Electronic Supplementary Information (ESI)

for

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

Nan Song, Dai-Xiong Chen, Meng-Chan Xia, Xi-Long Qiu, Ke Ma, Bin Xu,

Wenjing Tian and Ying-Wei Yang*

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, International Joint Research Laboratory of Nano-Macro Architecture Chemistry (NMAC), Jilin University, 2699 Qianjin Street, Changchun, 130012, P. R. China.
*Corresponding Author, E-mail: ywyang@jlu.edu.cn
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1. Materials and Methods

Materials. p-Hydroxyl anisole, paraformaldehyde (CH₂O)ₙ, potassium iodide (KI) and 1,4-dibromobutane were reagent grade and purchased from Aladdin Reagents or Sigma-Aldrich. Potassium carbonate (K₂CO₃) 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.¹

Methods. ¹H NMR and ¹³C 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. 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. ⁹ 9,10-Bis(4-hydroxystyryl)anthracene (120 mg, 0.29 mmol) and K₂CO₃ (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%. ¹H NMR (300 MHz, CDCl₃, 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). ¹³C NMR (125 MHz, CDCl₃, 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-hydroxystyril) anthracene (150 mg, 0.36 mmol) and K$_2$CO$_3$ (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; $\lambda_{\text{ex}} = 415$ nm; $\lambda_{\text{em}} = 543$ 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; $\lambda_{ex} = 415$ nm; $\lambda_{em} = 543$ 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 S11. Plot of fluorescence intensity of DSA-(monomer)$_2$ at 543 nm vs the fraction of H$_2$O in their mixed solvents.
Figure S12. Photograph of DSA-(P5)$_2$ in H$_2$O/THF mixtures for the fraction of H$_2$O 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 ($\lambda_{ex} = 365$ 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\(_{\text{DSA-(P5)2}}\) and NG2\(_{\text{DSA-(P5)2}}\) observed by fluorescence microscopy (\(\lambda_{\text{em}} = 543\) 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

