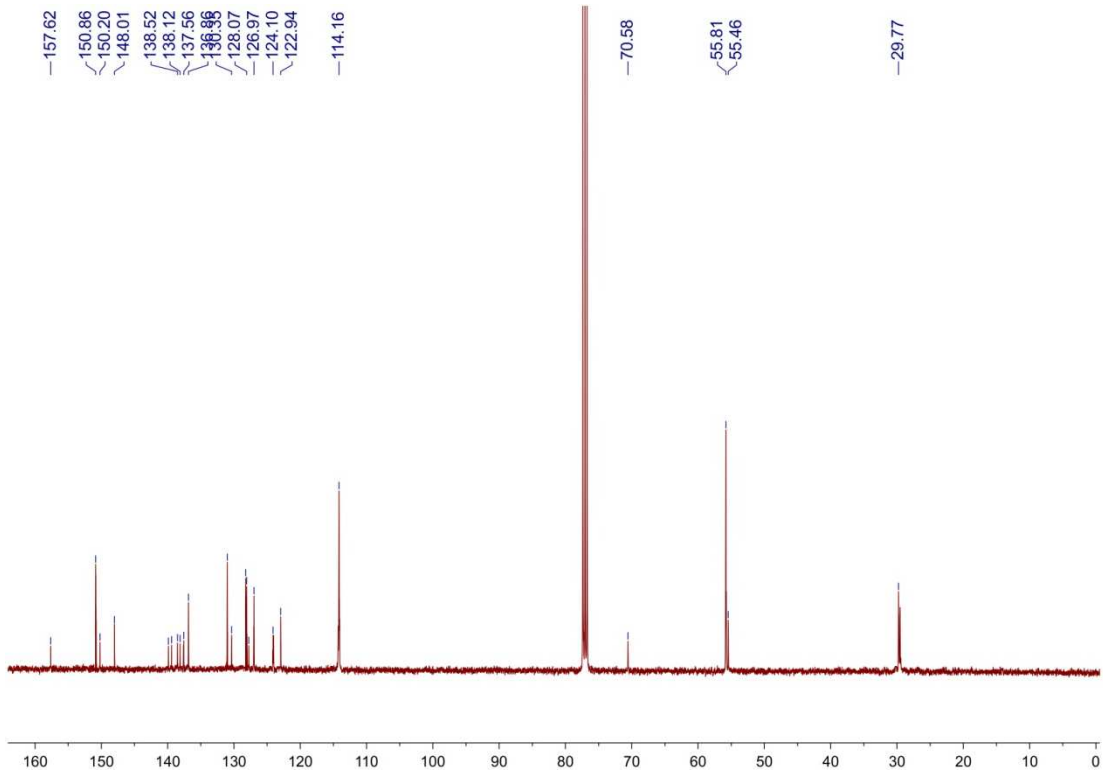


Figure S8. ^{13}C NMR spectrum of **H2** (100 MHz, $CDCl_3$, 298 K)

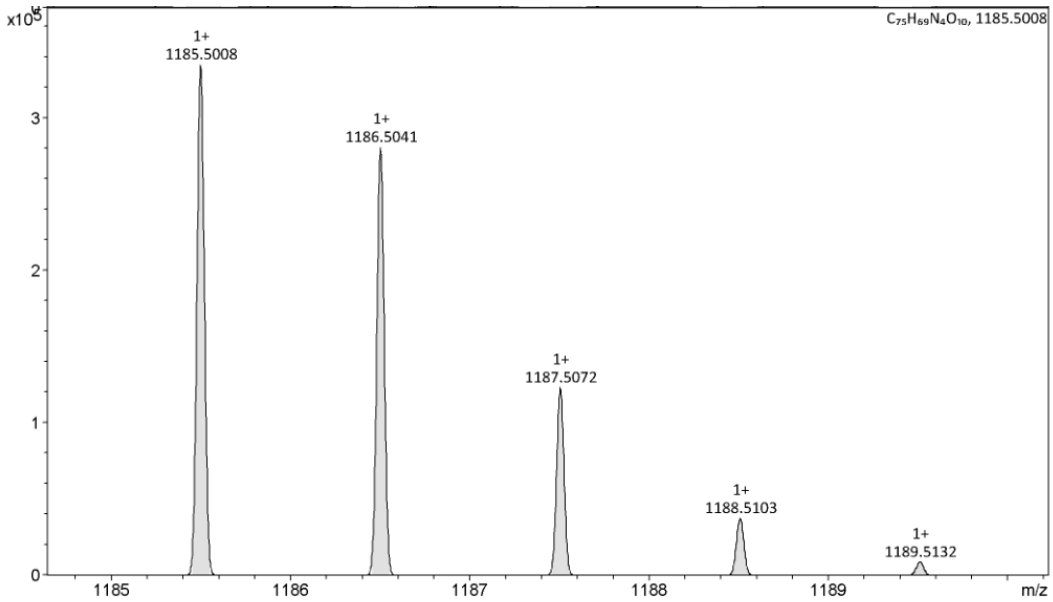


Figure S9. HRMS (ESI) spectrum of compound **H2+1**

1.6 Preparation of nanoparticles

20 μL of the stock solution of **G2** (or **H1** or **H1-G2** mixture or **H1-G1** mixture or **H1-G2-G1** mixture) in chloroform was rapidly injected into 2 mL aqueous solution containing 1 mM cetyltrimethyl ammonium bromide (CTAB). After sufficient ultrasonication of the solution and being washed three times with water, the water-dispersible nanoparticles were obtained.

2. Supplementary Figures

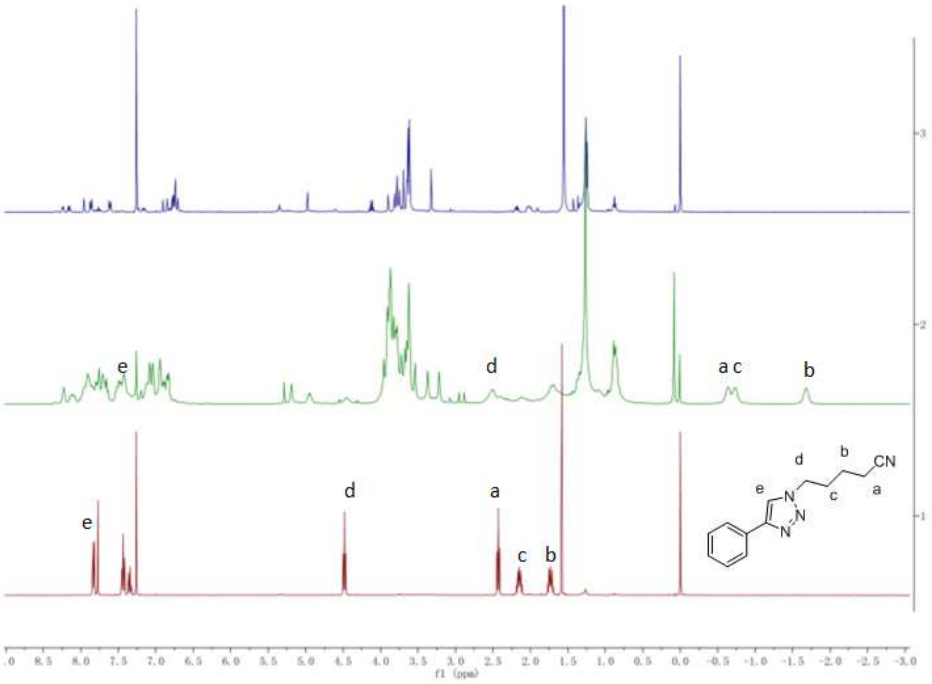


Figure S10. ^{1}H NMR spectra for the binding of **H1** and the guest in $CDCl_3$ (400 MHz, 298 K). From the bottom to the top: ^{1}H NMR spectra for free **G**, for the mixture of **G** and **H1** with the concentration ratio of 2:1, and for free **H1**. [**H1**] = 25 μM. (The alkyl protons *a*, *b*, *c*, *d* and triazole protons *e* of the guest shifted upfield upon the binding to the host **H1**. The signal peaks of **H1** were broadened upon the host-guest complexation due to the shielding effect of the pillar[5]arene cavity.

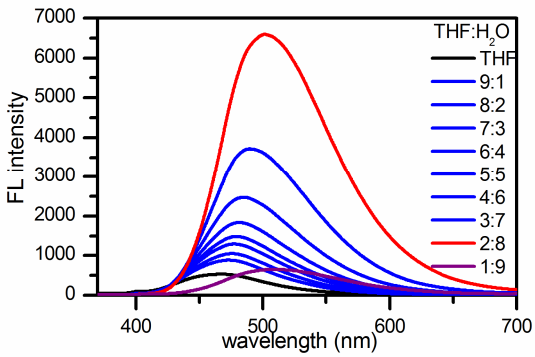


Figure S11. Fluorescence spectra of **C1** in THF–H_2O mixtures with different solvent ratios (λ_{exc} = 350 nm)

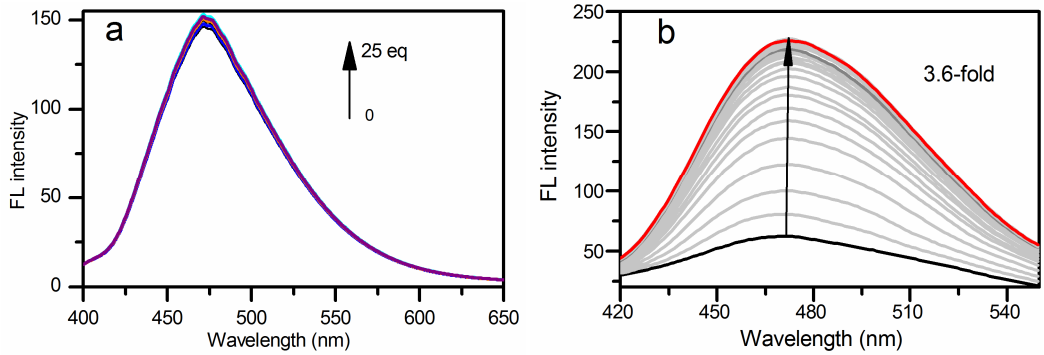


Figure S12. (a) Fluorescence response of **C1** toward the guest butanedinitrile in chloroform; (b) Fluorescence response of **H1** toward the guest butanedinitrile in chloroform. [**C1**] = 10 μM. [**H1**] = 10 μM. λ_{exc} = 350 nm.

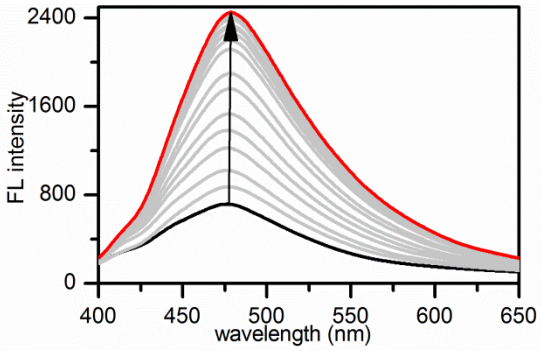


Figure S13. Fluorescence response of **H1** toward the guest **G1** in $CHCl_3$. λ_{exc}=350 nm. [**H1**] = 10 μM.

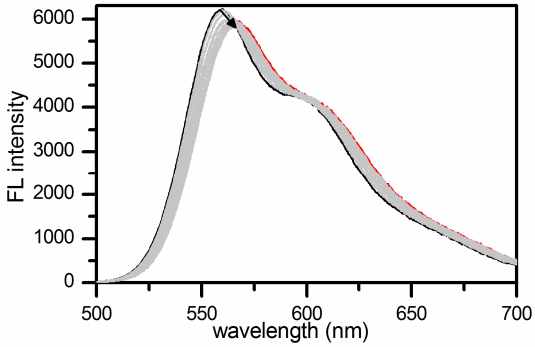


Figure S14. Fluorescence response of **G2** toward the host **H1** in $CHCl_3$. [**G2**] = 2.5 μM. [**H1**] = 0 – 25 μM. λ_{exc} = 490 nm.

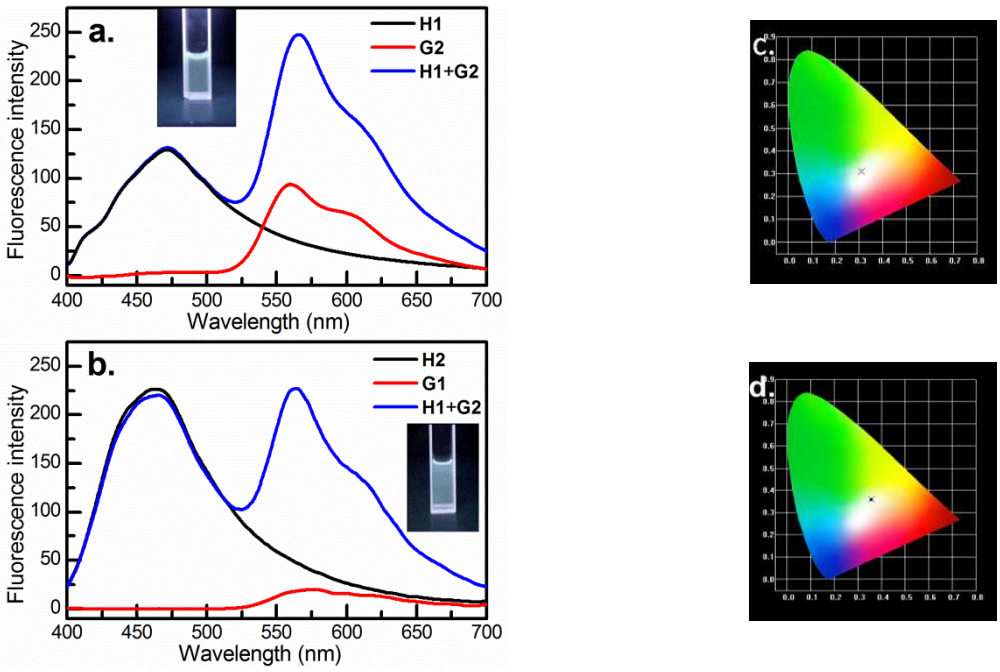


Figure S15. (a) Fluorescence spectra of **H1**, **G2**, and the mixture of **H1** and **G2** in chloroform. λ_{exc} = 390 nm. (b) CIE chromaticity of the fluorescence spectra for the **H1**/**G2** mixture shown in a. (c) Fluorescence spectra of **H1**, **G2**, and the mixture of **H1** and **G2** in a mixture of chloroform/n-hexane (1/99, v/v). λ_{exc} = 380 nm. (d) CIE chromaticity of the fluorescence spectra for the **H1**/**G2** mixture shown in c. [**H1**] = 10 μM. [**G2**] = 0.1 μM.

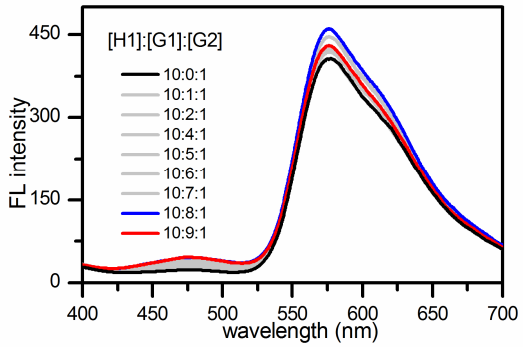


Figure S16. Fluorescence spectra of the mixture of **H1**, **G1**, and **G2** in $CHCl_3$ with different concentration ratio. λ_{exc}=390 nm. [**H1**] = 10 μM.

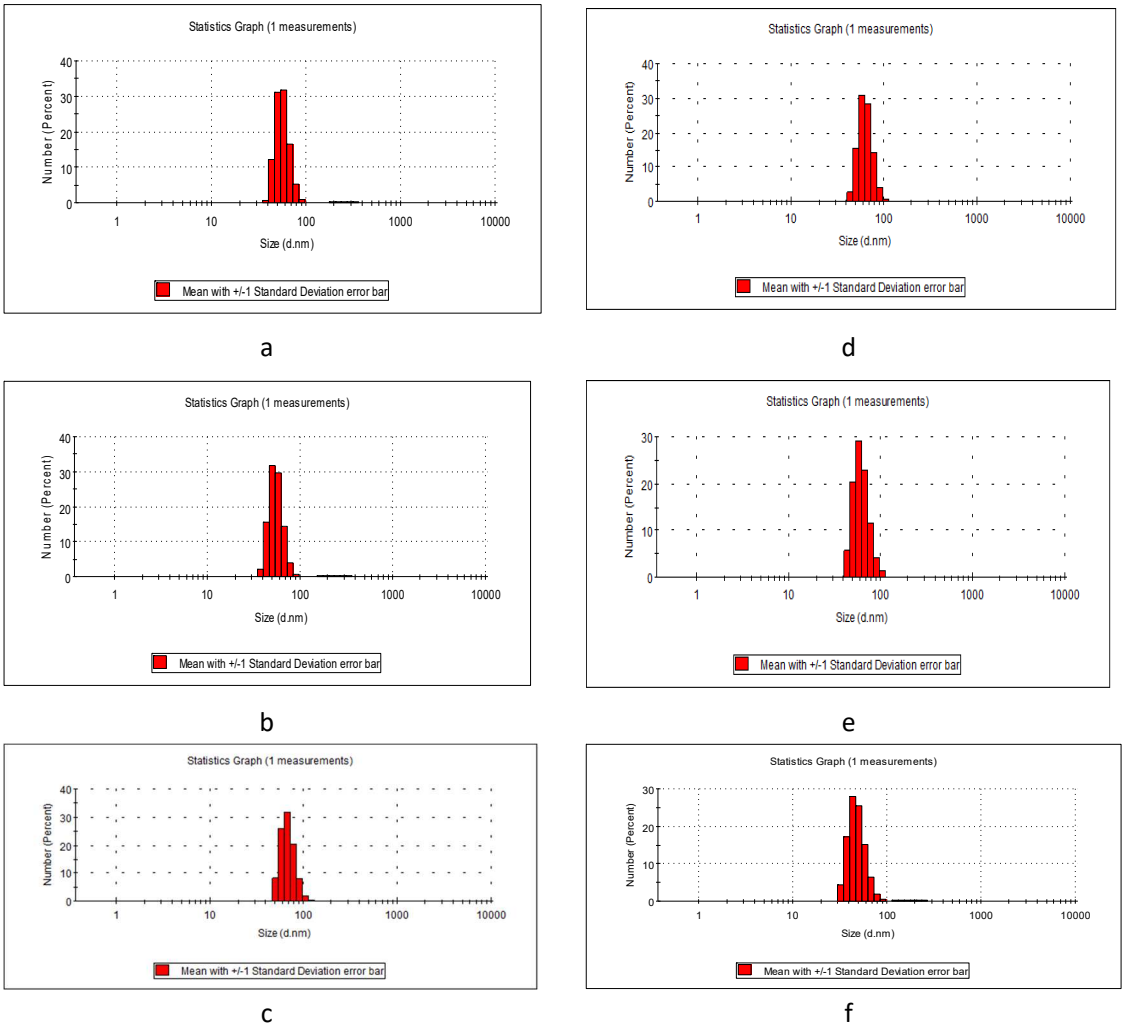


Figure S17. DLS data for nanoparticles with different ratios of compounds in CTAB aqueous solution. (a) [**H1**]/[**G2**] = 10/1 (b) [**H1**]/[**G1**]/[**G2**] = 10/3/1 (c) [**H1**]/[**G1**]/[**G2**] = 10/5/1 (d) [**H1**]/[**G1**]/[**G2**] = 10/7/1 (e) [**H1**]/[**G1**]/[**G2**] = 10/9/1 (f) [**H1**]/[**G2**] = 0/1. [**G2**] = 1 μM.

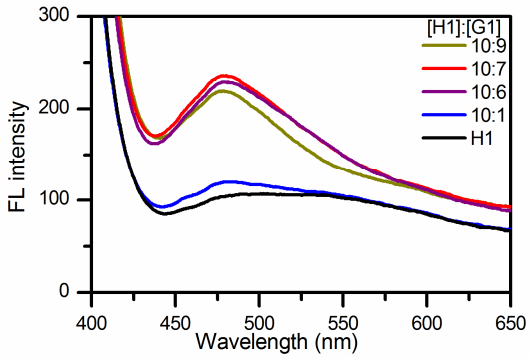


Figure S18. Fluorescence spectra of nanoparticles with different molar ratios of **H1**/**G1**. [**H1**] = 10 μM. λ_{exc} = 390 nm.

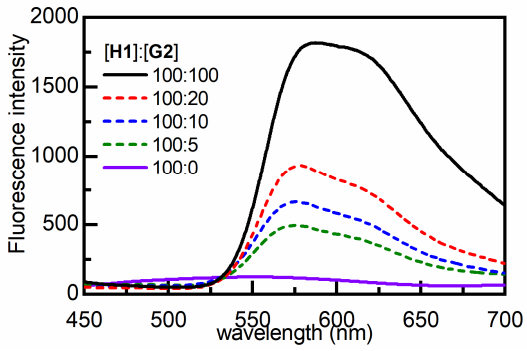


Figure S19. Fluorescence spectra of **BNP**s and **UNP** in water with the different ratios of components. λ_{exc} = 390 nm. [**H1**] = 10 μM.

The calculation of the energy transfer efficiency. When the molar ratio of **[H1]:[G1]:[G2]** reach to 100:0:100, the FRET efficiency for this sample could be treated as 100%, and the fluorescence intensity at 480 nm was determined as the value of a.

The energy transfer efficiency for each sample *i* was calculated with the following equation:

$$\varphi_{\mathrm{ET}} = \frac{I_0 - I_i}{I_0 - \mathrm{a}}$$

where I_i was determined as the fluorescence intensity at 480 nm for the sample with different concentration of **G2**, and I_0 was determined as the fluorescence intensity at 480 nm for the corresponding sample without **G2**.

The calculation of the Antenna effects. The antenna effect was calculated by the following equation:

$$\text{Antenna effect} = \frac{I_{390}}{I_{470}}$$

where I_i was the fluorescence intensity at 570 nm determined for sample excited at i nm.

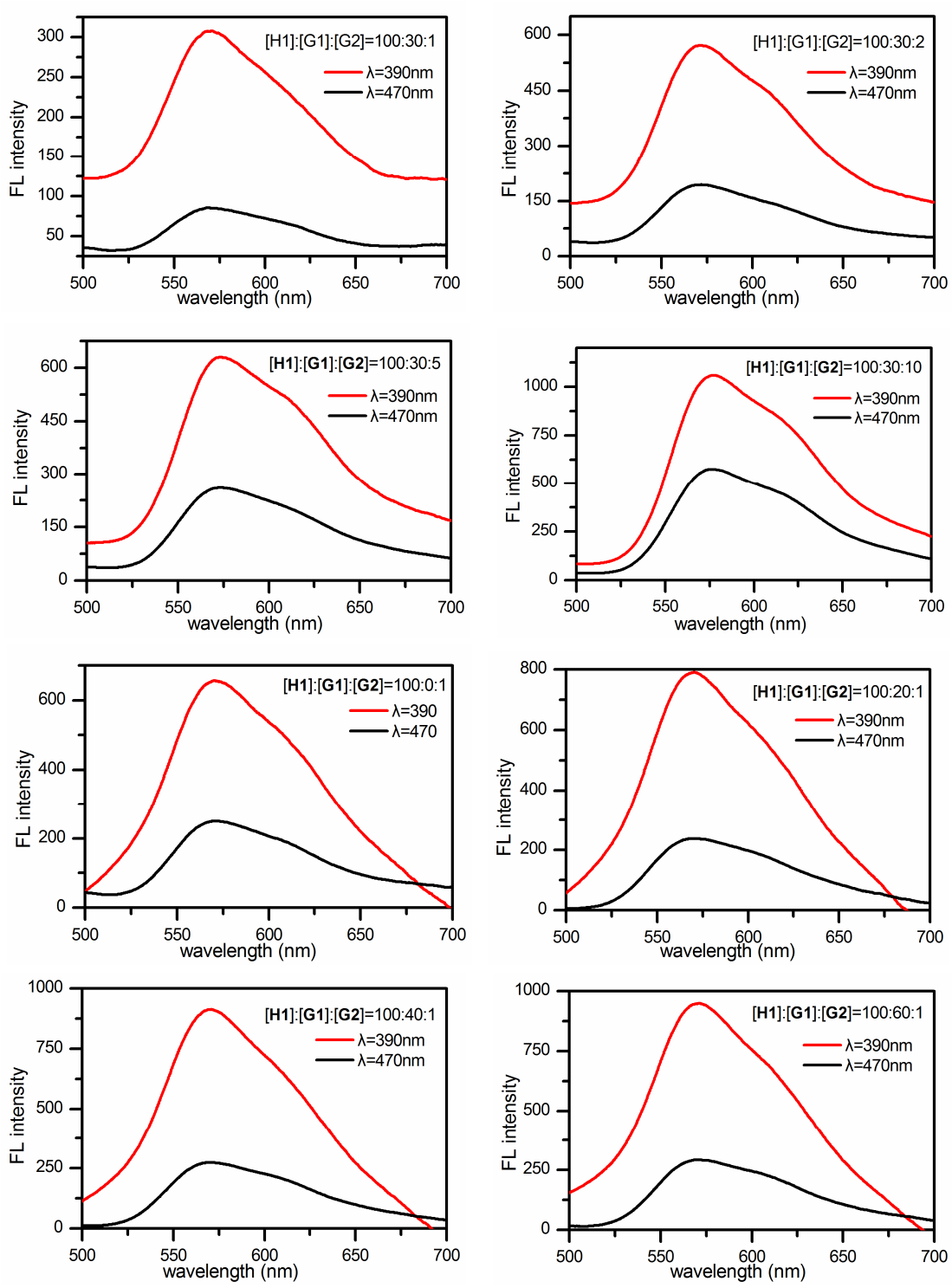


Figure S20. Fluorescence spectra of nanoparticles excited at 390 nm and 470 nm. Molar ratios of **H1/G1/G2** were shown in the spectra.

Table S1. Antenna effects calculated for different nanoparticles.

[**H1**]:[**G1**]:[**G2**]	100:0:1	100:20:1	100:30:1	100:30:2	100:30:5	100:30:10	100:40:1	100:60:1
Antenna effect	2.6	3.4	3.7	3.0	2.4	1.9	3.4	3.2

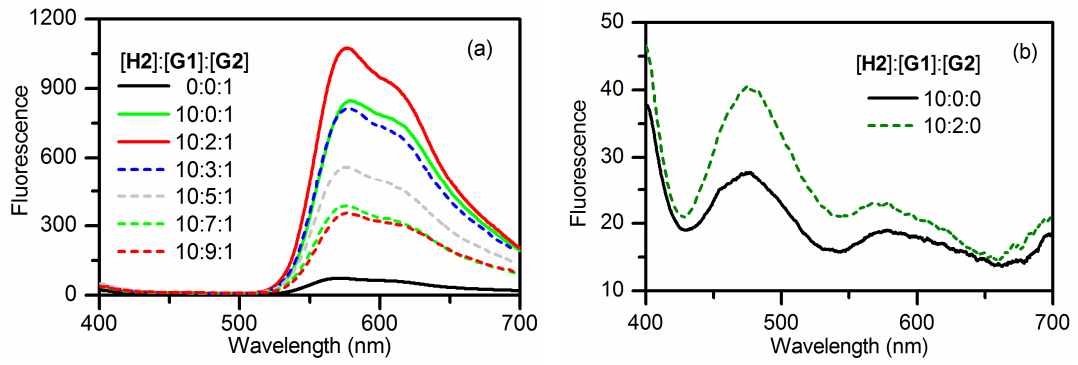


Figure S21. Fluorescence spectra of nanoparticles in CTAB aqueous solutions with different ratios of [**H2**]:[**G1**]:[**G2**] in the presence (a) and absence of **G2** (b). λ_{exc} = 390 nm. [**H2**] = 10 μM. [**G2**] = 1 μM.

3. Reference

1. L. Xu, R. Wang, W. Cui, L. Wang, H. Meier, H. Tang and D. Cao, *Chem. Commun.*, 2018, **54**, 9274-9277;
2. L. Xu, Z. Wang, R. Wang, L. Wang, X. He, H. Jiang, H. Tang, D. Cao, B. Tang, *under consideration*.