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Supporting Information

Polysaccharide Restriction on Bipyridyl Isomers for Multicolor Emissions

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Contents

1. Experimental details

General. ^{1}H NMR spectra were measured with a Bruker AV-400 spectrometer in D_2O at 25 °C. Chemical shifts are reported in δ ppm using D_2O (7.26 ppm) for ^{1}H NMR as an internal standard. UV-vis absorption spectra were measured with a Shimadzu UV-3600 spectrometer in the spectral-grade solvent. Fluorescence spectra were measured with a Hitachi F-4500 spectrometer in spectral-grade solvents. The morphologies and structures of the samples were characterized by using field emission scanning electron microscopy (FESEM; JSM-7001F, JEOL, Tokyo, Japan) with an energy dispersive X-ray spectrometer (EDS) and the transmission electron microscopy (TEM; JEM-1011; JEOL Co., Japan) operated at an accelerating voltage of 100 kV. The molecular packing was investigated by powder X-ray diffraction (PXRD). PXRD data were collected on a Bruker D8. Empyrean powder diffractometer using a Cu Kα source (λ = 1.5418 Å) over the range of 2θ = 2.0–30.0° with a step size of 0.02° and 2 s per step. The structural optimizations and DFT calculations of **OSA-3-Apy** and **OSA-5-Apy** were performed using Gaussian 09 program at the B3LYP/6-31G* level of theory.[1]

Synthesis

All solvents for synthesis were purchased from the Sinopharm Chemical Reagent limited corporation and used without further purification unless otherwise stated.

Synthesis of OSA: Sodium alginate (2.0 g, 10.1 mmol) was dissolved in 200 ml of deionized water and stirred at room temperature for 3 h to obtain the alginate solution of 1wt%. Sodium periodate (4.3 g, 20.2 mmol) solution of 5wt% was added to the above alginate solution and stirred for 24 h without light. Ethylene glycol (1.0 ml, 20.2 mmol) was added and stirred for 1 h to quench the remaining sodium periodate. After adding a large amount of anhydrous ethanol, a large amount of white precipitate was formed. After filtered and freeze-dried treatments, the white powder of OSA was obtained and preserved in a low-temperature and dry environment.

Synthesis of OSA-Apy: OSA (2.0 g, 10.2 mmol) was dissolved in 200 ml of

deionized water and 3-APy/5-APy with different feed ratios was dissolved in 20 ml of anhydrous ethanol. The 3-APy/5-APy and OSA solutions were mixed and stirred for 3 h. After adding a large amount of anhydrous ethanol, the flocculent solid precipitates were obtained, which were filtered and washed with anhydrous ethanol several times to remove the unreacted Apy. The OSA-3-APy/OSA-5-APy was obtained after the drying process.

Preparation of fibers: OSA (20.0 g, 102.3 mmol) with an oxidation degree of 2:1 was dissolved in 500 mL deionized water and stirred at room temperature for 6 h to form 4% OSA solution. 3-Apy with different molar ratio of the 3-Apy to the OSA repeating unit (1, 0.0001 and 0.00001) were added into their respective 500 mL OSA solution and reacted at room temperature for 2 h. Anhydrous calcium chloride (40.0 g, 3.7 mol) was dissolved in 8 L water to form 5% calcium chloride solution as coagulation bath. The 4% OSA-3-Apy solution was placed in the spinning machine liquid storage tank and stood for 12 h at atmospheric pressure to remove bubbles in the spinning solution. Positive pressure was added to make the spinning solution enter calcium chloride solution solidification bath through spinneret to form fluorescent fibers. The spun fluorescent fibers were soaked in 95% ethanol for filament splitting, soaked for 3 hours, and then dried to obtain fluorescent fibers.

Preparation of Rubik's cube: First, OSA-3-Apy solution with different molar ratio of the 3-Apy to the OSA repeating unit (1 and 0.0001) was injected into the mold with a syringe and put into the refrigerator for 10 h. Then, frozen gel was put into 4% $CaCl_2$ solution together with the mold for 5 h calcium cross-linking to form fluorescent gel. After that, 9 pieces of the same fluorescent gel were inserted into the same surface of the foam cube with a fine needle, and different fluorescent gels were used on different surfaces to make the colorful luminous Rubik's cube.

2. Structure and photophysical properties

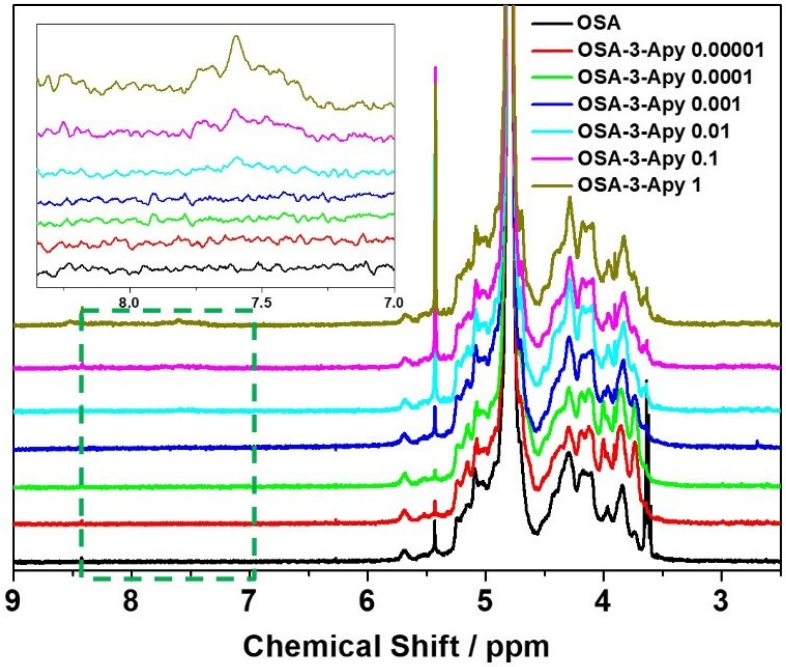

Figure S1. The ^{1}H NMR spectra of OSA-3-Apy with different 3-Apy feed ratios.

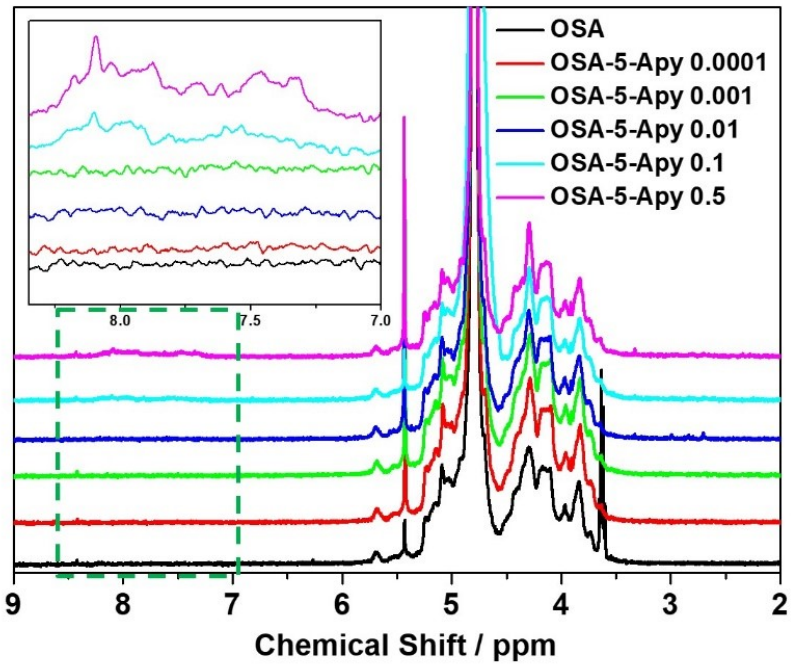

Figure S2. The ^{1}H NMR spectra of OSA-5-Apy with different 5-Apy feed ratios.

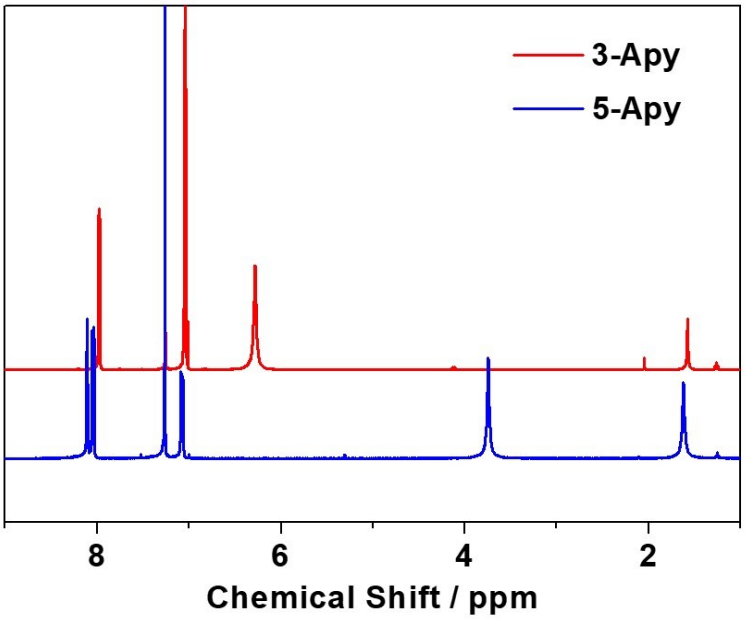

Figure S3. The ^{1}H NMR spectra of 3-Apy and 5-Apy.

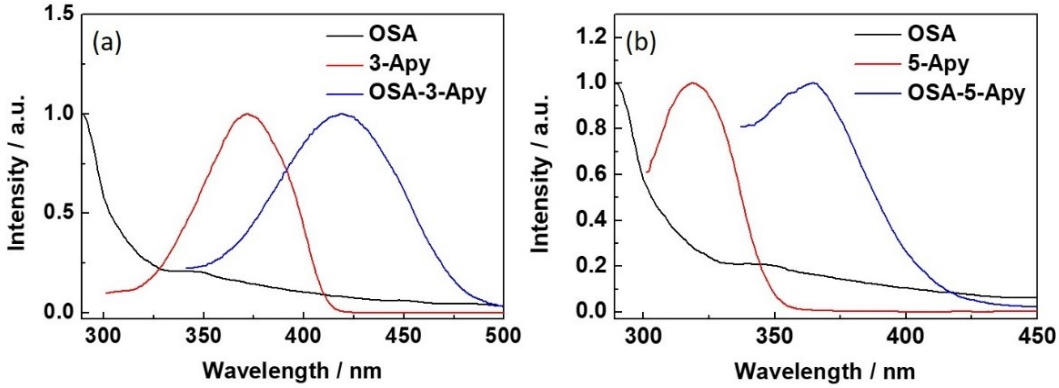

Figure S4. The UV-vis absorption spectra of OSA, 3-Apy, OSA-3-Apy (a) and OSA, 5-Apy, OSA-5-Apy (b).

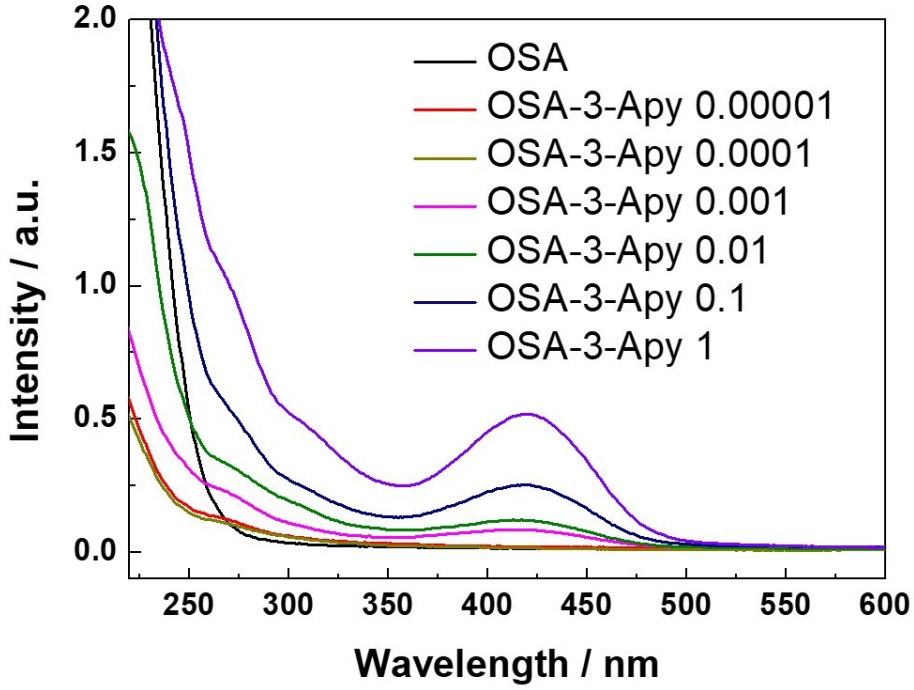

Figure S5. The UV-vis absorption spectra of OSA-3-Apy with different 3-Apy feed ratios.

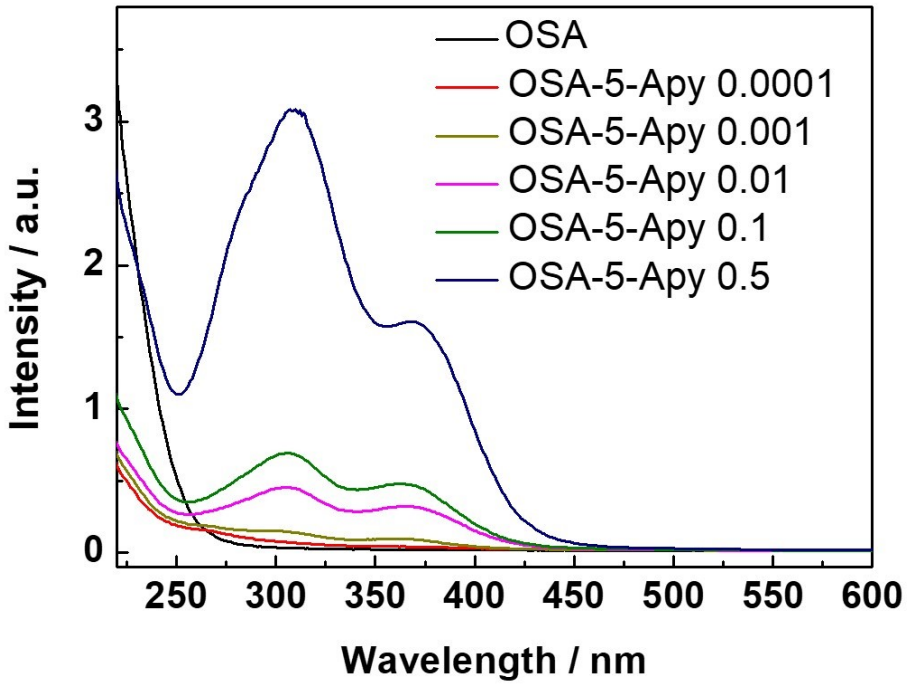

Figure S6. The UV-vis absorption spectra of OSA-5-Apy with different 5-Apy feed ratios.

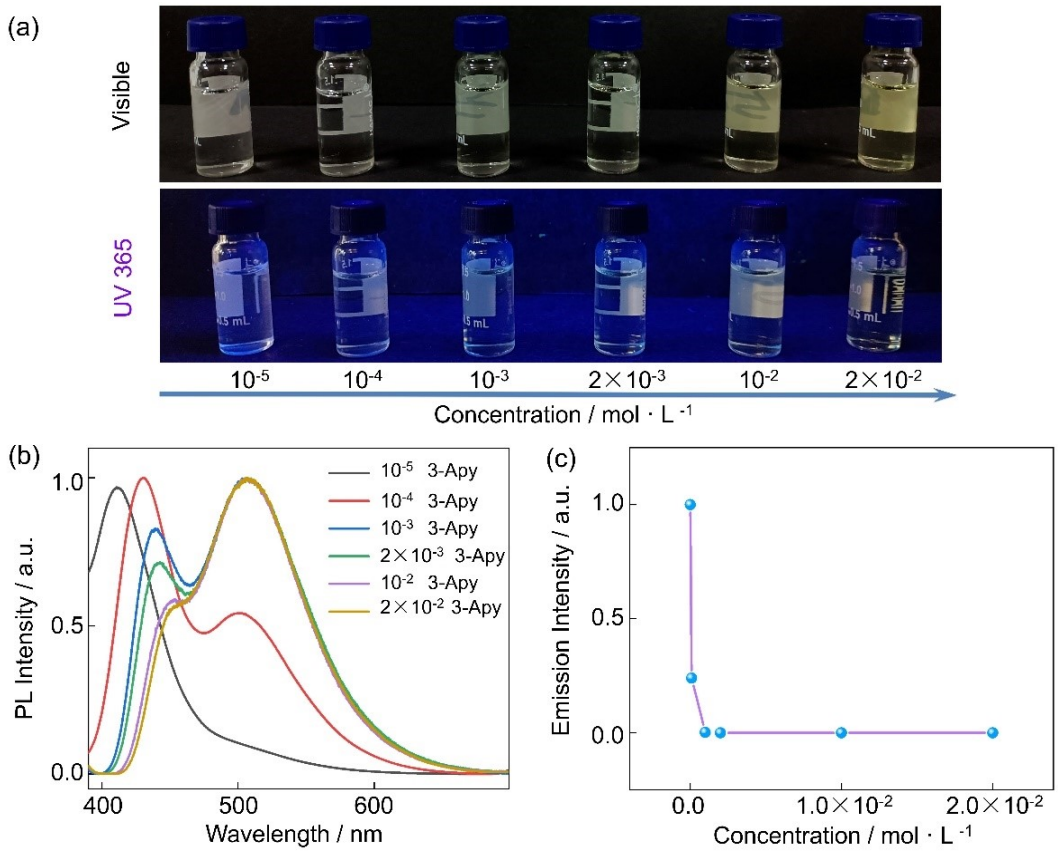

Figure S7. The photos of 3-Apy with different concentrations in daylight and UV light (a) Fluorescence emission spectra (b) and emission intensity (c) of 3-Apy with varying concentrations.

Both the fluorescent images (Figure S7a) and the curve of emission intensity variation (Figure S7c) reveal that the emission intensity deteriorates rapidly with the increase of the 3-Apy concentration, which indicates that ACQ phenomenon has occurred in its solutions. Moreover, the corresponding emission spectra also reveal red-shift emissions and an obviously low energy peak at about 510 nm, which is reasonably ascribed to the excimer emission. In all, herein the 3-Apy exhibits an ACQ behavior.

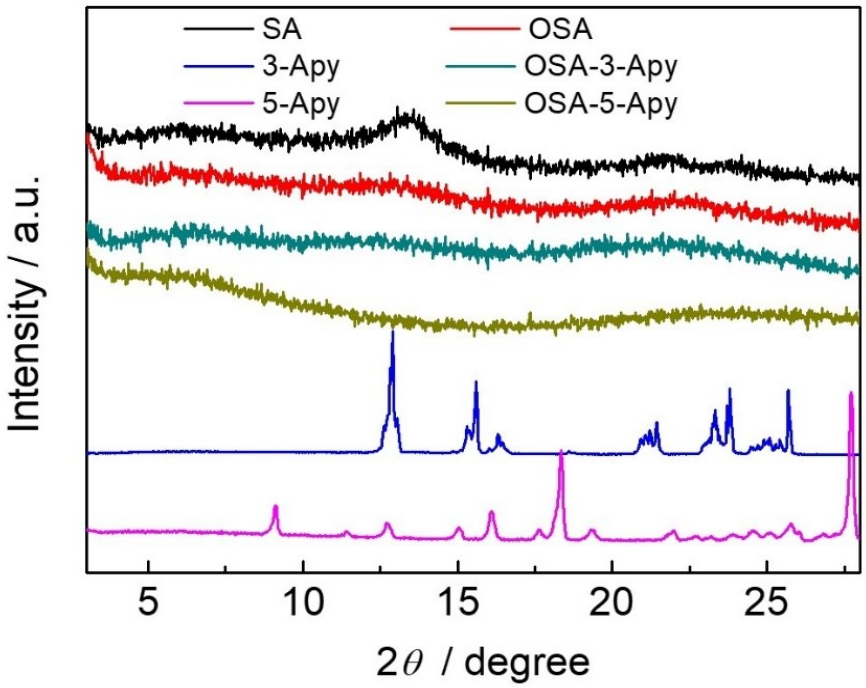

Figure S8. The XRD curves of SA, OSA, 3-Apy, 5-Apy, OSA-3-Apy, and OSA-5-Apy.

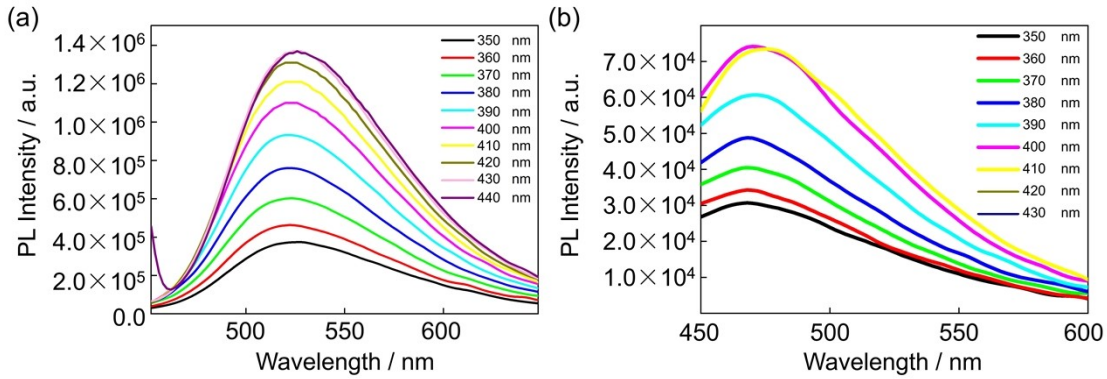

Figure S9. The excitation spectra of OSA-3-Apy (a) and OSA-5-Apy (b).

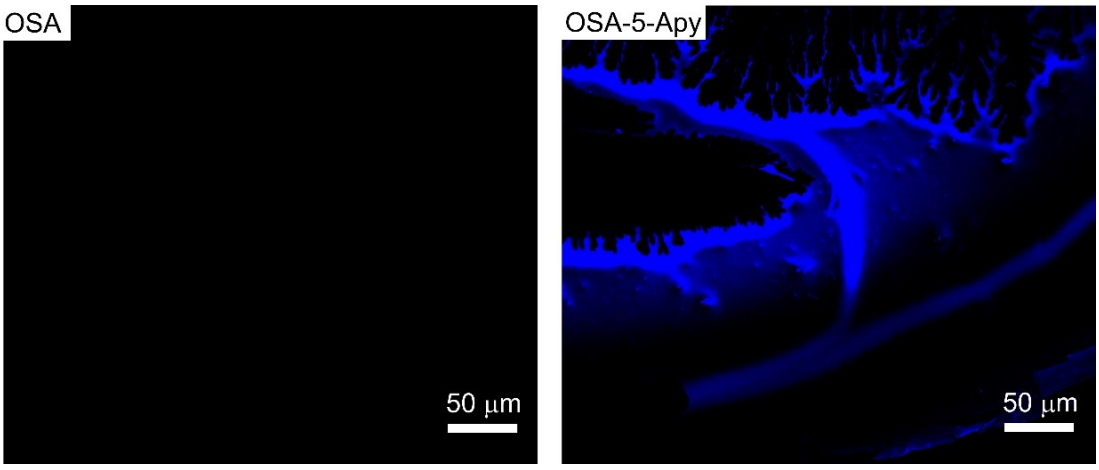

Figure S10. The fluorescence microscopy photos of OSA and OSA-3-Apy with the same concentration.

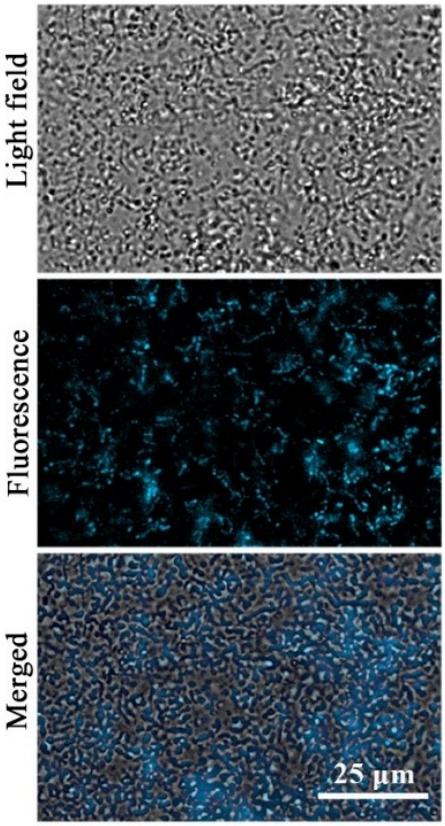

Figure S11. The photos of the living E. coli stained by OSA-3-Apy in imaging experiments.

Table S1. GPC comparative analyses for SA, OSA, and OSA-3-Apy.

Sample	M_n (kDa)	M_w (KDa)	PDI
SA	77	176	2.29
OSA	12	19	1.57
OSA-3-Apy	29	39.7	1.93

3. References

[1] (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.,* 2003, **54**, 724-728.

(b) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 2003, **56**, 2257-2261.