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for

Supramolecular Assembly-Induced Yellow Emission of 9,10-Distyrylanthracene Bridged Bis(pillar[5]arene)s†

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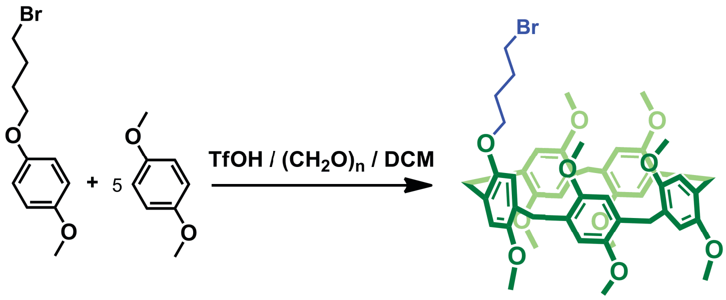
1. Materials and Methods

Materials. p-Hydroxyl anisole, paraformaldehyde $(CH_2O)_n$, potassium iodide (KI) and 1,4-dibromobutane were reagent grade and purchased from Aladdin Reagents or Sigma-Aldrich. Potassium carbonate (K_2CO_3) was obtained from J&K Co. Ltd. All of the solvents used in the study were reagent grade and used without further purification. **NG1** and **NG2** were prepared according to the previous literature report.[S1]

Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 300 MHz or 500 MHz NMR spectrometer. MALDI-TOF MS spectra were obtained from an autoflex TOF/TOF mass spectrometer (Bruker, Germany), equipped with a nitrogen laser (337 nm, 3 ns pulse). SEM images were collected on a JEOL JSM 6700F instrument with an accelerating voltage of 3 kV. The fluorescence microscopy images were obtained on an Olympus BX51 fluorescence microscopy. Fluorescence spectra were obtained on a Shimadzu RF-5301PC spectrofluorometer. The time-resolved fluorescence decay curves and quantum yields were obtained on a FLS920 instrument (Edinburgh Instrument) with the excitation of 405 nm. Quantum yields were calculated by means of an integrating sphere.

2. Syntheses and Characterization

2. 1 Synthesis of copillar[5]arene



Copillar[5]arene was prepared according to our previous report.[S2] Briefly, the reaction of 4-bromobutyl-anisole and 1,4-dimethoxybenzene and paraformaldehyde in dry dichloromethane, in the presence of 5% mmol of trifluoromethanesulfonate (TfOH) as catalyst. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C) δ (ppm): 6.76 (m, 10 H), 3.84 (t, 2 H), 3.77 (s, 10H), 3.68 (m, 27H), 3.28 (t, 2H), 1.83 (m, 4H).

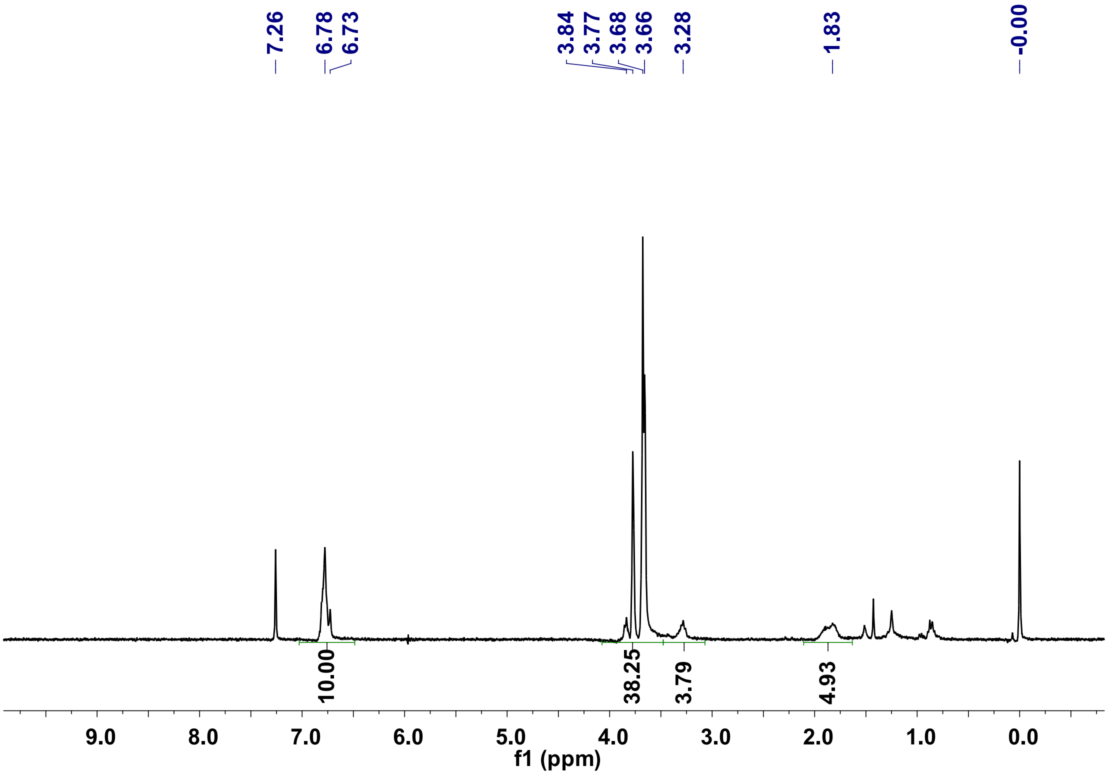
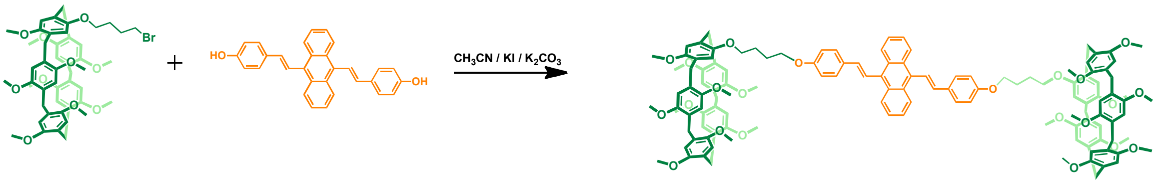


Figure S1. ^{1}H NMR spectrum of copillar[5]arene.

2.2 Synthesis and characterization of **DSA-(P5)$_2$**.



9,10-Bis(4-hydroxystyryl)anthracene was synthesized according to our reported method.[S3] 9,10-Bis(4-hydroxystyryl)anthracene (120 mg, 0.29 mmol) and K_2CO_3 (480 mg) were dispersed in acetonitrile (50 mL) and the mixture was stirred at room temperature for 30 min. Then, KI (20 mg) and excess copillar[5]arene (757 mg, 0.87 mmol) were added to the solution. The mixture was heated to reflux and reacted for 12 h. The mixture was filtered while it was hot and washed with dichloromethane for three times. The filtrate was collected and concentrated by rotary evaporation. The crude product was then isolated by flash column chromatography (silica gel, n-hexane : dichloromethane : acetone = 60:4:1) to give a yellow solid. Yield: 140 mg, 24%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.427-8.394 (m, 4H), 7.794 (d, J = 16.2 Hz, 2H), 7.620 (d, J = 8.7 Hz, 4H), 7.488-7.455 (m, 4H), 6.990 (d, J = 8.7 Hz, 4H), 6.880 (d, J = 16.8 Hz, 2H), 6.787-6.752 (m, 20H), 4.101 (t, J = 6.0 Hz, 4H), 3.929 (t, J = 4.8 Hz, 4H), 3.781 (s, 20H), 3.650 (s, 54H), 2.012 (s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ (ppm): 159.1, 150.8, 150.0, 136.9, 132.8, 130.2, 129.7, 128.3, 127.8, 126.6, 125.2, 122.9, 114.8, 114.1, 68.0, 67.7, 55.8, 29.8, 26.5, 26.4. MS (MALDI-TOF), *m/z* 1994.5926 (found); 1994.9054 [M] (calcd); 2033.5673 (found); 2033.8685 $[M + K]^+$ (calcd).

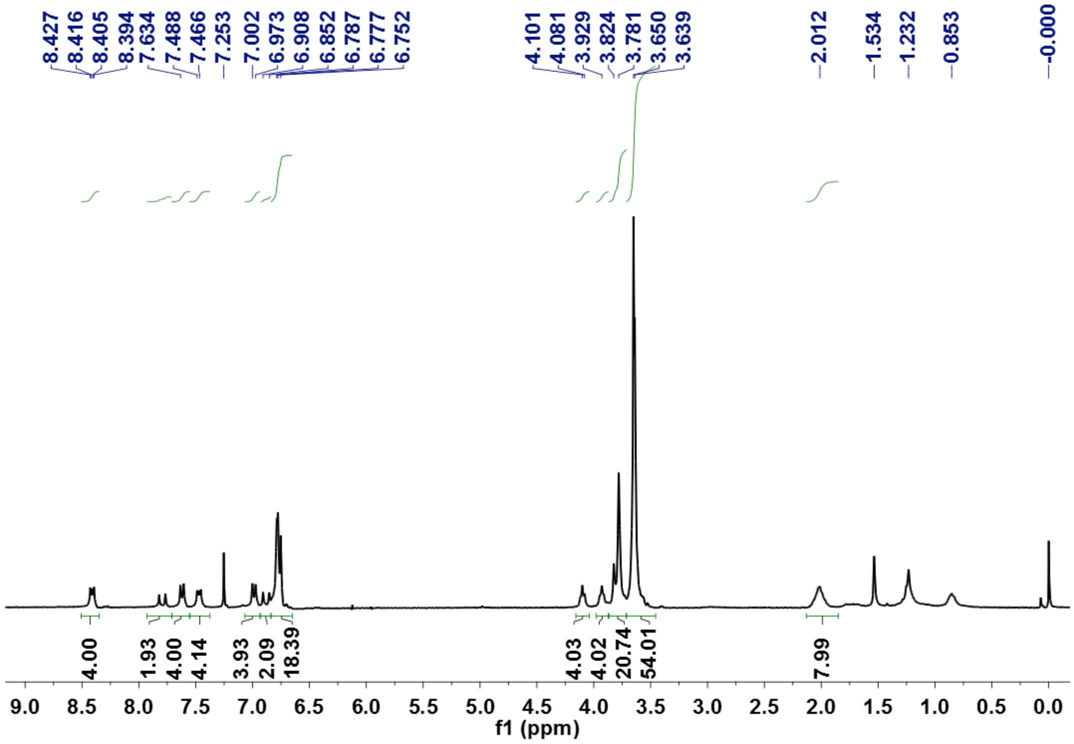


Figure S2. ^{1}H NMR spectrum of **DSA-(P5)$_2$**.

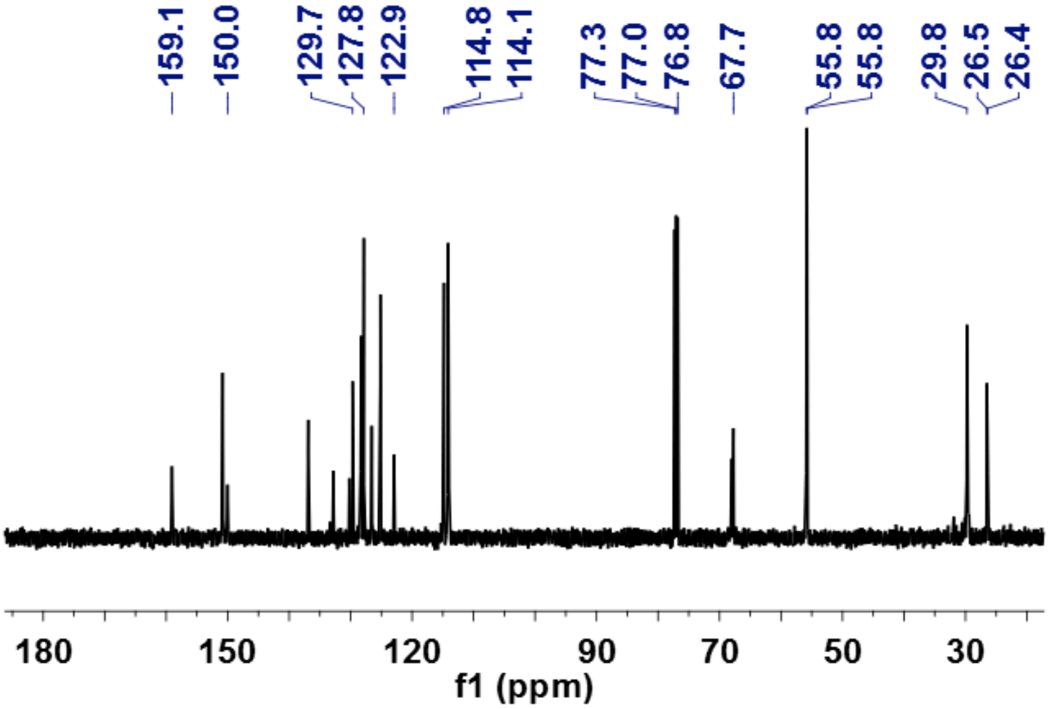


Figure S3. ^{13}C NMR spectrum of **DSA-(P5)$_2$**.

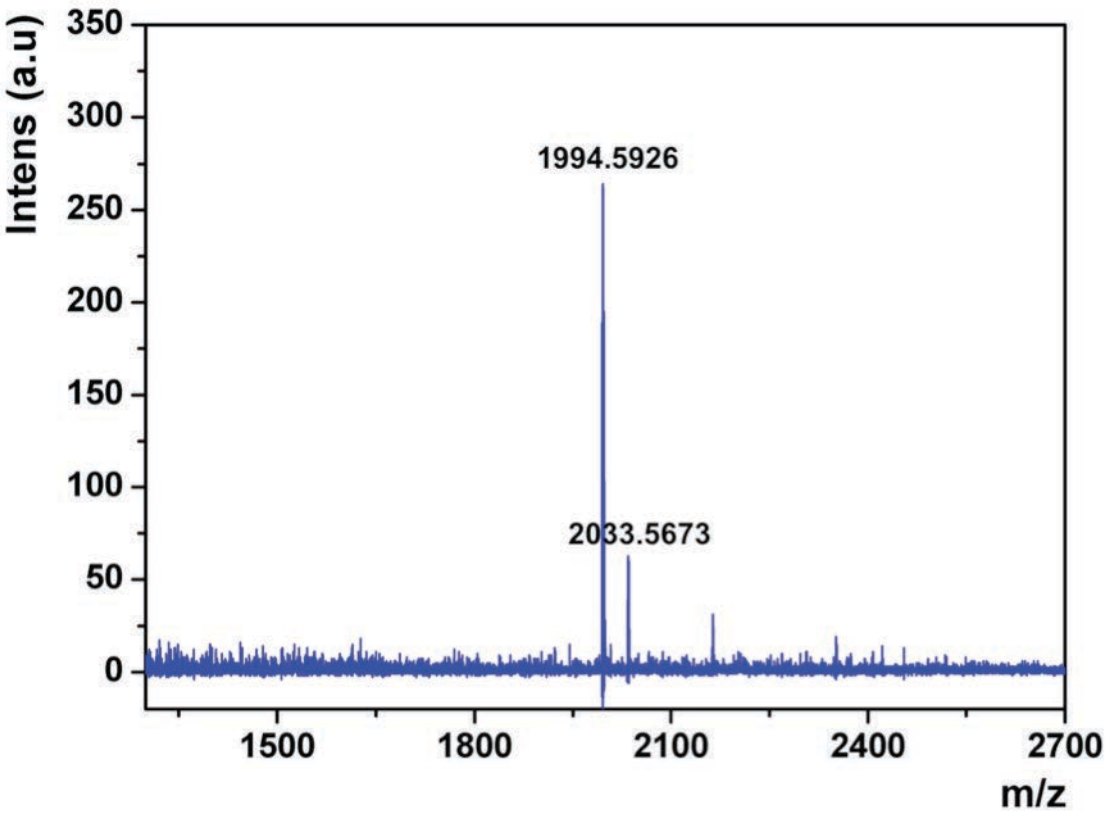
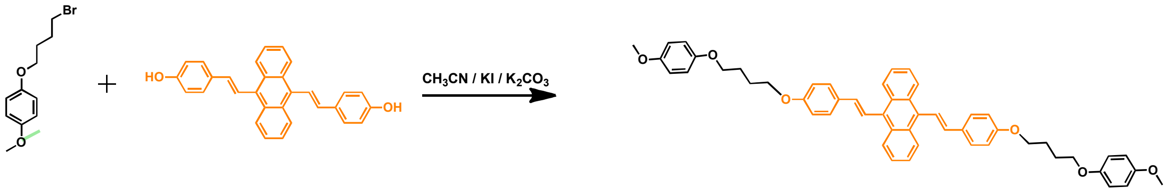


Figure S4. MOLDI-TOF MS spectrum of **DSA-(P5)$_2$**.

2. 3 Synthesis and characterization of **DSA-(monomer)$_2$**.



9,10-Bis (4-hydroxystyryl) anthracene (150 mg, 0.36 mmol) and K_2CO_3 (201 mg) were added in acetonitrile (30 mL) and activated at room temperature for 30 min. KI (10 mg) and excess monomer of copillar[5]arene, *i.e.*, 1-(4-bromobutoxy)-4-methoxybenzene (284 mg, 1.10 mmol), were then added to above mixture solution. The dispersion was reacted for 12 h at 85 °C for reflux. The mixture was filtered while it was hot and washed with dichloromethane for several times. The filtrate was collected and concentrated by rotary evaporation. The crude product was then isolated by flash column chromatography (silica gel, n-hexane : dichloromethane : hexane = 2:1) to give a yellow solid. Yield: 70 mg, 25%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.422-8.389 (m, 4H), 7.789 (d, J = 16.5 Hz, 2H), 7.619 (d, J = 8.4 Hz, 4H), 7.481-7.448 (m, 4H), 6.994 (d, J = 8.4 Hz, 4H), 6.871 (d, J = 20.0 Hz, 2H), 6.859 (m, 8H), 4.117 (t, J = 5.7 Hz, 4H), 4.024 (t, J = 5.4 Hz, 4H), 3.781 (s, 6H), 2.014 (s, 8H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C) δ (ppm): 159.0, 153.2, 136.9, 133.3, 132.8, 130.1, 129.7, 128.6, 127.8, 126.6, 126.5, 125.3, 125.1, 124.3, 122.8, 115.5, 115.4, 114.9, 114.7, 114.6, 114.1, 68.1, 68.0, 67.7, 55.8, 29.7, 26.1, 26.0, 25.9. MS (MALDI-TOF), *m/z* 770.3806 (found); 770.3607 [M] (calcd).

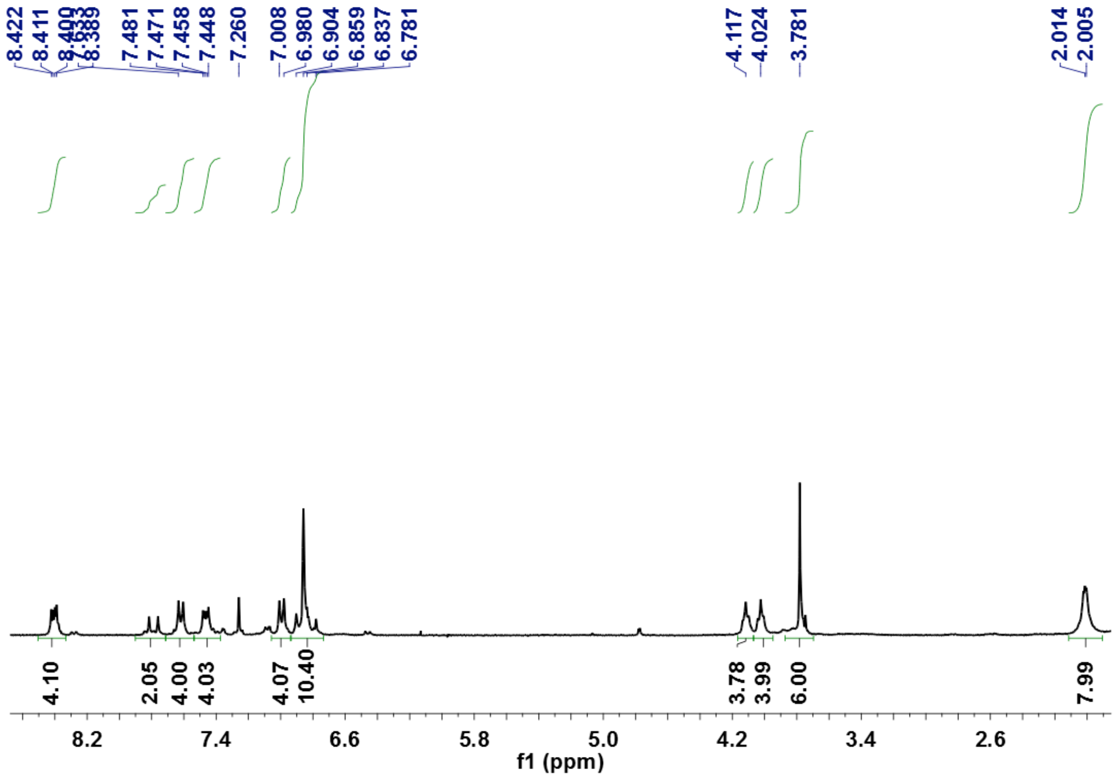


Figure S5. ^{1}H NMR spectrum of **DSA-(monomer)$_2$**.

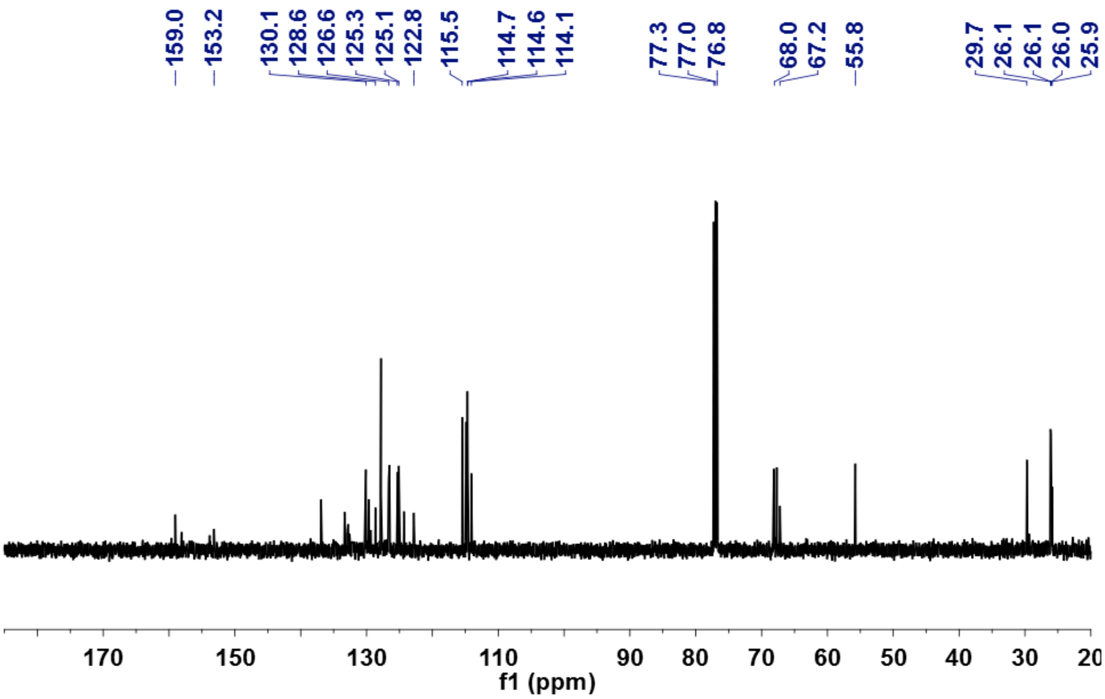


Figure S6. ^{13}C NMR spectrum of **DSA-(monomer)$_2$**.

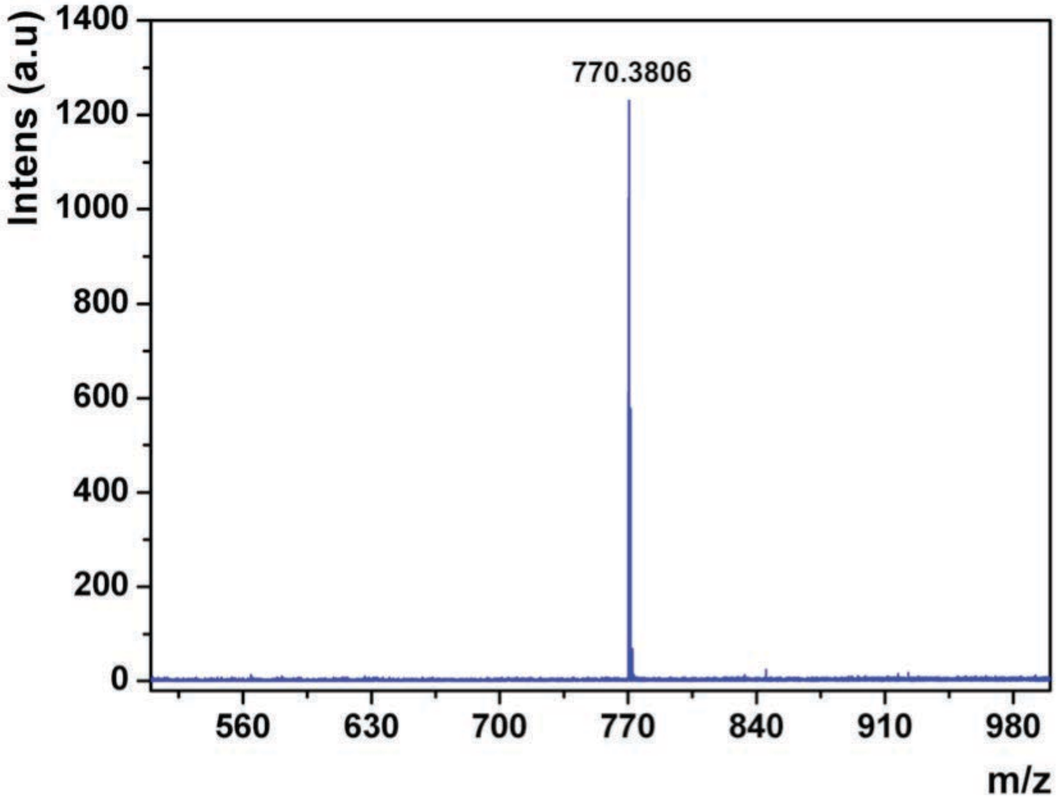


Figure S7. MOLDI-TOF MS spectrum of **DSA-(monomer)$_2$**.

3. AIE Properties of DSA-(P5)$_2$ and DSA-(monomer)$_2$ in H$_2$O/THF

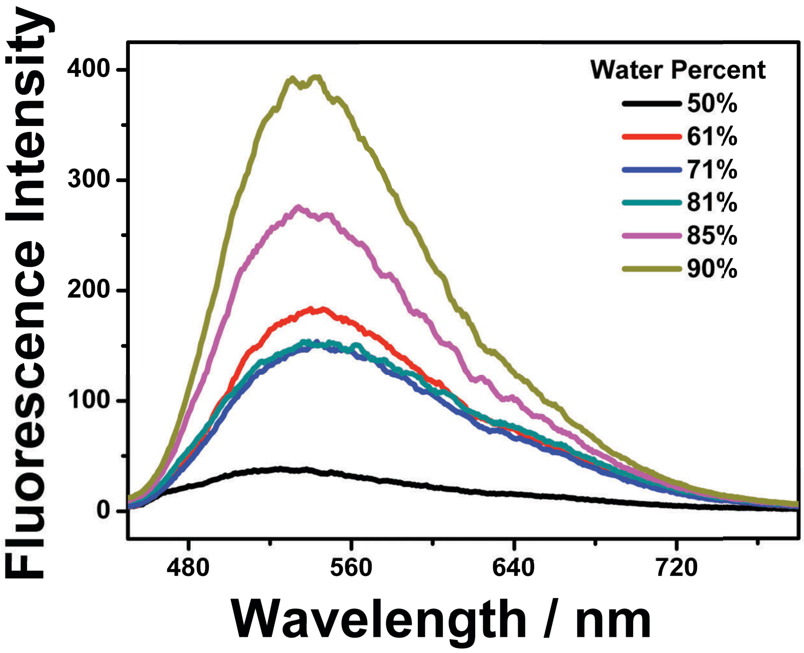


Figure S8. Fluorescent emission spectra of **DSA-(P5)$_2$** (1 μM; λ_{ex} = 415 nm; λ_{em} = 543 nm; slit widths: Ex. 10 nm, Em. 10 nm; 25 °C) in the mixed solvents of H$_2$O/THF with different fraction of hexane ranging from 50% to 90%.

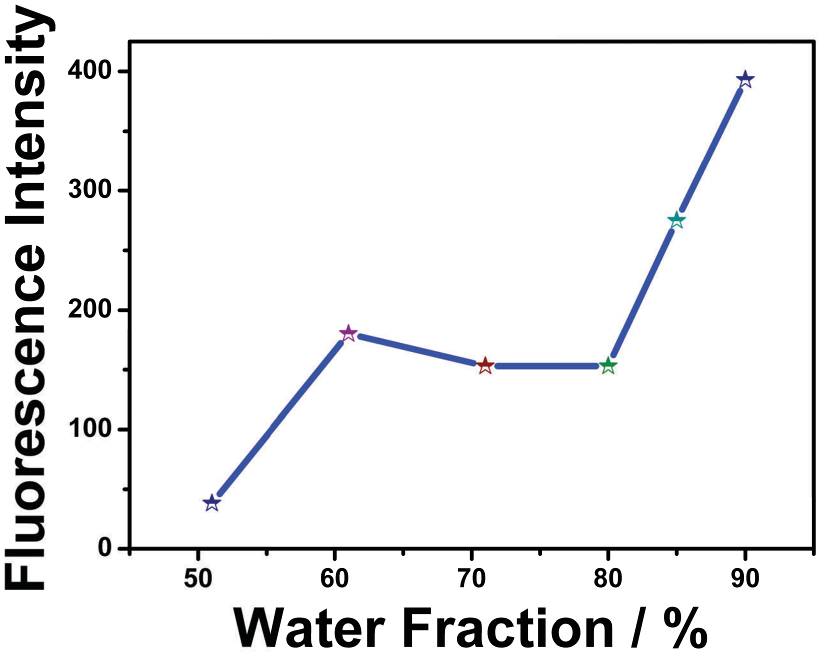


Figure S9. Plot of fluorescence intensity of **DSA-(P5)$_2$** at 543 nm *vs* the fraction of H$_2$O in their mixed solvents.

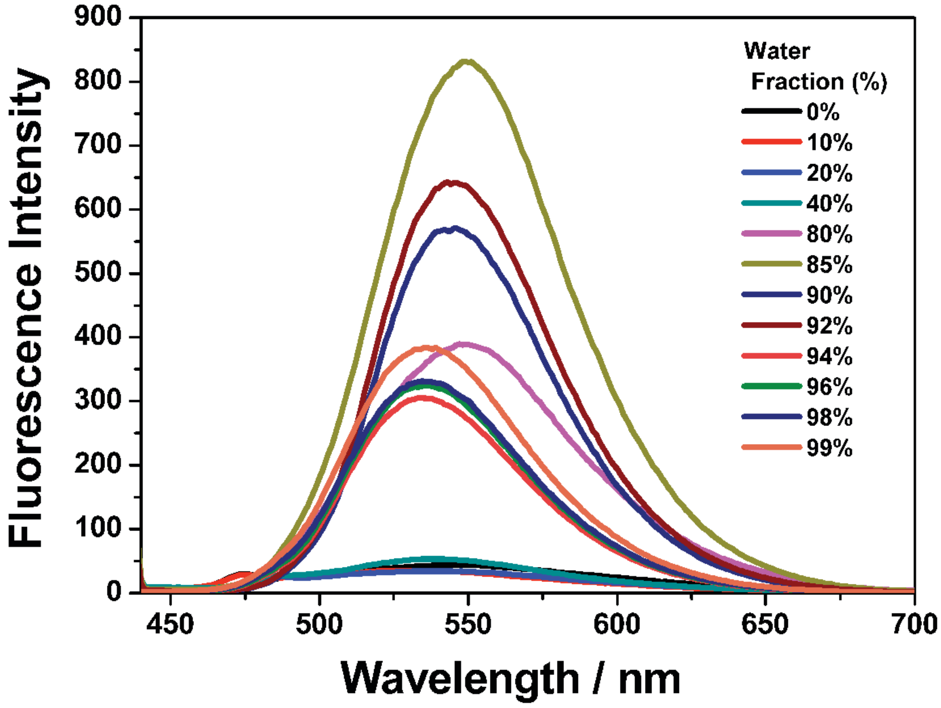


Figure S10. Fluorescent emission spectra of **DSA-(monomer)$_2$** (1 μM; λ_{ex} = 415 nm; λ_{em} = 543 nm; slit widths: Ex. 10 nm, Em. 10 nm; 25 °C) in the mixed solvents of H_2O/THF with different fraction of hexane ranging from 50% to 90%.

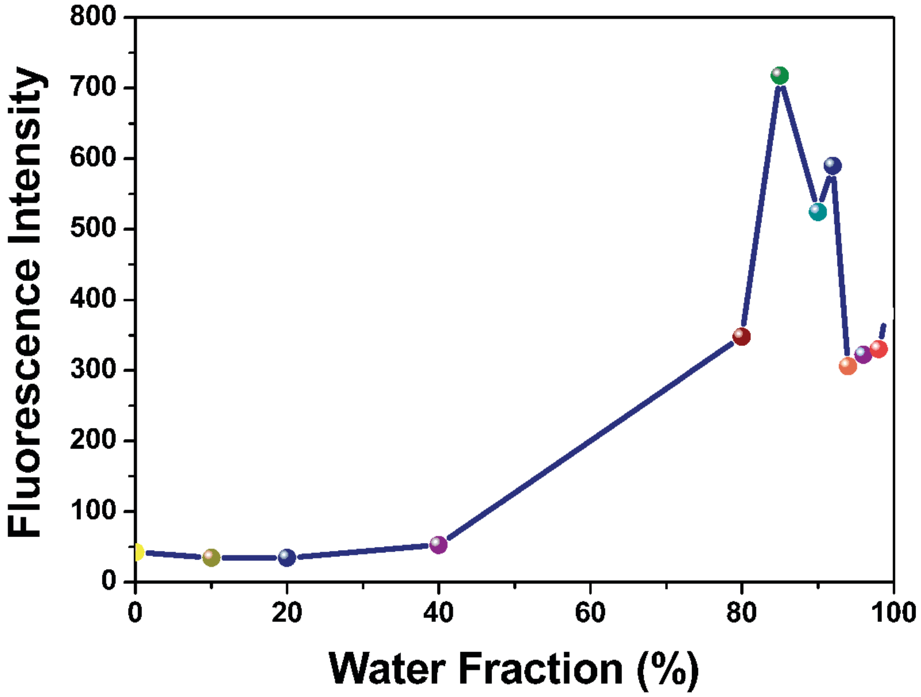


Figure S11. Plot of fluorescence intensity of **DSA-(monomer)$_2$** at 543 nm *vs* the fraction of H_2O in their mixed solvents.

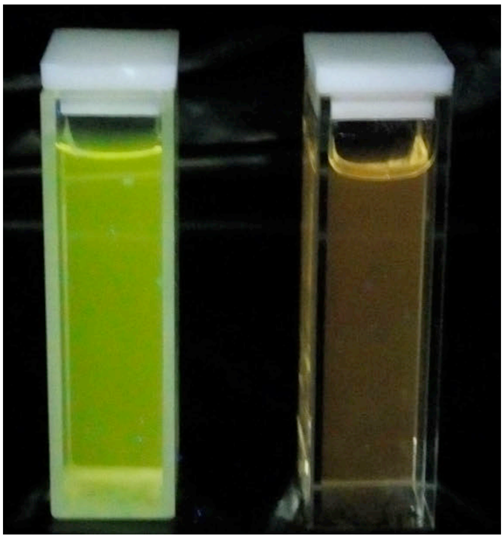


Figure S12. Photograph of **DSA-(P5)$_2$** in H_2O/THF mixtures for the fraction of H_2O is 90% (left) and 0% (right) under 365 nm UV irradiation.

4. Time-Resolved Fluorescence Decay

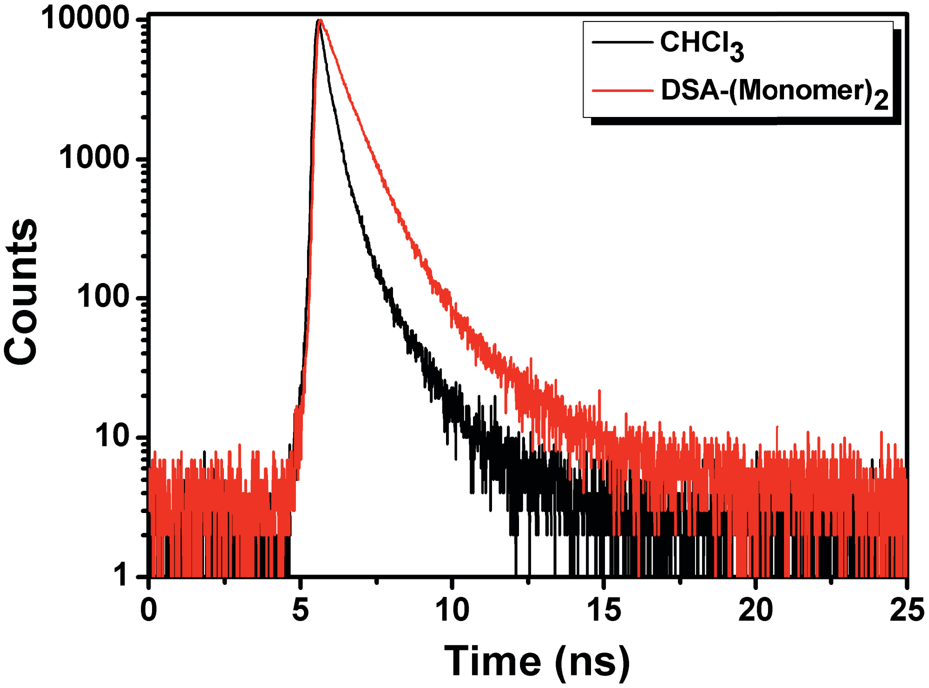


Figure S13. Time-resolved fluorescence decay curves of **DSA-(Monomer)$_2$**.

5. SEM and Fluorescence Microscopy Images

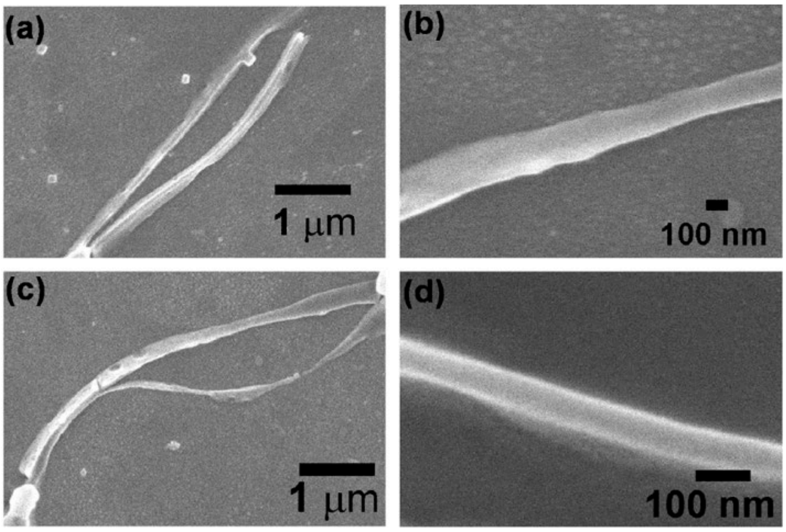


Figure S14. Scanning electron microscopy images of supramolecular polymer of **NG2⊂DSA-(P5)$_2$**. (a-d) several representative areas of samples.

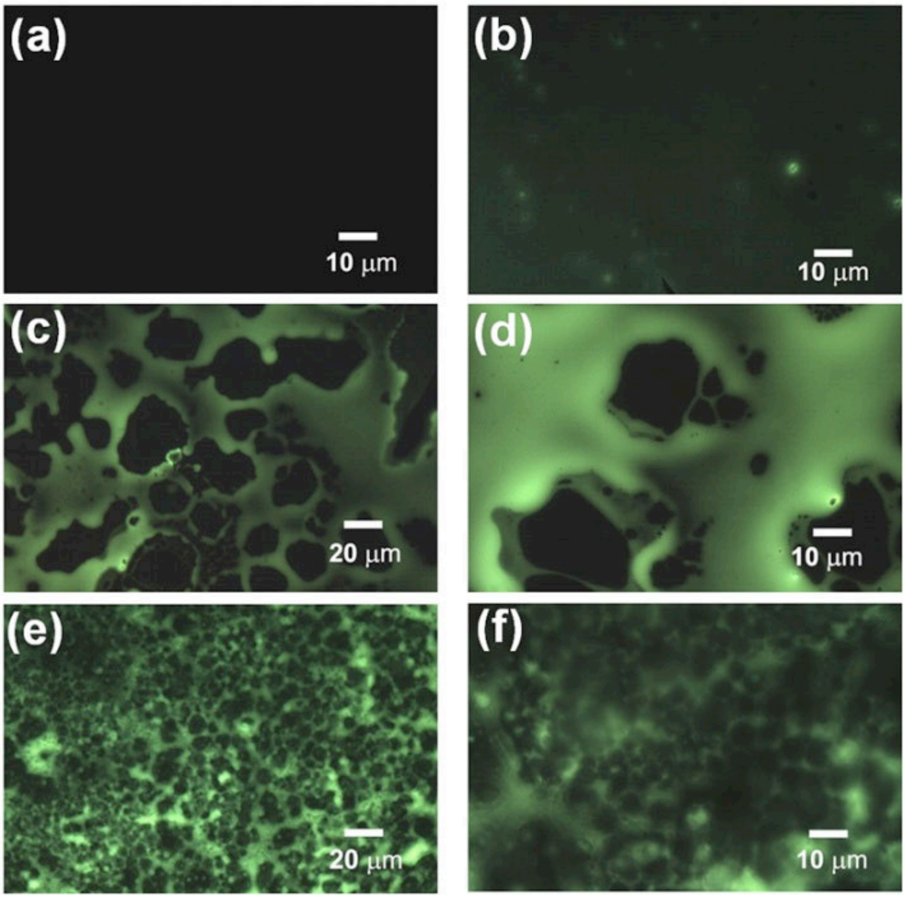


Figure S15. Fluorescent images observed by the fluorescence microscopy (λ_{ex} = 365 nm). (a) **NG2** (at magnification: ×1000); (b) **NG1⊂DSA-(P5)$_2$** (at magnification: ×1000); (c) **DSA-(P5)$_2$** (at magnification: ×500); (d) **DSA-(P5)$_2$** (at magnification: ×1000); (e) **NG2⊂DSA-(P5)$_2$** (at magnification: ×500); (f) **NG2⊂DSA-(P5)$_2$** (at magnification: ×1000).

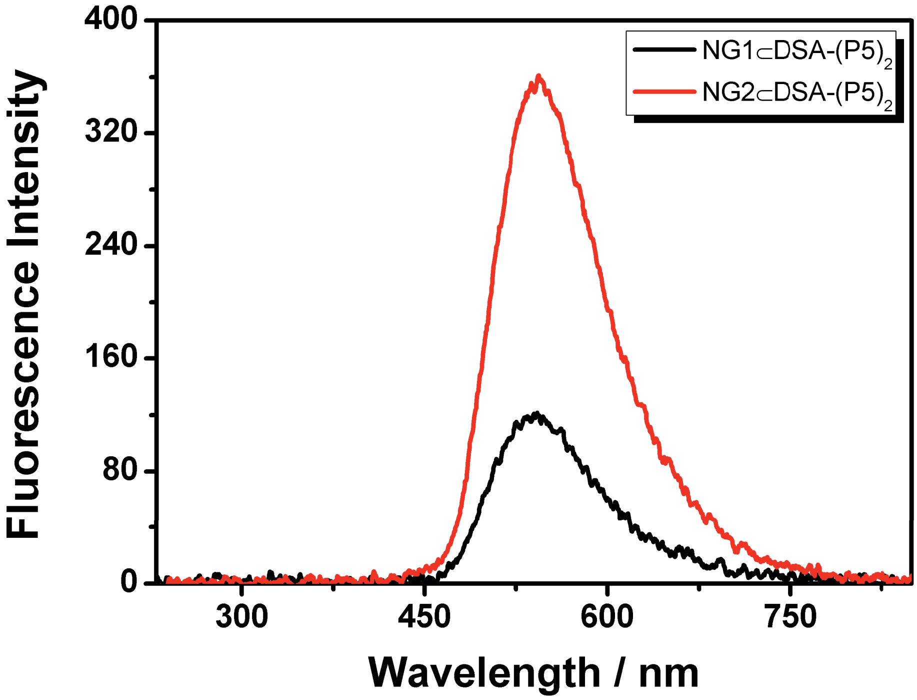


Figure S16. Solid-state fluorescence emission spectra of **NG1⊂DSA-(P5)₂** and **NG2⊂DSA-(P5)₂** observed by fluorescence microscopy (λ_{em} = 543 nm).

6. MTT Assay

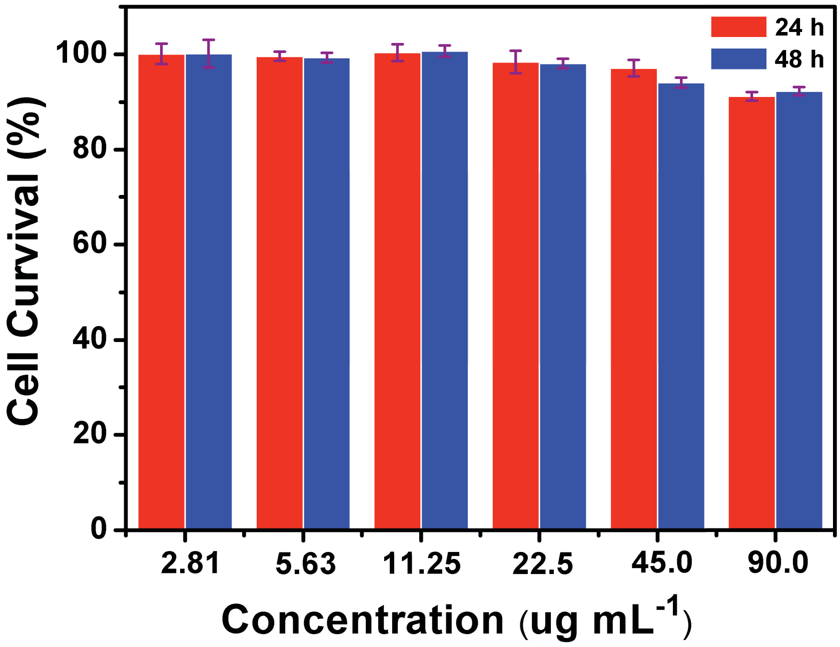


Figure S17. Cytotoxicity of **DSA-(P5)₂** to 293T cells.

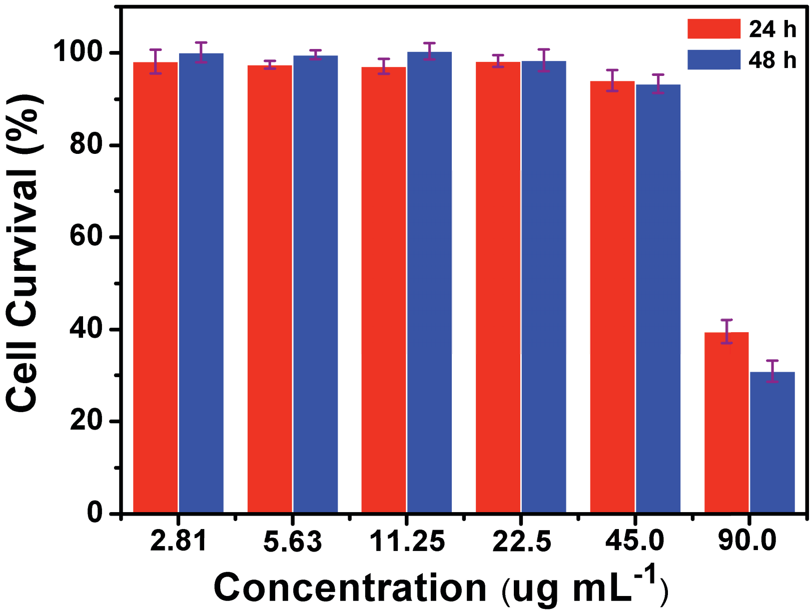


Figure S18. Cytotoxicity of **DSA-(OH)$_2$** to 293T cells.

7. References

S1. N. Song, D.-X. Chen, Y.-C. Qiu, X.-Y. Yang, B. Xu, W. Tian and Y.-W**.** Yang, *Chem. Commun.,* 2014, **50**, 8231.

S2. K. Wang, L.-L. Tan, D.-X. Chen, N. Song, G. Xi, S. X.-A. Zhang, C. Li and Y.-W. Yang, *Org. Biomol. Chem.*, 2012, **10**, 9405.

S3. H. Lu, B. Xu, Y. Dong, F. Chen, Y. Li, Z. Li, J. He, H. Li and W. Tian, *Langmuir,* 2010, **26**, 6838.