

## Supporting Information

# Assembly-Induced-Emission Orthogonal Supramolecular Network with Spirobifluorene, Pillararene and Tetraphenylethylene Units for Efficient Light Harvesting

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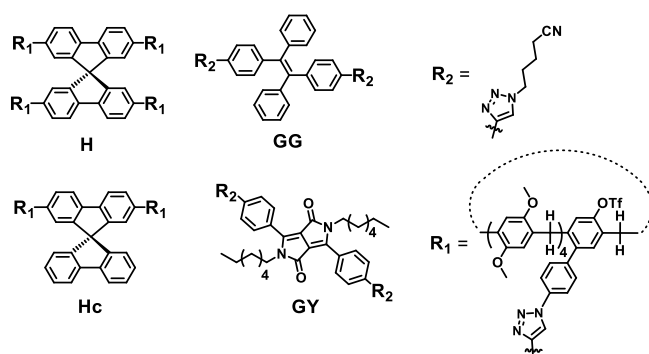
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# 1. Experimental Procedures

## 1.1 Materials and Methods

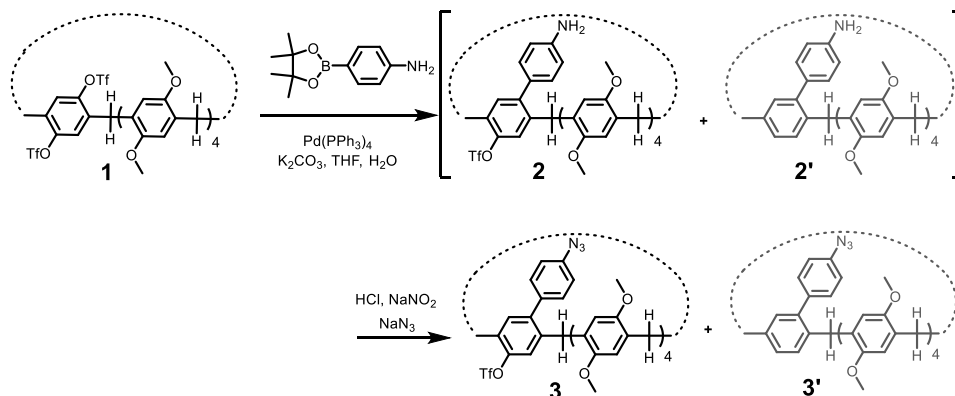
All solvents were obtained from commercial resources or dried according to the standard procedure. Other materials were purchased from Aladdin, Adamas, Energy Chemical and J&K were used for synthesis without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were collected on a Bruker DRX-400 spectrometer and chemical shifts were expressed in ppm using TMS as an internal standard. High resolution mass spectrometry (HRMS) was performed with a Bruker maXis impact instrument. Fluorescence spectra were recorded on Hitachi F-7000 fluorescence spectrophotometer. The UV-Vis absorption spectra were recorded using a Shimadzu UV-2600 UV-Vis scanning spectrophotometer. Dynamic light scattering experiments were performed with a Malvern Zetasizer Nano ZS system. Scanning electron microscope (SEM) was carried out on a Zeiss LEO1530VP field-emission scanning electron microscope system. Viscosity measurements were carried out with an Ubbelohde viscometer at 293K (capillary bore 0.4 mm).

1,4-Dimethoxypillar[5]arene, compound **1**,<sup>[1]</sup> compound **4**,<sup>[2]</sup> compound **5**,<sup>[2b, 2d]</sup> compound **6**,<sup>[1e, 3]</sup> and **GY**<sup>[1e, 4]</sup> were prepared according to the reported procedures.



Scheme S1. Molecules in this work: the orthogonal host **H**, the control host **Hc**, the guests **GG** and **GY**.

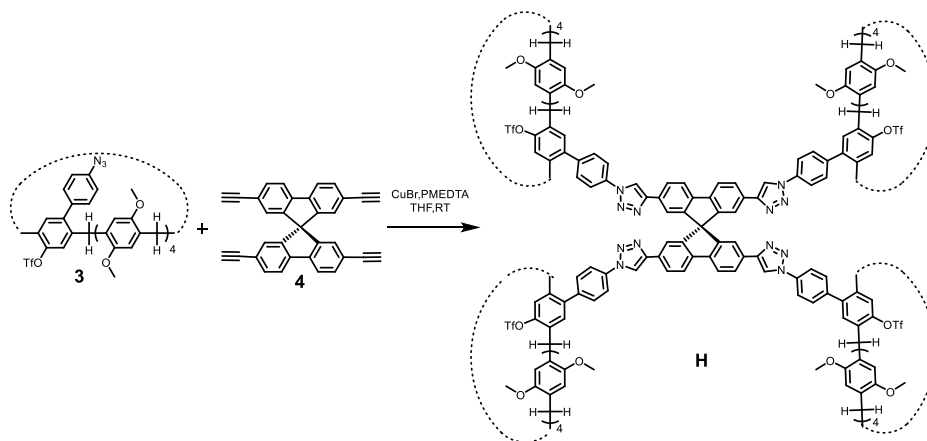
## 1.2 Synthesis of compound 3



Synthesis of compound **2**. Ditrifluoromethylsulfonyl pillar[5]arene **1** was prepared according to the reported procedures.<sup>[1e]</sup> **2** was synthesized by the Suzuki reaction. Compound **1** (868.9 mg, 1 mmol), 4-aminophenylboronic acid pinacol ester (241.0 mg, 1.1 mmol), potassium carbonate (1382.1 mg, 10 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (57.8 mg, 0.05 mmol, purchased from J&K in bright yellow color) were dispersed in a mixed solution of 20 mL THF and 5 mL H<sub>2</sub>O. The mixture was degassed with nitrogen and stirred under 85 °C for 8 hours. The mixture was concentrated under reduced pressure, then purified by column chromatography (petroleum ether/dichloromethane/ethyl acetate 20:1:1 as eluent) to get a mixture of **2** and a by-product **2'** as a brown powder. Note: because this reaction yields a by-product **2'** with the same polarity and solubility as compound **2**, the purification just yielded a mixture of them which was used for the next reaction without further purification. So no spectra are provided in this paper for the structural characterization of compound **2**.

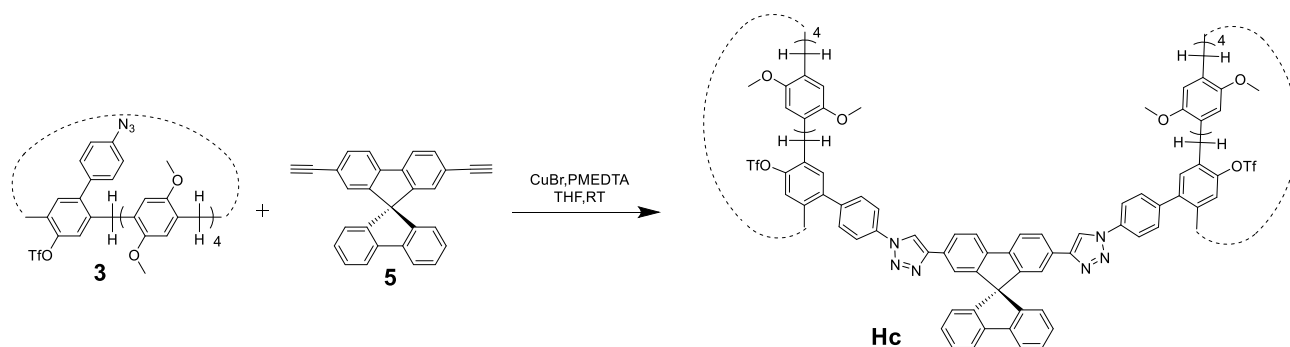
Synthesis of compound **3**. The above mixture (929.3 mg) and concentrated hydrochloric acid (0.25 mL, 3 mmol) were dispersed in 20 mL THF in an ice-salt bath for 0.5 hours. Sodium nitrite solution (NaNO<sub>2</sub>, 103.5 mg, 1.5 mmol; H<sub>2</sub>O, 1.5 mL) was slowly added into the mixture within 20 min in an ice-salt bath, then the mixture was stirred for 30 min. Then sodium azide solution (NaN<sub>3</sub>, 97.5 mg, 1.5 mmol; H<sub>2</sub>O, 1.5 mL) was slowly added into the mixture within 20 min in an ice-salt bath, and then reacted for 6 hours under room temperature. The mixture was concentrated under reduced pressure, then extracted with brine and CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was concentrated by the rotary evaporation and then purified by column chromatography (petroleum ether/dichloromethane/ethyl acetate 10:2:1 as eluent) to get the product **3** as brown powder (878.9 mg) in about 64% yield for the two steps. Note: a by-product **3'** was obtained and its structural characterization spectra are available in our previous publication (*Angew. Chem. Int. Ed.*, 2020, **59**, 9908-9913).<sup>[1e]</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K), δ (ppm): 7.20 (s, 1H), 7.00 (s, 1H), 6.97-6.92 (m, 4H), 6.77-6.76 (m, 2H), 6.74-6.73 (m, 3H), 6.64 (s, 2H), 5.84 (s, 1H), 3.86 (s, 2H), 3.82 (s, 4H), 3.77 (s, 2H), 3.72 (s, 2H), 3.69 (m, 6H), 3.66 (s, 3H), 3.62 (s, 6H), 3.52 (s, 3H), 3.46 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 151.1, 151.1, 151.1, 150.9, 150.9, 150.9, 150.6, 150.4, 147.5, 140.2, 139.7, 139.0, 137.7, 133.7, 130.9, 130.7, 129.7, 129.0, 128.7, 128.5, 128.4, 128.0, 126.8, 125.2, 122.7, 118.8 (*J*<sub>CF</sub> = 318.3 Hz), 118.8, 114.6, 114.2, 114.2, 114.1, 114.0, 113.9, 113.7, 113.3, 56.1, 56.0, 55.9, 55.8, 55.8, 55.5, 55.4, 55.3, 33.1, 31.3, 30.2, 29.5, 27.0. HRMS (ESI, m/z): calcd for [M+Na]<sup>+</sup> C<sub>50</sub>H<sub>48</sub>F<sub>3</sub>N<sub>3</sub>NaO<sub>11</sub>S: 978.2859, found: 978.2854.

### 1.3 Synthesis of **H**



Synthesis of compound **H**. **H** was synthesized by a Click reaction. Compound **3** (477.7 mg, 0.5 mmol), compound **4** (41.2 mg, 0.1 mmol), CuBr (2.9 mg, 0.02 mmol) and 1, 1, 4, 7, 7-pentamethyldiethylenetriamine (PMDETA, 6.9 mg, 0.04 mmol) were dispersed in 30 ml dry THF. The mixture was degassed and stirred under room temperature for 12 hours. After the reaction was completed, the mixture was concentrated by the rotary evaporation and the crude product was purified by column chromatography (petroleum ether/dichloromethane/ethyl acetate 5:2:1 as eluent) and got the product **H** as white powder (372.5 mg, 0.088 mmol) in 88% yield.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 298 K),  $\delta$  (ppm): 8.16 (s, 4H), 8.14-8.08 (m, 8H), 7.63 (s, 4H), 7.25 (s, 4H), 7.14-7.12 (m, 8H), 6.79 (s, 4H), 6.67 (s, 4H), 6.64-6.64 (m, 8H), 6.59-6.58 (m, 16H), 6.48 (s, 4H), 6.44 (s, 4H), 5.64 (s, 4H), 3.86 (br.s, 24H), 3.75 (br.s, 8H), 3.67 (s, 12H), 3.66 (s, 12H), 3.61 (s, 8H), 3.45 (s, 12H), 3.44 (s, 12H), 3.42 (s, 12H), 3.32 (s, 12H), 3.30 (s, 12H), 3.24 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , 298 K),  $\delta$  (ppm): 151.2, 151.2, 151.2, 150.9, 150.8, 150.5, 150.5, 150.3, 149.6, 148.2, 147.1, 142.0, 141.4, 140.1, 139.8, 135.4, 132.5, 131.4, 130.3, 130.3, 129.7, 129.7, 129.2, 128.4, 128.1, 128.1, 127.8, 126.7, 126.1, 125.2, 123.2, 121.8, 121.1, 119.5, 119.5, 118.7 ( $J_{\text{CF}} = 318.2$  Hz), 117.7, 115.1, 115.0, 114.6, 114.5, 113.9, 113.8, 113.0, 113.0, 66.2, 56.4, 56.1, 55.9, 55.6, 55.5, 55.4, 55.3, 55.0, 34.8, 30.9, 30.5, 29.1, 28.7. HRMS (MALDI,  $m/z$ ): calcd for  $[\text{M}+\text{Na}]^+ \text{C}_{233}\text{H}_{208}\text{F}_{12}\text{N}_{12}\text{NaO}_{44}\text{S}_4$ : 4258.3063, found: 4258.8530.

#### 1.4 Synthesis of **Hc**



Synthesis of compound **Hc**. **Hc** was synthesized by a Click reaction. Compound **3** (238.9 mg, 0.25 mmol), compound **5** (36.4 mg, 0.1 mmol), CuBr (1.5 mg, 0.01 mmol) and 1, 1, 4, 7, 7-pentamethyldiethylenetriamine (PMDETA, 3.5 mg, 0.02 mmol) were added in 20 ml dry THF. The mixture was degassed and stirred under room temperature for 12 hours. After the



## 2. Supplementary Figures

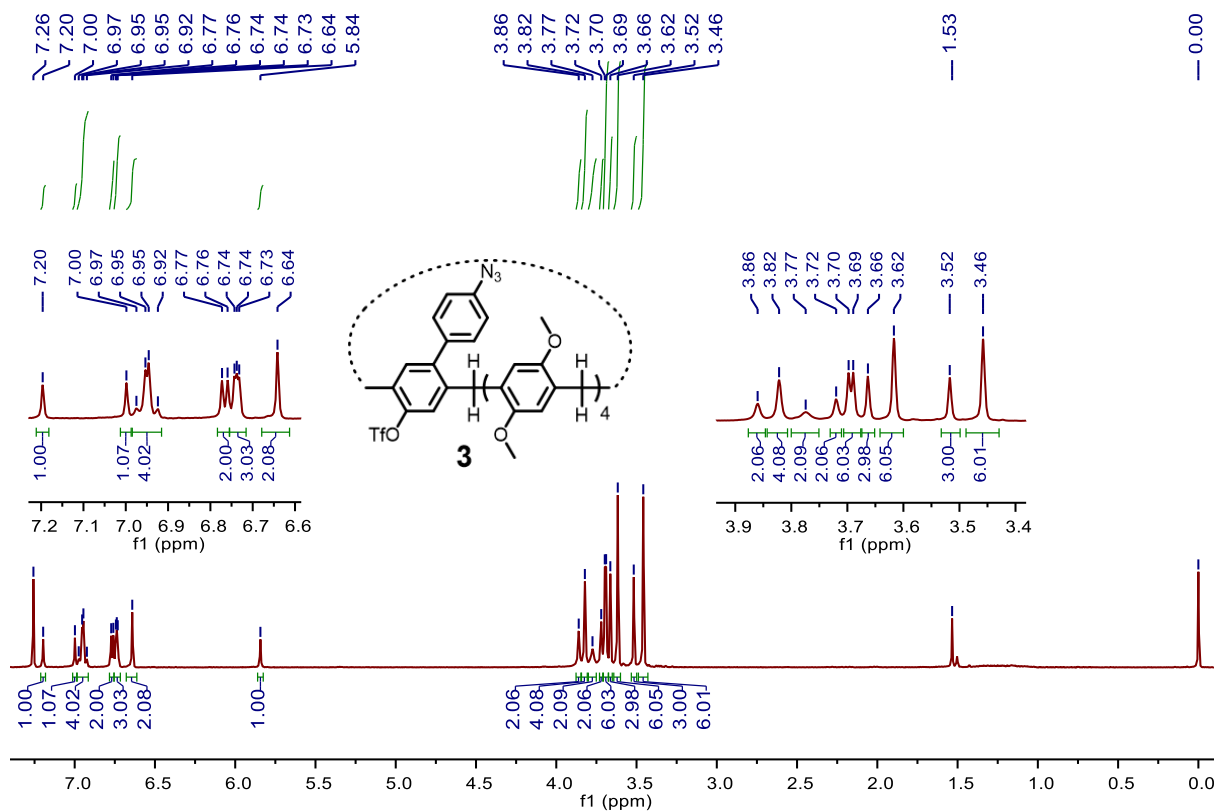


Fig. S1. <sup>1</sup>H NMR spectrum of compound **3** (400 MHz, CDCl<sub>3</sub>, 298 K).

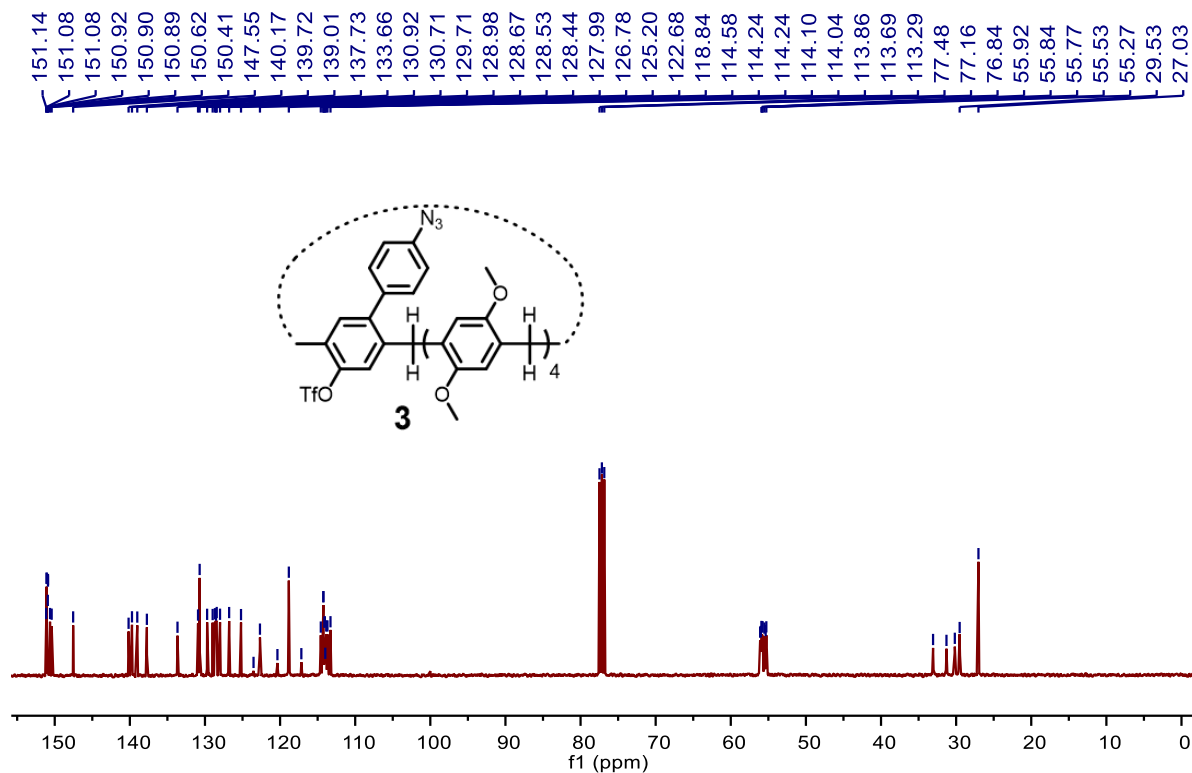


Fig. S2. <sup>13</sup>C NMR spectrum of compound **3** (100 MHz, CDCl<sub>3</sub>, 298 K).

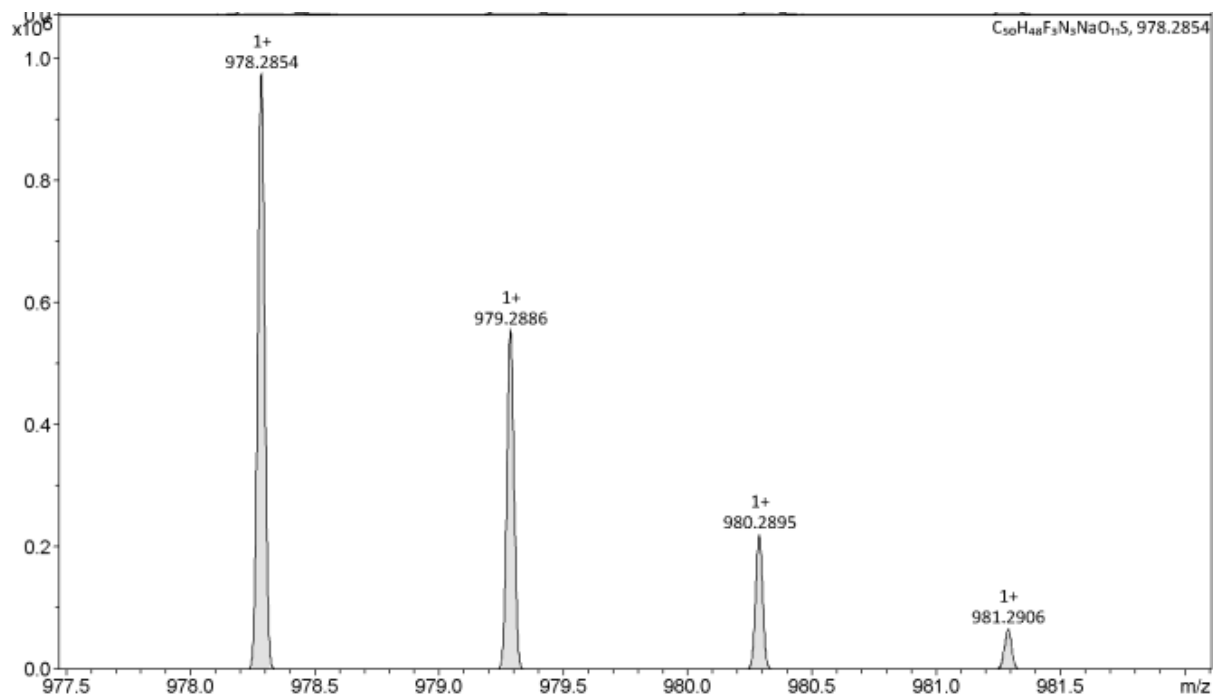


Fig. S3. HRMS (ESI) spectrum of compound **3**.

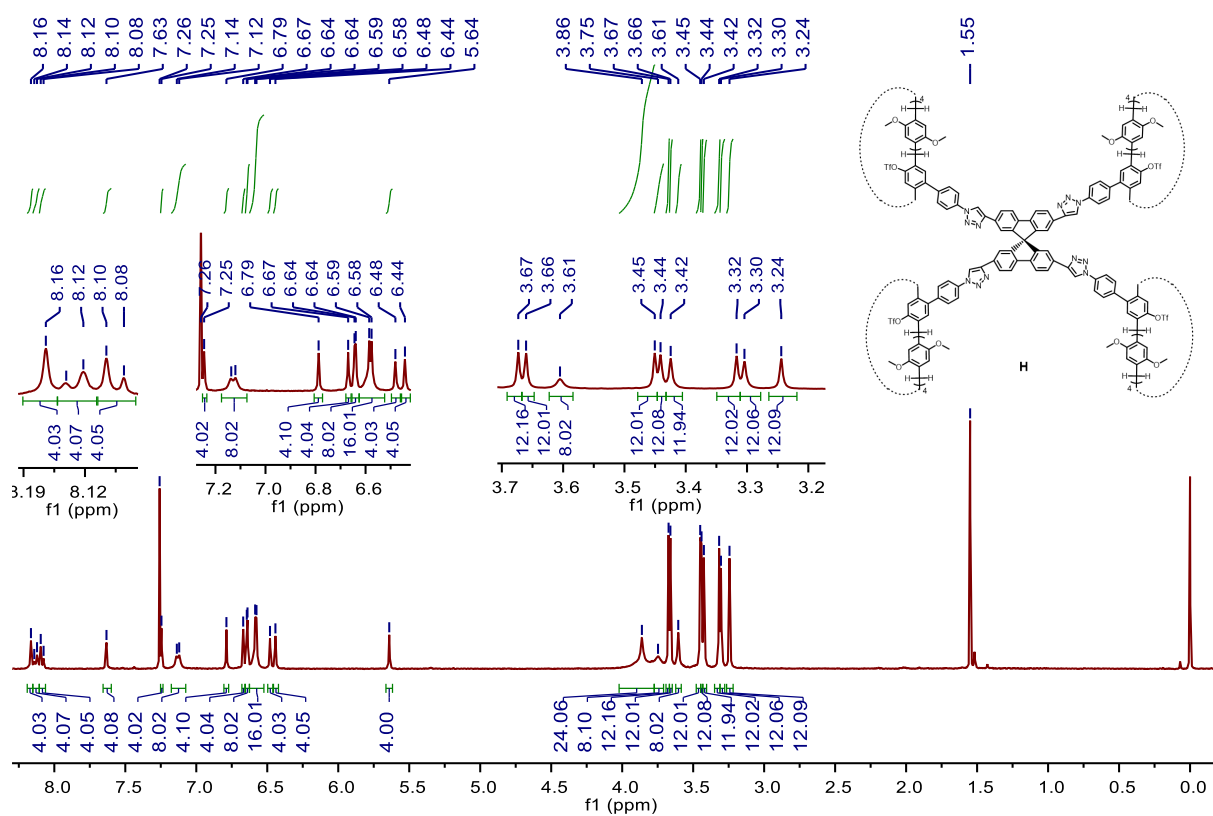


Fig. S4.  $^1H$  NMR spectrum of compound **H** (400 MHz,  $CDCl_3$ , 298 K).

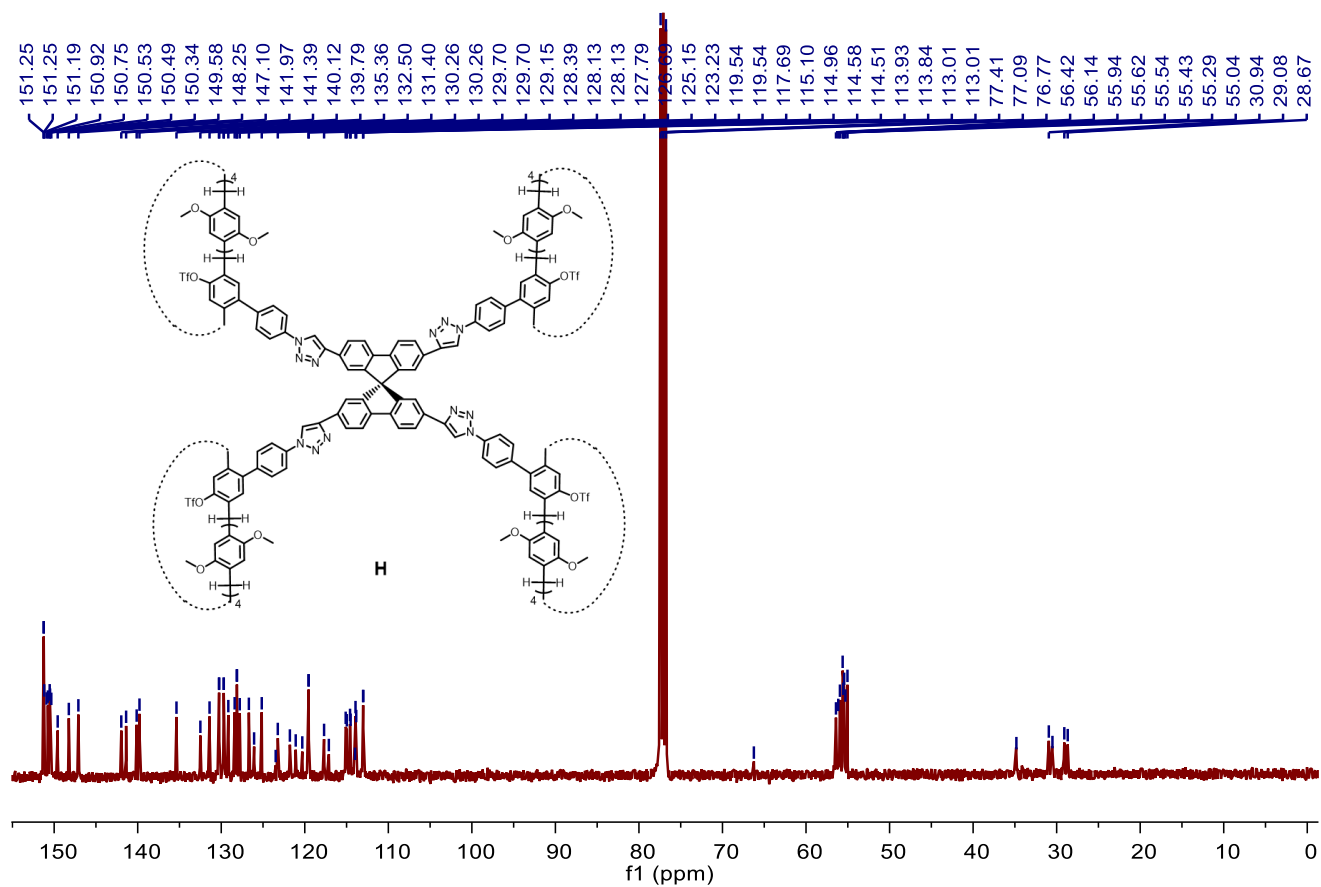


Fig. S5.  $^{13}\text{C}$  NMR spectrum of compound **H** (100 MHz,  $\text{CDCl}_3$ , 298 K).

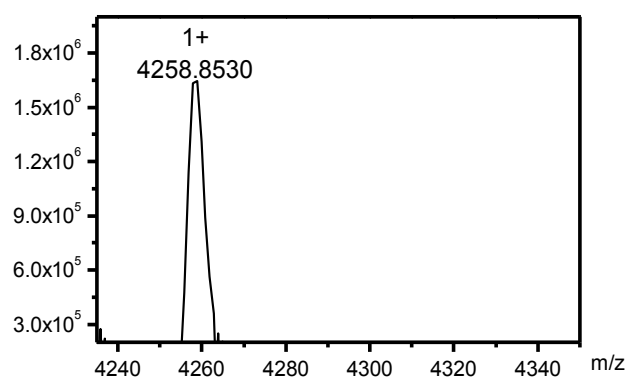


Fig. S6. TOF spectrum of compound **H**.



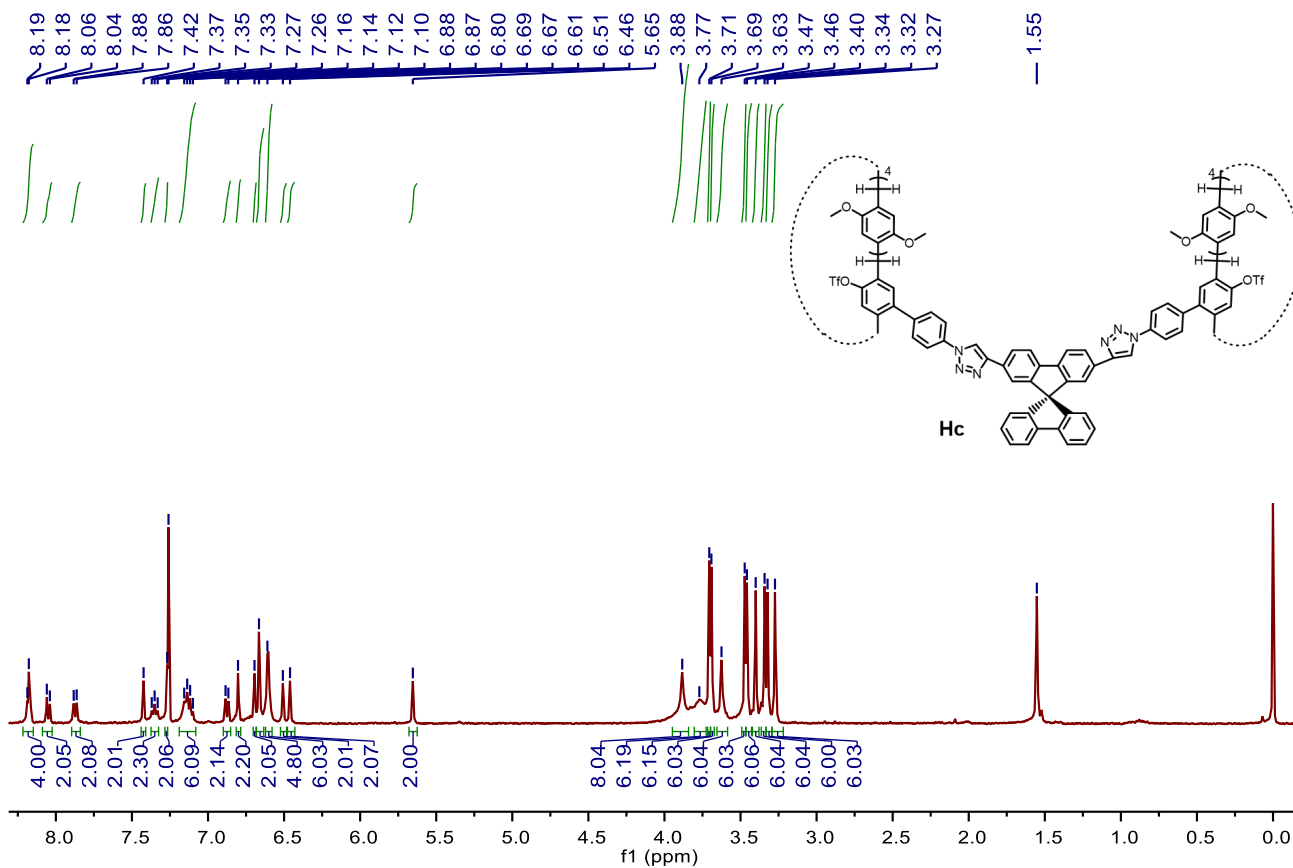


Fig. S7. <sup>1</sup>H NMR spectrum of compound **Hc** (400 MHz, CDCl<sub>3</sub>, 298 K).

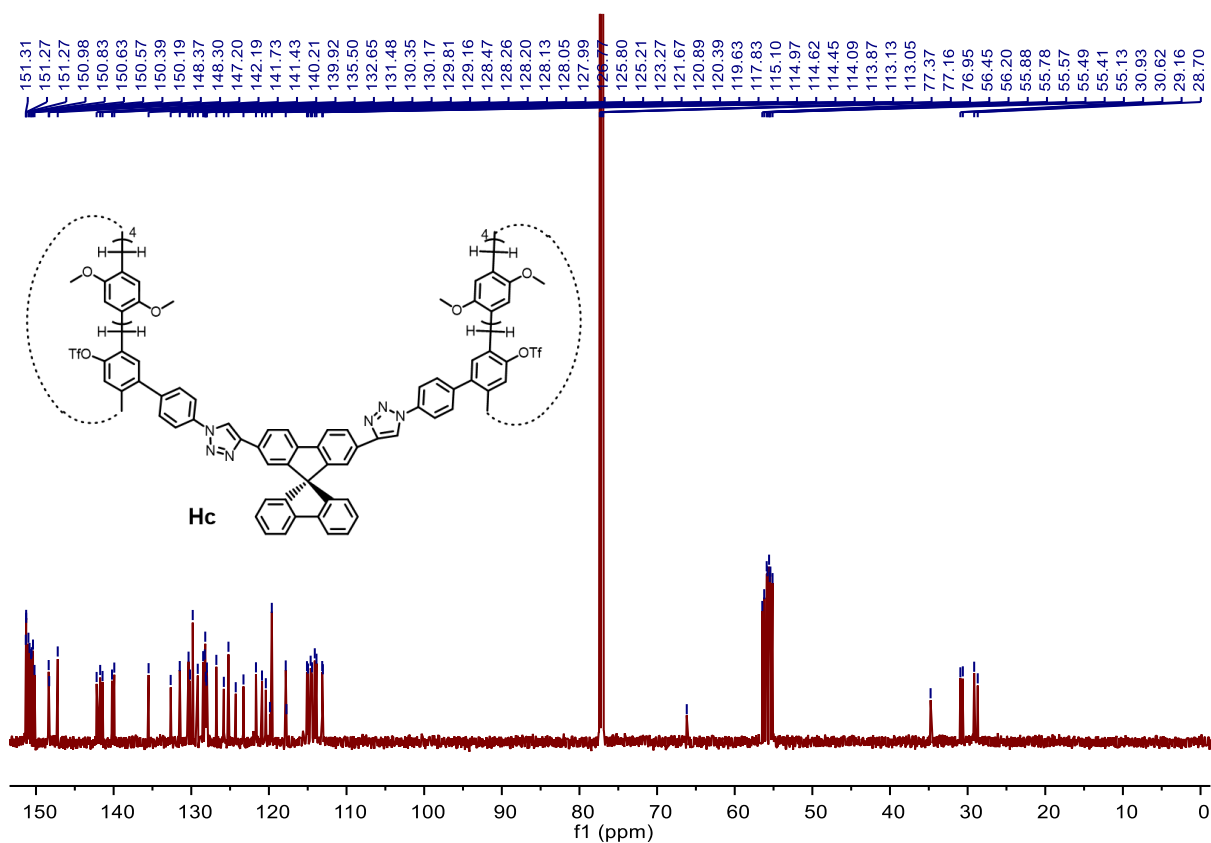


Fig. S8. <sup>13</sup>C NMR spectrum of compound **Hc** (100 MHz, CDCl<sub>3</sub>, 298 K).

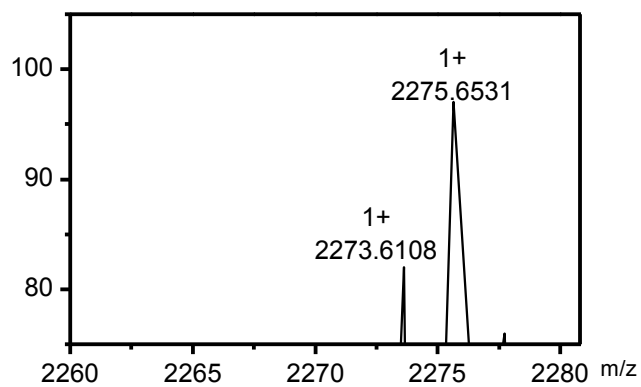


Fig. S9. TOF spectrum of compound **Hc**.

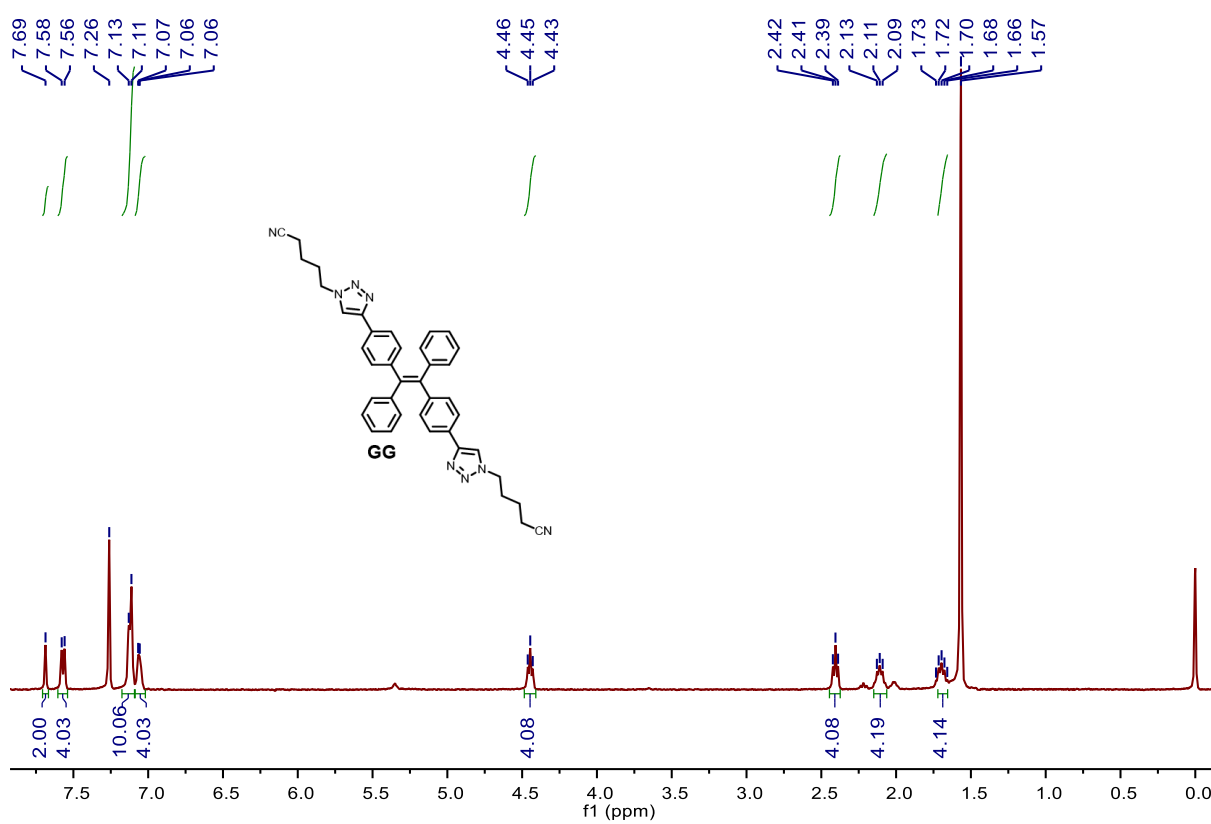


Fig. S10. <sup>1</sup>H NMR spectrum of compound **GG** (400 MHz, CDCl<sub>3</sub>, 298 K).

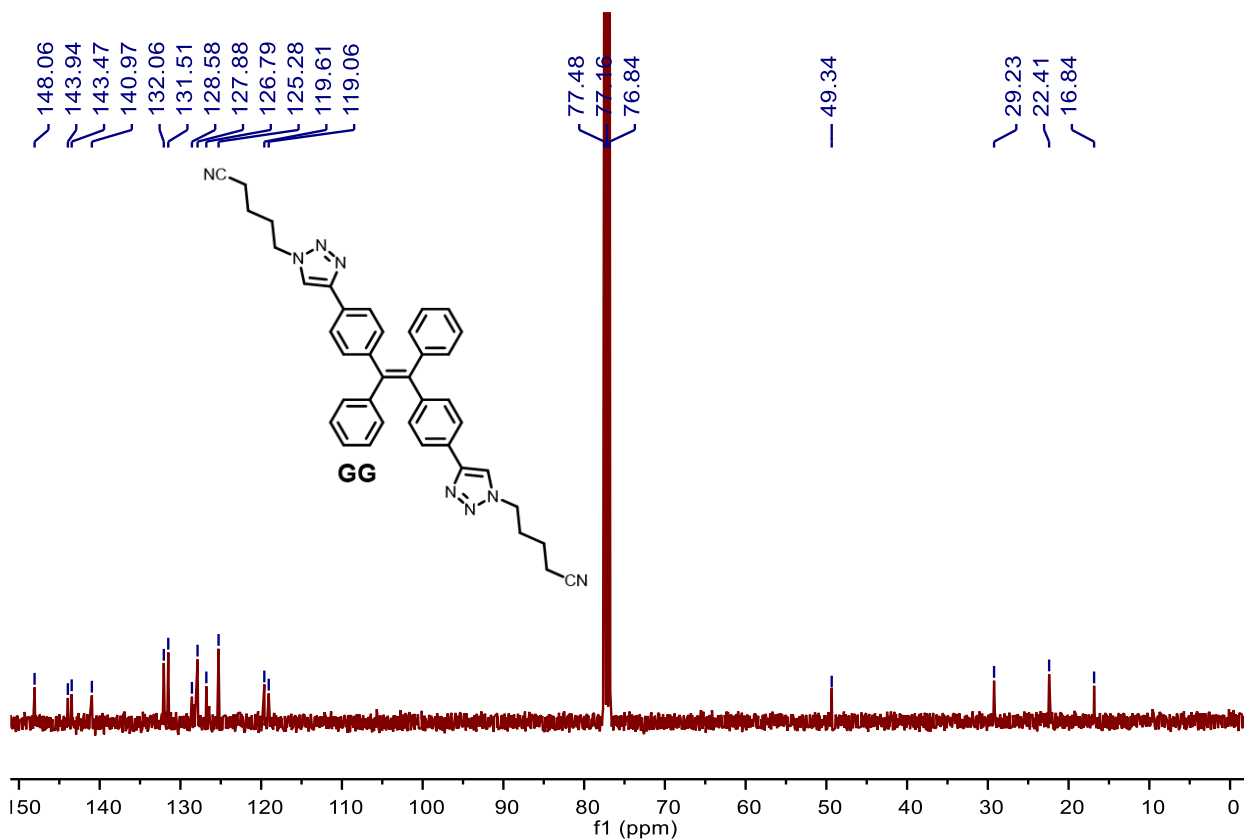


Fig. S11. <sup>13</sup>C NMR spectrum of compound **GG** (100 MHz, CDCl<sub>3</sub>, 298 K).

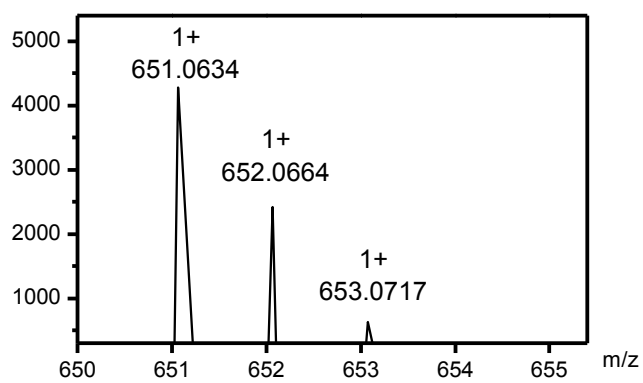


Fig. S12. TOF spectrum of compound **GG**.

The absorption spectra of **H** barely changed with the addition of a “poor” solvent of water until the ratio of H<sub>2</sub>O/THF reached 1:1 by volume. Further addition of H<sub>2</sub>O led to a broad increase of absorption in the whole spectra, which is a typical sign for the formation of aggregates (Fig. S13b). The intensity of the fluorescence peak of **H** decreased with the addition of H<sub>2</sub>O (Fig. S13a), which is probably related to the solvent-polarity-induced fluorescence quenching<sup>[5]</sup> and the aggregation-caused quenching.

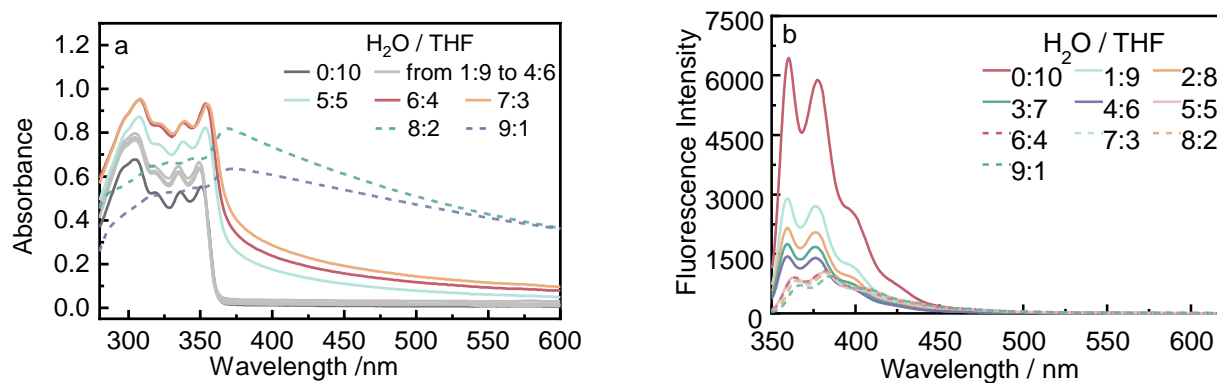


Fig. S13. Fluorescence (a) and absorption spectra (b) of **H** in H<sub>2</sub>O/THF mixtures with different solvent ratios.

$$[\mathbf{H}] = 5.0 \mu\text{M}, \lambda_{\text{ex}} = 335 \text{ nm}.$$

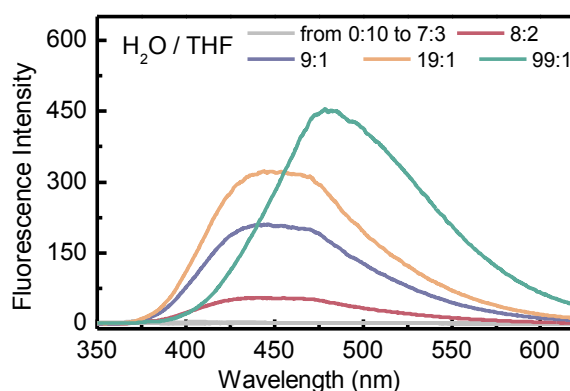


Fig. S14. Fluorescence spectra of **GG** in H<sub>2</sub>O/THF mixtures with different solvent ratios.

$$[\mathbf{GG}] = 5.0 \mu\text{M}, \lambda_{\text{ex}} = 335 \text{ nm}.$$

The media were adjusted to optimize the fluorescent property of the **AOSNs**. With the addition of H<sub>2</sub>O, the emission of **H-GG-crosslinked AOSN** at ca. 485 nm increased remarkably while the emission of **H** at ca. 383 nm gradually decreases owing to the solvation effect of **H** (Fig. S19). In order to keep the fine photophysical properties of the **AOSNs** and avoid precipitation in poor solvents, an 8:2 H<sub>2</sub>O/THF co-solvent was chosen for the further investigation of the **AOSNs**.

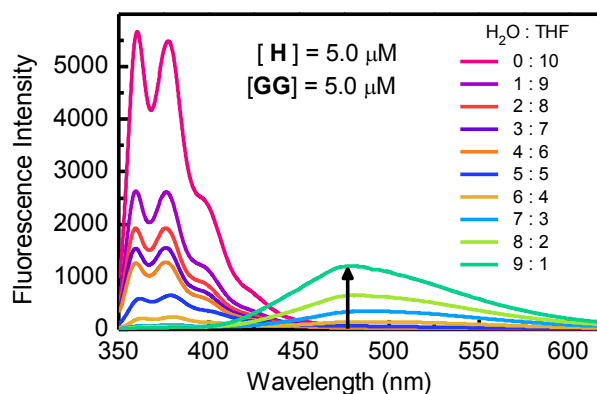


Fig. S15. Fluorescence spectra of **H-GG-crosslinked AOSNs** in H<sub>2</sub>O/THF mixtures with different solvent ratios. [**H**] = 5.0 μM, [**GG**] = 5.0 μM,  $\lambda_{\text{ex}} = 335$  nm.

Job plot was used to determine the binding stoichiometry between the tetratopic host **H** and the ditopic guests. A series of **H-GG-crosslinked AOSNs** were prepared with the total concentration of **H** and **GG** keeping at 10.0 μM in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). Excited by 335 nm, the fluorescence intensity values of the **H-GG-crosslinked AOSNs** with different **H/GG** ratios were recorded at 485 nm. The job plot can be obtained with the fluorescence intensity values against the concentration ratios [**GG**]/([**GG**]+[**H**]) (Fig. S16). It can be seen from Fig. S16, that the fluorescence intensity value at 485 nm reaches the maximum at [**GG**]/([**GG**]+[**H**]) ratio of 0.67, implying that the binding stoichiometry of **H** to **GG** is 1:2.

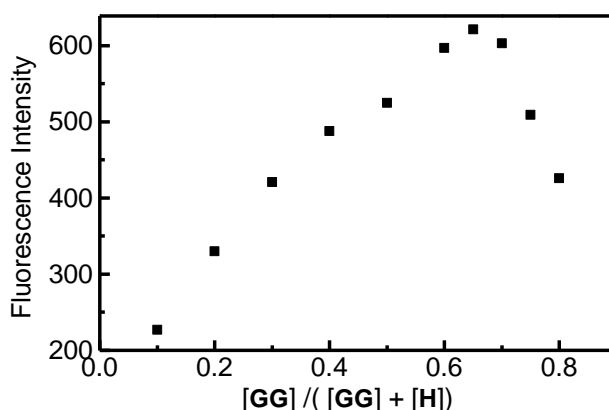


Fig. S16. Job plot of guest **GG** binding to host **H** in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). [**H**] + [**GG**] = 10.0 μM.

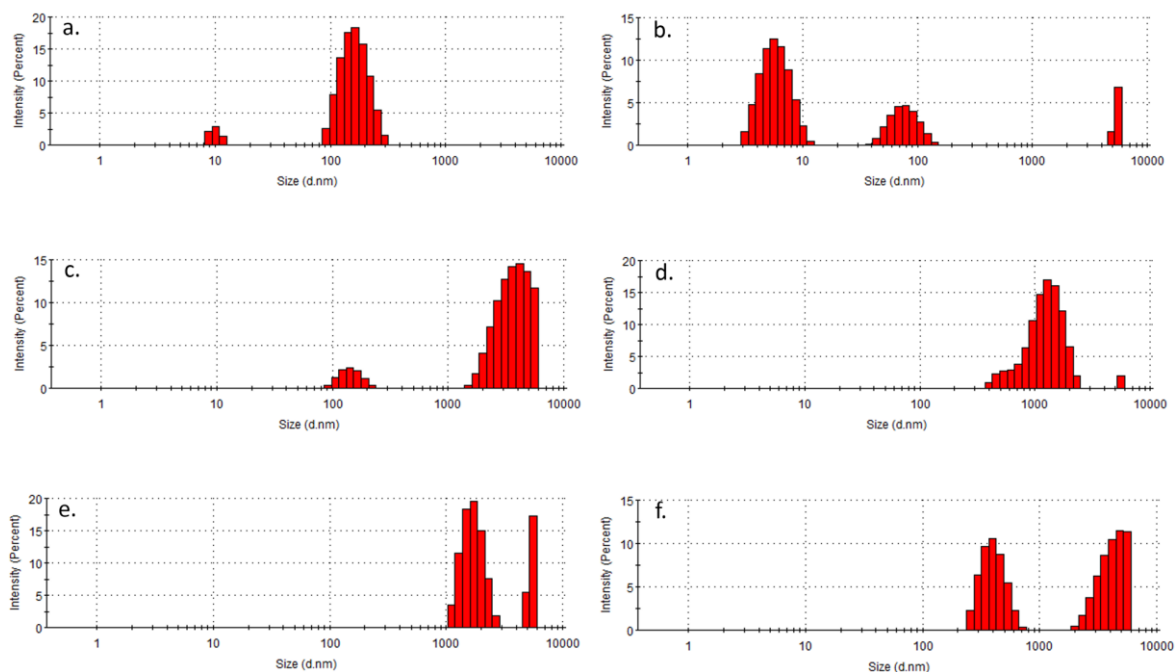


Fig. S17. DLS results of (a) **H** unary system,  $[\mathbf{H}] = 5.0 \mu\text{M}$ ; (b) **GG** unary system,  $[\mathbf{GG}] = 5.0 \mu\text{M}$ ; (c) **GY** unary system,  $[\mathbf{GY}] = 5.0 \mu\text{M}$ ; (d) binary **H-GG**-crosslinked AOSN system,  $[\mathbf{H}] = 5.0 \mu\text{M}$ ,  $[\mathbf{GG}] = 10.0 \mu\text{M}$ ; (e) binary **H-GY**-crosslinked supramolecular network system,  $[\mathbf{H}] = 5.0 \mu\text{M}$ ,  $[\mathbf{GY}] = 10.0 \mu\text{M}$ . (f) ternary **H-GG-GY**-crosslinked AOSN system,  $[\mathbf{H}] = 2.5 \mu\text{M}$ ,  $[\mathbf{GG}] = 7.5 \mu\text{M}$ ,  $[\mathbf{GY}] = 0.05 \mu\text{M}$ . The co-solvent is  $\text{H}_2\text{O}/\text{THF}$  (8:2 by volume).

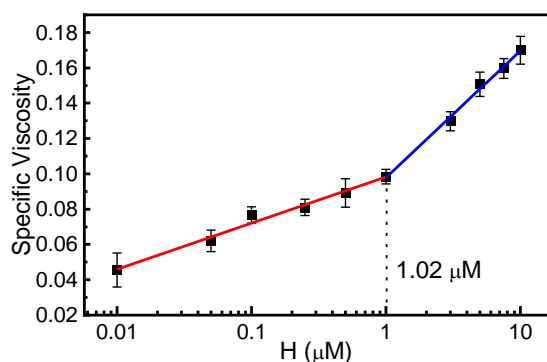


Fig. S18. Specific viscosities of the **H-GG** system (**H:GG** was kept at 1:2 molar ratio) in the  $\text{H}_2\text{O}/\text{THF}$  (8:2 by volume) co-solvent versus the concentration of **H** monomer (293 K). The critical polymerization concentration (CPC) value is  $1 \mu\text{M}$ .

Each viscosity data is the average of the three tests.

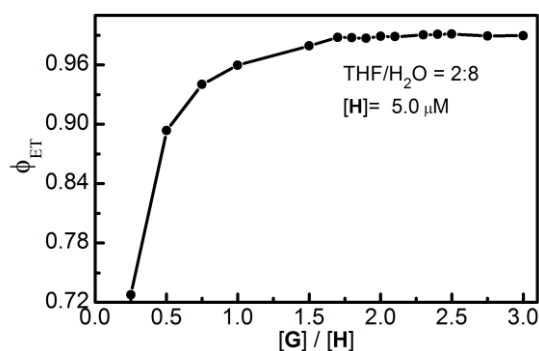


Fig. S19. The energy-transfer efficiency of the **H-GG**-crosslinked AOSNs with a different ratio of **GG**.  $[\mathbf{H}] = 5.0 \mu\text{M}$ ,  $\lambda_{\text{ex}} = 335 \text{ nm}$ , the co-solvent is  $\text{H}_2\text{O}/\text{THF}$  (8:2 by volume).

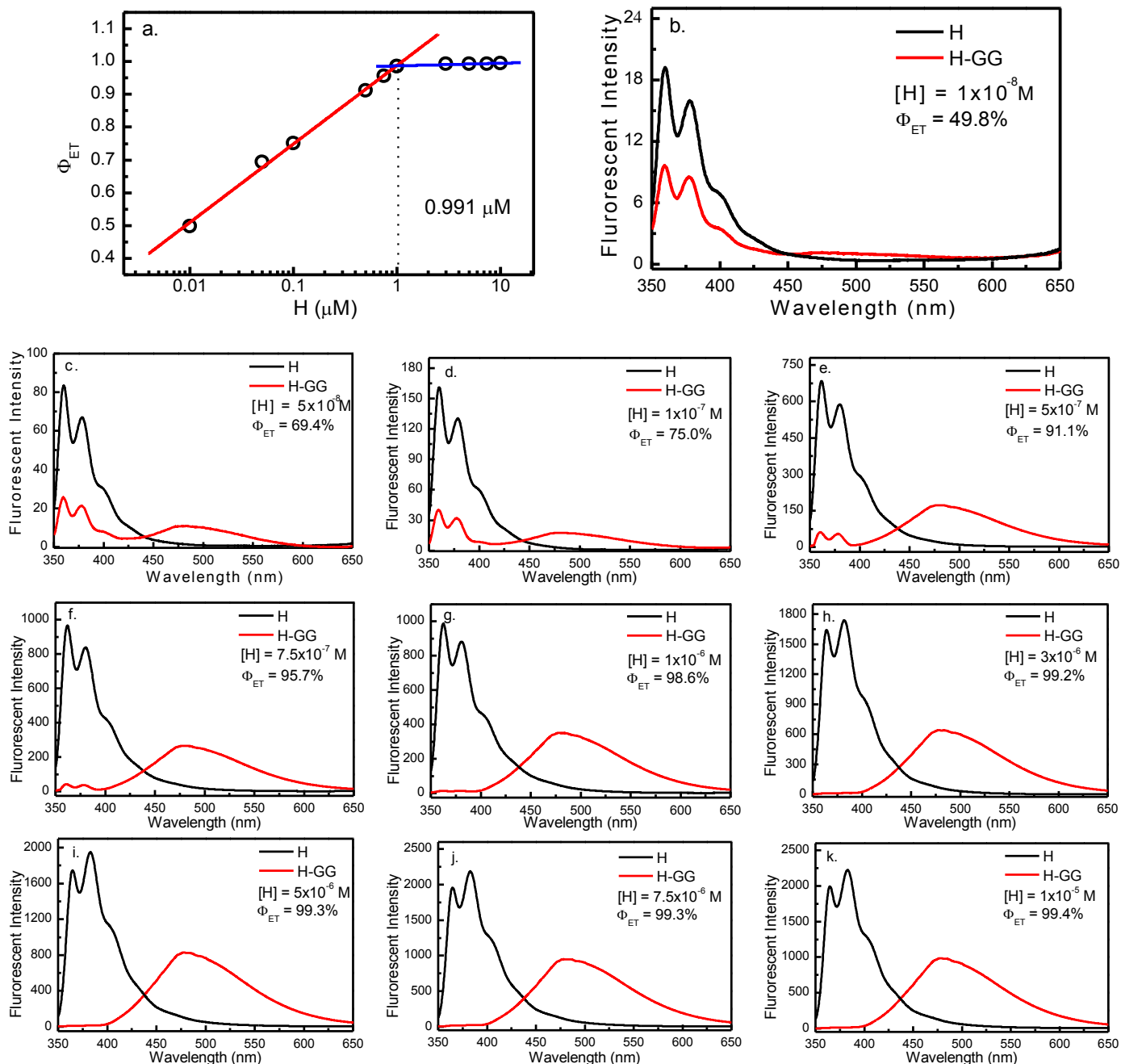


Fig. S20. Relationship between energy-transfer efficiency ( $\Phi_{ET}$ ) and concentration. a. The energy-transfer efficiency of the **H-GG** system with a different concentration (**H:GG** was kept at 1:2 molar ratio) in the  $\text{H}_2\text{O}/\text{THF}$  (8:2 by volume) co-solvent. b-k. Fluorescence spectra of **H** (black curve) and **H-GG** system (red curve) with a different concentration (**H:GG** was kept at 1:2 molar ratio) in the  $\text{H}_2\text{O}/\text{THF}$  (8:2 by volume) co-solvent.

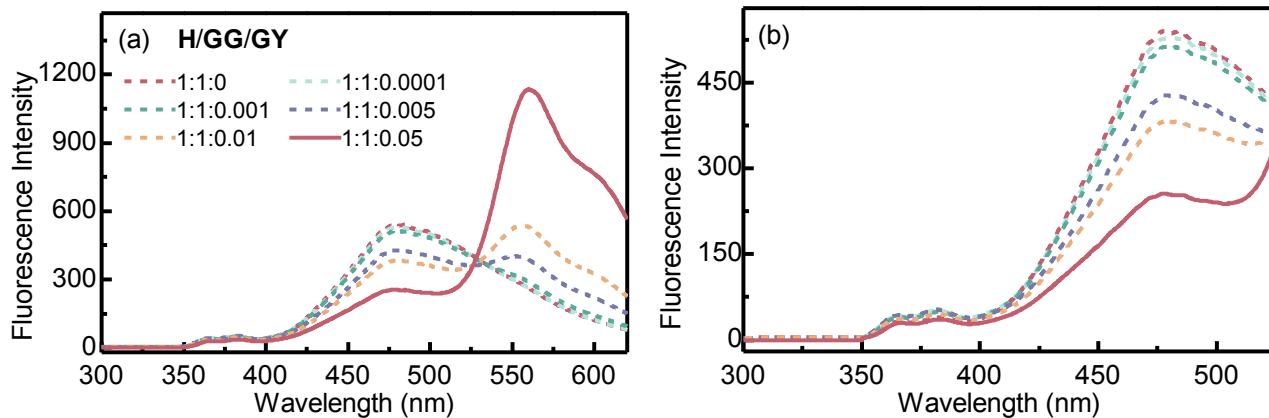
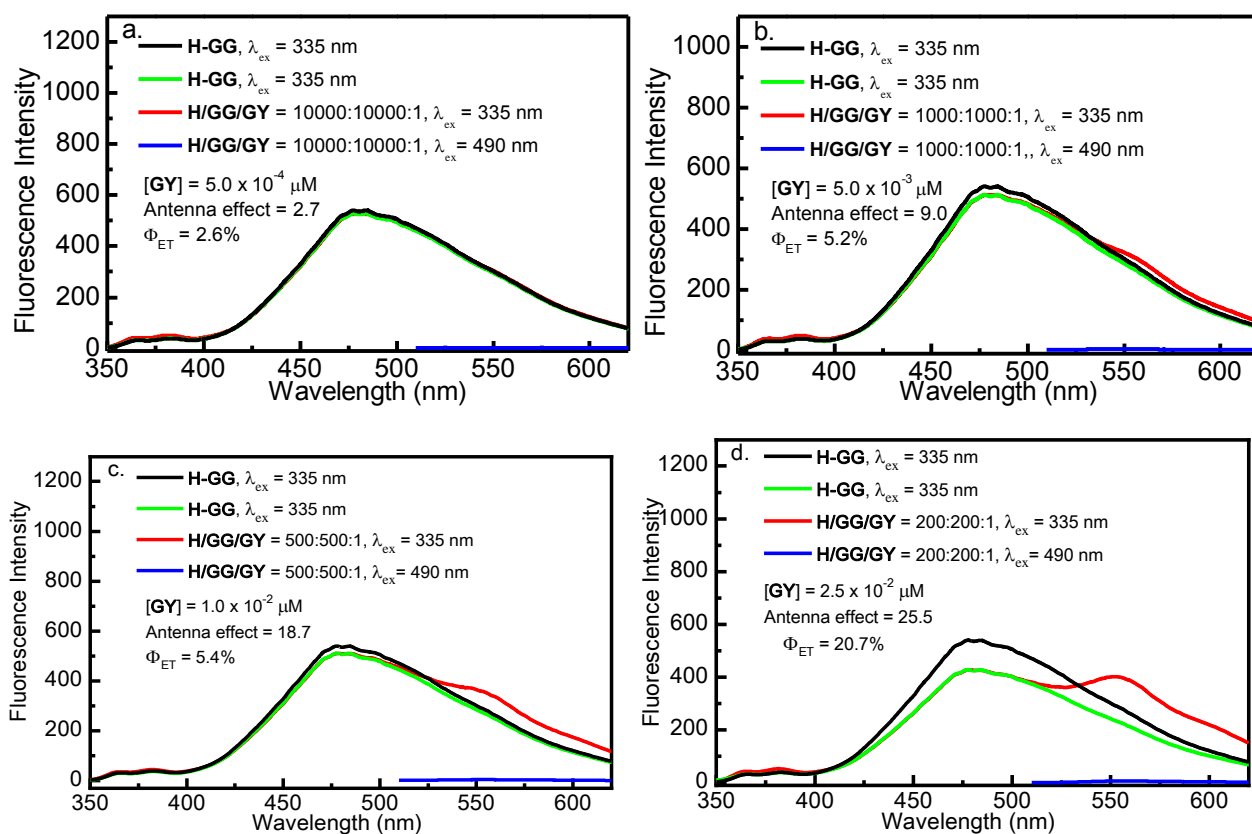


Fig. S21. Fluorescence spectra of the ternary **H-GG-GY**-crosslinked AOSNs with different concentrations of **GY** in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). **[H]** = 5.0 μM. **[GG]** = 5.0 μM.  $\lambda_{\text{ex}}$  = 335 nm. The panel (b) shows the zoom-in view of the fluorescence band of **GG**.





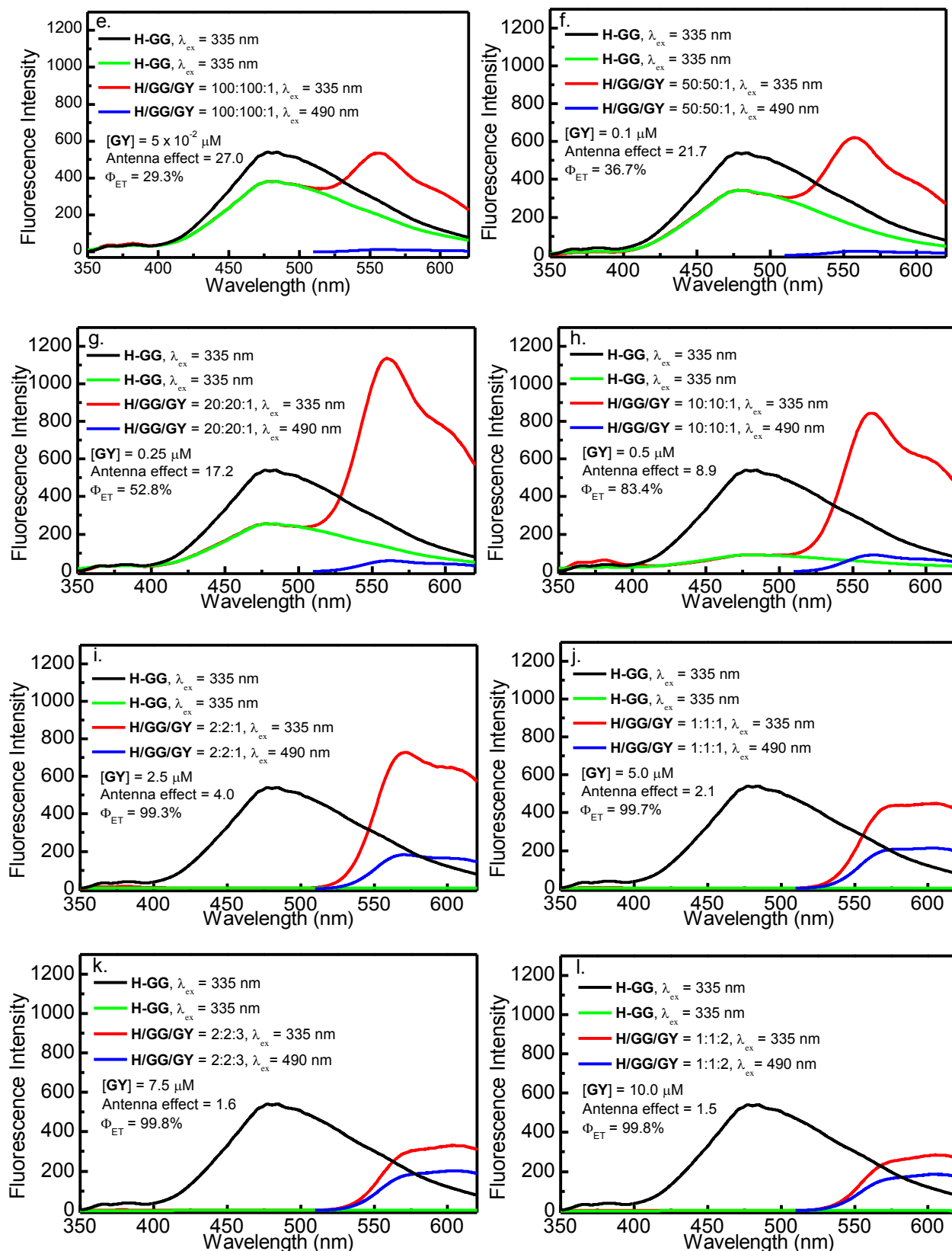


Fig.S22. Fluorescence spectra of ternary **H-GG-GY**-crosslinked **AOSNs** with different donor/acceptor ratios in the co-solvent of  $\text{H}_2\text{O}/\text{THF}$  (8:2 by volume).  $[\text{H}] = 5.0 \mu\text{M}$ ,  $[\text{GG}] = 5.0 \mu\text{M}$ ,  $[\text{GY}] = 5.0 \times 10^{-4} \mu\text{M} \sim 10.0 \mu\text{M}$ .  $\lambda_{\text{ex}} = 335 \text{ nm}$  for **H-GG**-crosslinked **AOSNs** (black),  $\lambda_{\text{ex}} = 335 \text{ nm}$  (red) and  $\lambda_{\text{ex}} = 490 \text{ nm}$  (blue) for **H-GG-GY**-crosslinked **AOSNs**. The fluorescence spectra for **H-GG**-crosslinked **AOSN** in the absence of **GY** were normalized so that the emission intensities at 480 nm were the same as in the presence of **GY** (green).

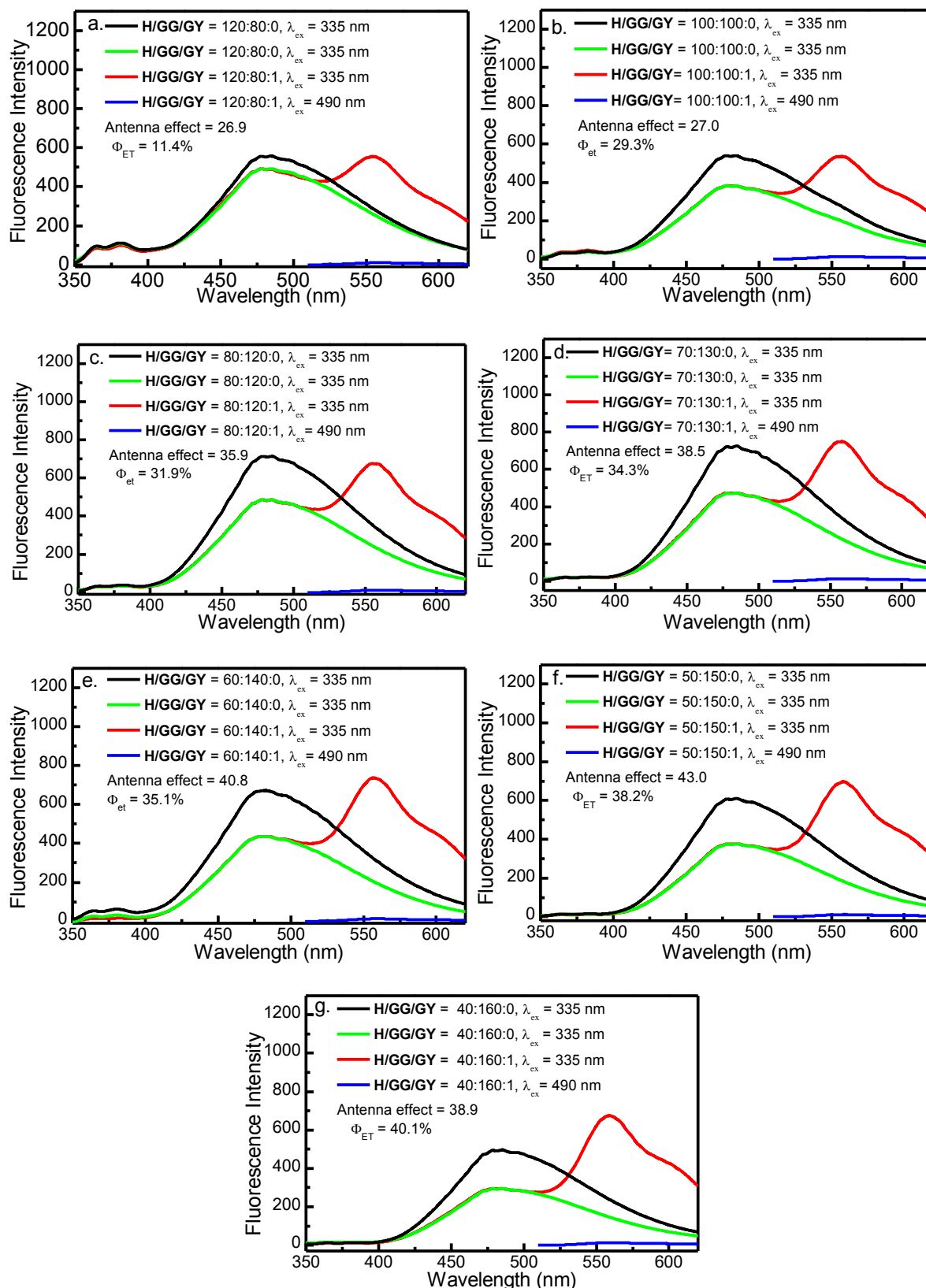


Fig. S23. Fluorescence spectra of ternary H-GG-GY-crosslinked AOSNs with different ratios of H/GG while the ratio of (H+GG)/GY was kept at 200:1 in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). [H] + [GG] = 10.0  $\mu$ M, [GY] =  $5.0 \times 10^{-2}$   $\mu$ M.  $\lambda_{ex}$  = 335 nm for H-GG-crosslinked AOSNs (black),  $\lambda_{ex}$  = 335 nm (red) and  $\lambda_{ex}$  = 490 nm (blue) for H-GG-GY-crosslinked AOSNs. The fluorescence spectra for H-GG-crosslinked AOSNs in the absence of GY were normalized such that the emission intensities at ca. 480 nm were the same as in the presence of GY (green).

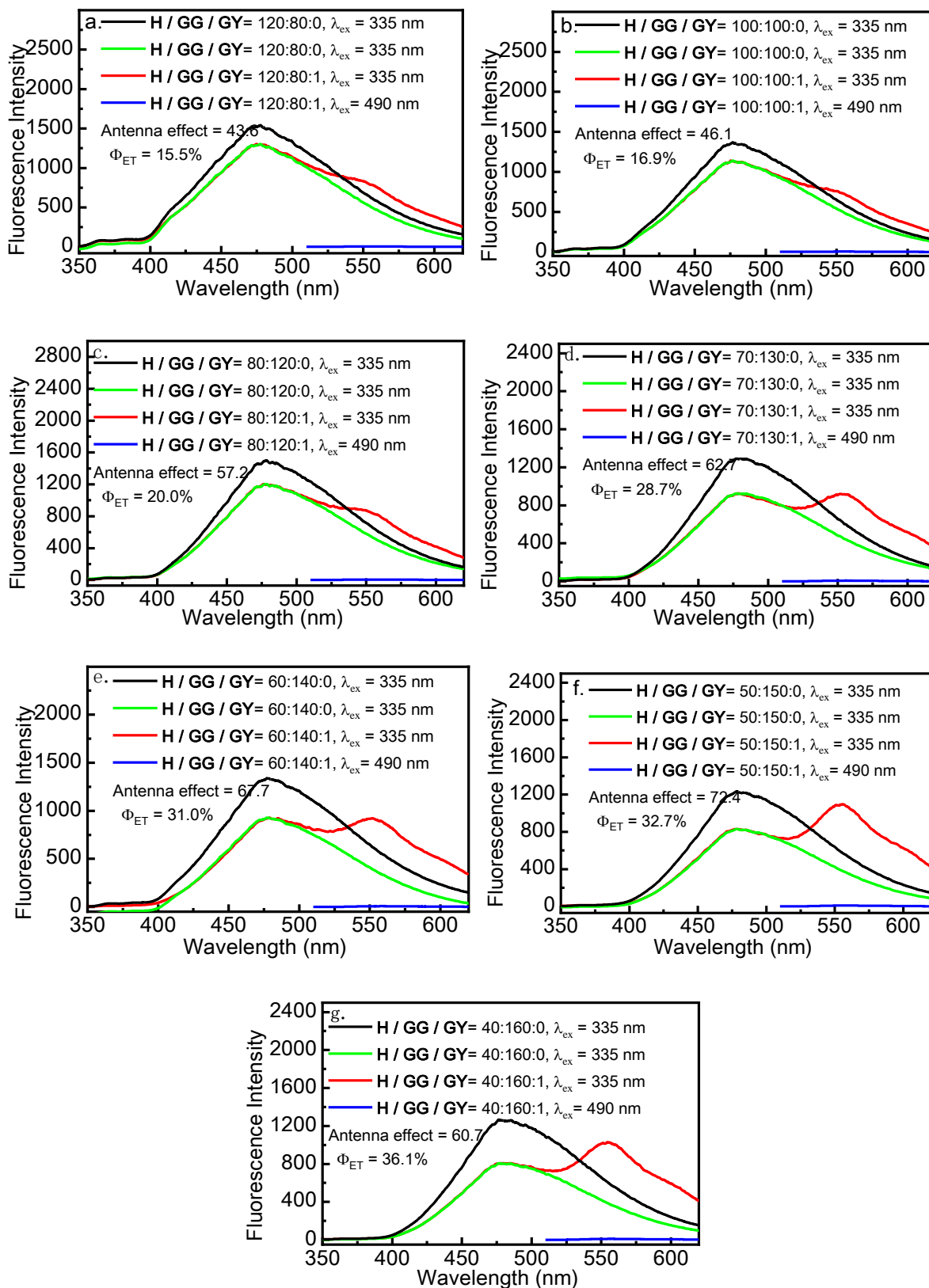


Fig. S24. Fluorescence spectra of **H-GG-GY**-crosslinked **AOSNs** with different ratios of **H/GG** in the co-solvent of  $\text{H}_2\text{O}/\text{THF}$  (9:1 by volume).  $[\text{H}] + [\text{GG}] = 10.0 \mu\text{M}$ ,  $[\text{GY}] = 5.0 \times 10^{-2} \mu\text{M}$ .  $\lambda_{\text{ex}} = 335 \text{ nm}$  for **H-GG**-crosslinked **AOSNs** (black),  $\lambda_{\text{ex}} = 335 \text{ nm}$  (red) and  $\lambda_{\text{ex}} = 490 \text{ nm}$  (blue) for **H-GG-GY**-crosslinked **AOSNs**. The fluorescence spectra for **H-GG**-crosslinked **AOSNs** in the absence of **GY** were normalized such that the emission intensities at ca. 480 nm were the same as in the presence of **GY** (green).

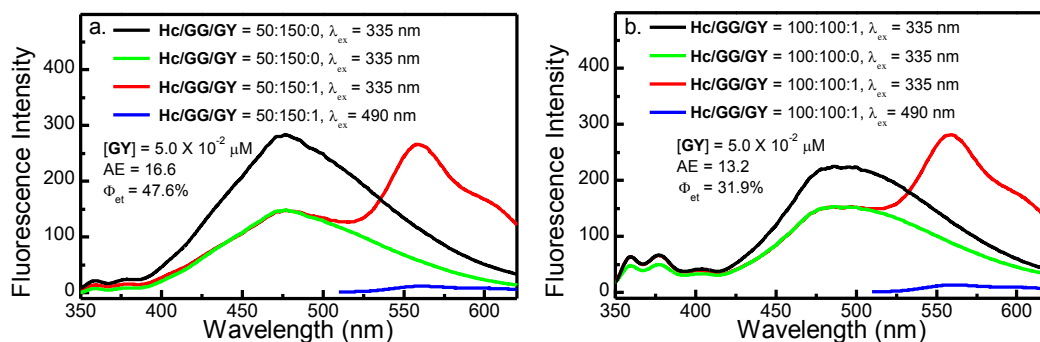


Fig. S25. Fluorescence spectra of the **Hc-GG-GY**-linked supramolecular polymers in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). (a) [**Hc**] = 2.5 μM, [**GG**] = 7.5 μM, (b) [**Hc**] = 5.0 μM, [**GG**] = 5.0 μM. [**GY**] = 5.0 × 10<sup>-2</sup> μM. λ<sub>ex</sub> = 335 nm for **Hc/GG** systems (black), λ<sub>ex</sub> = 335 nm (red) and λ<sub>ex</sub> = 490 nm (blue) for **Hc-GG-GY**-linked supramolecular polymers. The fluorescence spectra for **Hc-GG**-linked supramolecular polymers in the absence of **GY** were normalized so that the emission intensities at ca. 480 nm were the same as in the presence of **GY** (green).

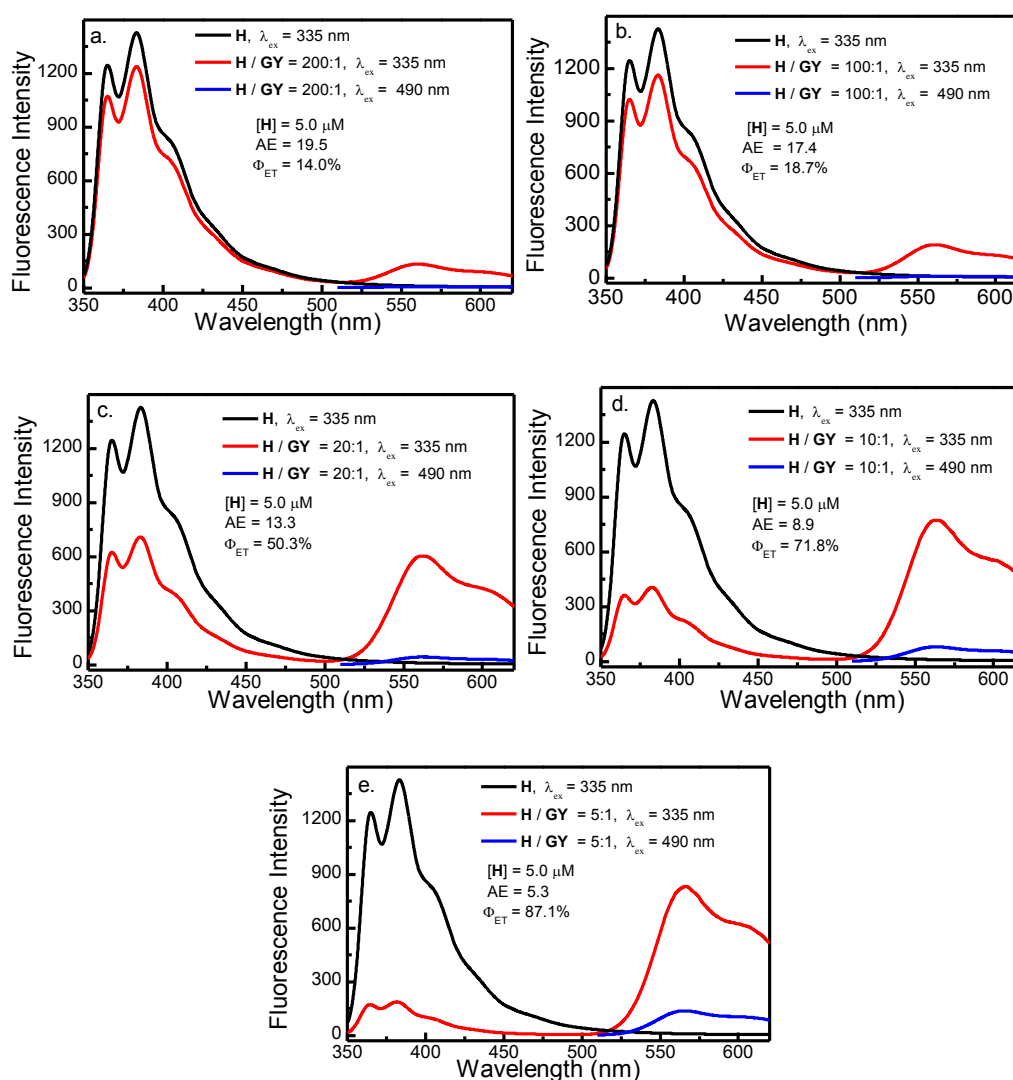


Fig. S26. Fluorescence spectra of **H-GY**-crosslinked supramolecular networks with different ratios of **H/GY** in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). [**H**] = 5.0 μM. λ<sub>ex</sub> = 335 nm for **H** (black), λ<sub>ex</sub> = 335 nm (red) and λ<sub>ex</sub> = 490 nm (blue) for **H-GY**-crosslinked supramolecular networks.

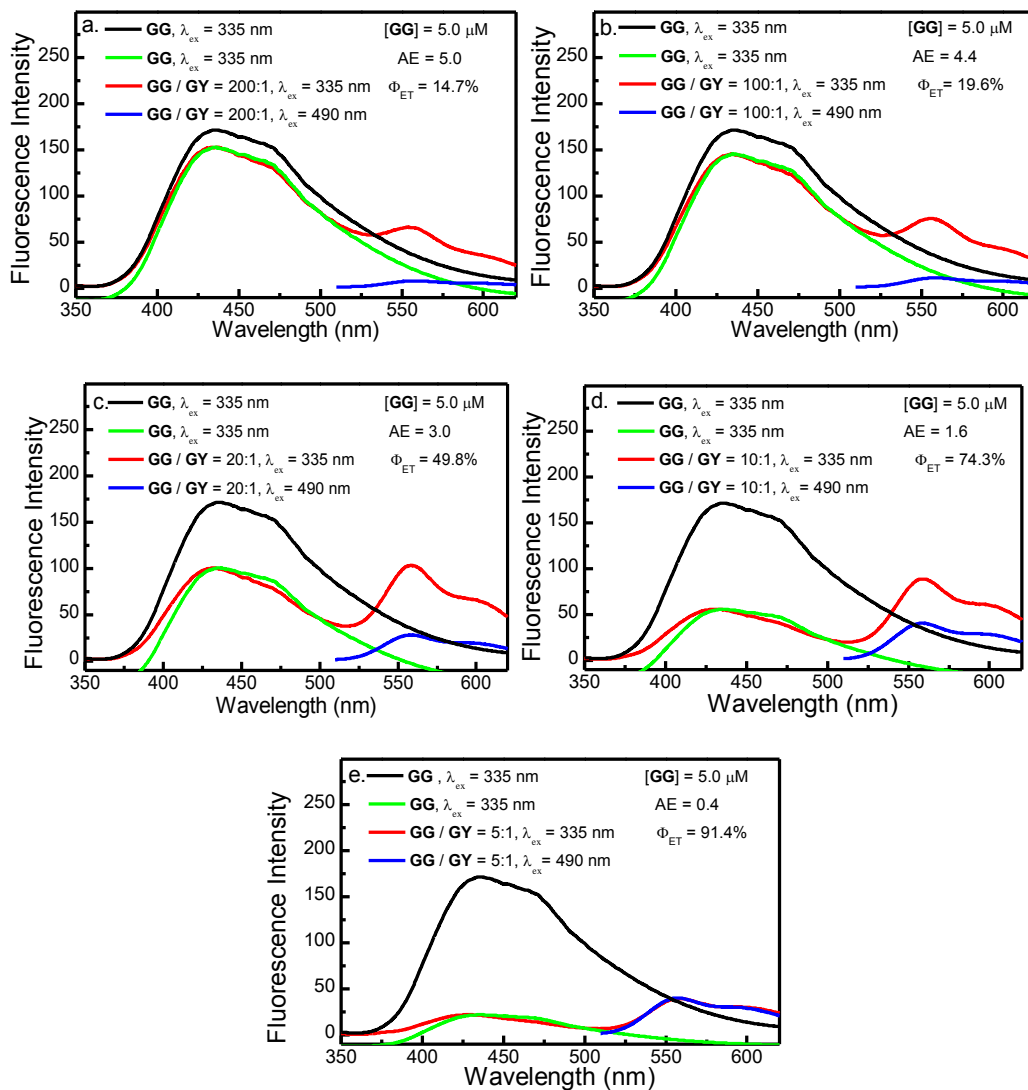


Fig.S27. Fluorescence spectra of **GG-GY**-mixed nanostructures with different ratios of **GG/GY** in the co-solvent of H<sub>2</sub>O/THF (8:2 by volume). **[GG]** = 5.0 μM, **[GY]** = 2.5 × 10<sup>-2</sup> ~ 1.0 μM. λ<sub>ex</sub> = 335 nm for **GG** (black), λ<sub>ex</sub> = 335 nm for **GG/GY** system (red) and λ<sub>ex</sub> = 490 nm for **GG-GY**-mixed nanostructures (blue) and the fluorescence spectra for **GG** in the absence of **GY** was normalized such that the emission intensity at ca. 480 nm was the same as in the presence of **GY** (green).

### 3. Supplementary Tables

Table S1. Antenna effect values and  $\Phi_{ET}$  values of **H-GG-GY**-crosslinked **AOSNs** with different ratios of **GY**.

<b>H/GG/GY</b>	10000:10000:1	1000:1000:1	500:500:1	200:200:1	100:100:1	50:50:1	20:20:1	10:10:1	2:2:1	1:1:1	2:2:3	1:1:2
AE	2.7	9.0	18.7	25.5	27.0	21.7	17.2	8.9	4.0	2.1	1.6	1.5
$\Phi_{ET}$ (%)	2.6	5.2	5.4	20.7	29.3	36.7	52.8	83.4	99.3	99.7	99.8	99.8

Note: **[H]** = 5.0  $\mu$ M. **[GG]** = 5.0  $\mu$ M. Media: H<sub>2</sub>O/THF co-solvent (8:2 by volume).

Table S2. Antenna effect values of **H-GG-GY**-crosslinked **AOSNs** with different ratios of **H/GG** in different media.

<b>H/GG/GY</b>		120:80:1	100:100:1	80:120:1	70:130:1	60:140:1	50:150:1	40:160:1
AE	In media A	43.6	46.1	57.2	62.7	67.7	72.4	60.7
	In media B	26.9	27	35.9	38.5	40.8	43	38.9

Note: **[H]**+**[GG]**=10.0  $\mu$ M. **[GY]** = 0.05  $\mu$ M. Media: H<sub>2</sub>O/THF mixture with the volume ratio of 9:1 (media A) and 8:2 (media B)

Table S3.  $\Phi_{ET}$  of **H-GG-GY**-crosslinked **AOSNs** with different ratios of **H/GG** in different media.

<b>H/GG/GY</b>		120:80:1	100:100:1	80:120:1	70:130:1	60:140:1	50:150:1	40:160:1
$\Phi_{ET}$ (%)	in media A	15.5	16.9	20.0	28.7	31.0	32.7	36.1
	in media B	11.4	29.3	31.9	34.3	35.1	38.2	40.1

Note: **[GY]** = 0.05  $\mu$ M. **[H]**+**[GG]**=10.0  $\mu$ M. Media: H<sub>2</sub>O/THF co-solvent with the volume ratio of 9:1 (media A) and 8:2 (media B).

Table.S4. Antenna effect and  $\Phi_{ET}$  values of **Hc-GG-GY**-linked supramolecular polymers with different ratios of **H/GG**.

<b>Hc/GG/GY</b>	100:00:1	50:150:1
AE	13.2	16.6
$\Phi_{ET}$ (%)	31.9	47.6

Note: **[GY]** = 0.05  $\mu$ M. **[Hc]**+**[GG]**=10.0  $\mu$ M. Media: H<sub>2</sub>O/THF co-solvent (8:2 by volume).

Table.S5. Antenna effect and  $\Phi_{ET}$  values of **H-GY**-crosslinked supramolecular networks with different ration of **GY**.

<b>H/GY</b>	200:1	100:1	20:1	10:1	5:1
AE	19.5	17.4	13.3	8.9	5.3
$\Phi_{ET}$ (%)	14.0	18.7	50.3	71.8	87.1

Note: [**H**] = 5.0  $\mu$ M. Media: H<sub>2</sub>O/THF co-solvent (8:2 by volume).

Table. S6. Antenna effect and  $\Phi_{ET}$  values of **GG-GY**-mixed nanostructures with different ration of **GY**.

<b>GG/GY</b>	200:1	100:1	20:1	10:1	5:1
AE	5.0	4.4	3.0	1.6	0.4
$\Phi_{ET}$ (%)	14.7	19.6	49.8	74.3	91.4

Note: [**GG**] = 5.0  $\mu$ M. Media: H<sub>2</sub>O/THF co-solvent (8:2 by volume).

## 5. References

- [1] a) D. Cao, Y. Kou, J. Liang, Z. Chen, L. Wang, H. Meier, *Angew. Chem. Int. Ed.* **2009**, *48*, 9721-9723; b) L. Liu, D. Cao, Y. Jin, H. Tao, Y. Kou, H. Meier, *Org. Biomol. Chem.* **2011**, *9*, 7007-7010; c) W. Cui, H. Tang, L. Xu, L. Wang, H. Meier, D. Cao, *Macromol. Rapid Commun.* **2017**, *38*, 1700161; d) W. Cui, L. Wang, L. Xu, G. Zhang, H. Meier, H. Tang, D. Cao, *The Journal of Physical Chemistry Letters* **2018**, *9*, 1047-1052; e) L. Xu, Z. Wang, R. Wang, L. Wang, X. He, H. Jiang, H. Tang, D. Cao, B. Z. Tang, *Angew. Chem. Int. Ed.* **2020**, *59*, 9908-9913.
- [2] a) J. Zhang, Y. Hua, B. Xu, L. Yang, P. Liu, M. B. Johansson, N. Vlachopoulos, L. Kloo, G. Boschloo, E. M. J. Johansson, L. Sun, A. Hagfeldt, *Advanced Energy Materials* **2016**, *6*, 1601062; b) S. Yuan, S. Kirklin, B. Dorney, D.-J. Liu, L. Yu, *Macromolecules* **2009**, *42*, 1554-1559; c) B. Xu, J. Zhang, Y. Hua, P. Liu, L. Wang, C. Ruan, Y. Li, G. Boschloo, E. M. J. Johansson, L. Kloo, A. Hagfeldt, A. K. Y. Jen, L. Sun, *Chem* **2017**, *2*, 676-687; d) C. Yu, Y. Xu, S. Liang, X. Jiang, G. Feng, C. Li, W. Li, *Chin. Chem. Lett.* **2018**, *29*, 325-327.
- [3] a) L. Xu, R. Wang, W. Cui, L. Wang, H. Meier, H. Tang, D. Cao, *Chem. Commun.* **2018**, *54*, 9274-9277; b) X. Sun, W. Shi, F. Ma, Y. Hui, L. Xu, H. Mi, Y. Tian, Z. Xie, *Sens. Actuators B Chem.* **2014**, *198*, 395-401.
- [4] Y. Zhu, L. Xu, L. Wang, H. Tang, D. Cao, *Chem. Commun.* **2019**, *55*, 5910-5913.
- [5] W. Cui, L. Wang, L. Xu, G. Zhang, H. Meier, H. Tang, D. Cao, *J. Phys. Chem. Lett.* **2018**, *9*, 1047-1052.