Electronic Supplementary Material (ESI) for Materials Horizons.

ELECTRONIC SUPPLEMENTARY INFORMATION

AIE-based universal super-resolution imaging for inorganic and organic nanostructures

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CONTENTS

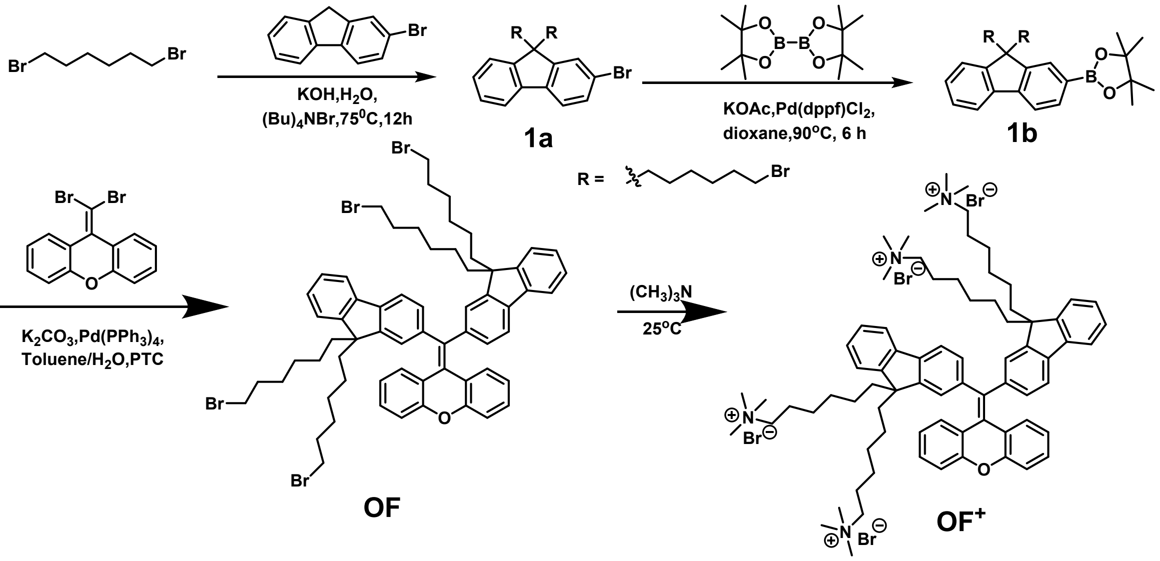
1. EXPERIMENTAL.

(a) INSTRUMENTATION.

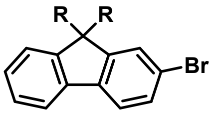
All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Energy, Aladdin, Alfa Aesar, J&K and Sinopharm Chemical Reagent Co. Ltd. All reactions were carried out under a dry nitrogen atmosphere and the temperatures were measured externally. Toluene, dioxane and tetrahydrofuran (THF) were dried using sodium wire and benzophenone as the indicator. Other solvents were dried over CaH_2 with stirring overnight followed by distillation under reduced pressure. Reported yields are isolated yields. Purification of all final products was accomplished by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot (visualized using UV-light at 254 nm and 365 nm) was obtained on thin film chromatography plate. The UV-Vis absorption and photoluminescence emission of the compounds were recorded on Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600) and Edinburgh instruments (FLS 920 spectrometers), respectively. The NMR spectra were recorded using a 600M Bruker AscendTM 600MHZ in $CDCl_3$ or CD_2Cl_2 and an internal standard of tetramethylsilane was used. The relative fluorescence quantum yields were estimated using N,N'-di(2,6-diisopropylphenyl)terrylene-3,4:11,12-tetracarboxdiimides in chloroform as standard material. The Mass spectra were recorded using an Agilent 1100 LC/MSD Trap. MALDI TOF mass spectra were recorded with a MALDI-TOF-TOF (Bruker ultrafleXtreme).

(b) SYNTHESIS PROCEDURES.

Scheme S1. The Synthesis of OF and OF^+



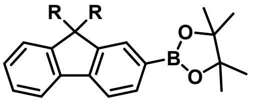
The synthesis of 1a.



Under a nitrogen atmosphere, 50 wt% sodium hydroxide aqueous solution (50 mL) was added to the mixture of 2-bromofluorene (9.8 g, 40 mmol), tetrabutylammonium bromide (1.28 g, 4 mmol) and 1, 6-Dibromohexane

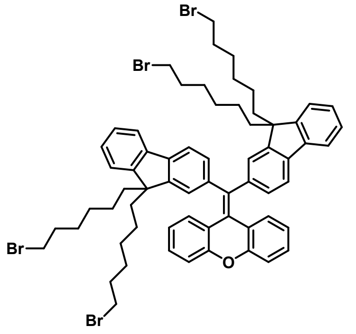
(150 mL). The reaction mixture was stirred at 70 °C for 12 h. After cooling down to room temperature, the organic layer was separated and the water layer was extracted with DCM. The combined organic solution was washed with water several times. After evaporation of the dichloromethane, the residual liquid reagent was removed under vacuum. The crude product was purified by column chromatography over silica gel with hexane as the eluent to give a colorless liquid (19.01 g, 83.2%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.29 (m, 3H), 3.28 (t, J = 6.8 Hz, 4H), 2.00 – 1.87 (m, 4H), 1.65 (p, J = 6.9 Hz, 4H), 1.19 (p, J = 7.6 Hz, 4H), 1.12 – 1.03 (m, 4H), 0.65 – 0.53 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.56, 149.90, 140.14, 140.01, 130.03, 127.57, 127.08, 126.03, 122.78, 121.10, 121.03, 119.82, 55.24, 40.12, 33.91, 32.61, 28.99, 27.75, 23.46.

The synthesis of 1b[2].



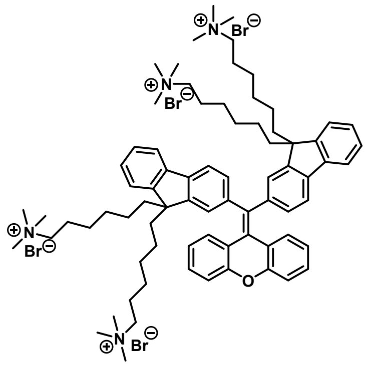
Under a nitrogen atmosphere, bis(pinacolato)diboron (11.43 g, 45 mmol), **1a** (17.14g, 30 mmol), KOAc (11.76 g, 120 mmol), and Pd(dppf)Cl_2 (1.10 g, 1.5 mmol) were dissolved in dioxane (300 mL) and heated to 90 °C and stirred for 6 h. After cooling down to room temperature, the solvent was evaporated under vacuum. The residue was dissolved with dichloromethane (100 mL), and washed with water three times, the organic layer was dried over magnesium sulfate. The solvent was removed under vacuum. The crude product was purified by column chromatography over silica gel with hexane/dichloromethane as the eluent to give a light white solid (13.73g, 74%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 1H), 7.75 – 7.66 (m, 3H), 7.33 (d, J = 5.8 Hz, 3H), 3.26 (t, J = 6.9 Hz, 4H), 2.06 – 1.92 (m, 2H), 1.63 (p, J = 7.0 Hz, 4H), 1.39 (s, 12H), 1.16 (p, J = 7.5 Hz, 4H), 1.09 – 1.01 (m, 4H), 0.63 – 0.51 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.90, 149.46, 144.10, 140.91, 133.83, 128.69, 127.59, 126.82, 122.82, 120.16, 119.03, 83.74, 54.95, 40.06, 33.95, 32.64, 29.00, 27.74, 24.96, 23.43.

The synthesis of OF



A mixture of 1, 1-dibromo-2,2-diphenylene (0.352 g, 1 mmol), **1b** (1.48 g, 2.4 mmol), Pd(PPh_3)$_4$ (0.120 g, 0.1 mmol), tetrabutylammonium hydrogen sulfate (0.034 g, 0.1 mmol), K_2CO_3 (0.414 g, 3 mmol) were stirred in toluene (30 mL) and water (15 mL) at 90 °C under nitrogen atmosphere overnight. After cooling down to room temperature, the organic layer was separated and dichloromethane (50 mL) was added. The organic solution was washed with water three times. The organic layer was dried over magnesium sulfate, and the solvent was removed under vacuum. After filtration, the residue was purified by column chromatography over silica gel with hexane/dichloromethane as the eluent to give a red solid (0.987 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 4H), 7.33 – 7.27 (m, 6H), 7.25 – 7.21 (m, 4H), 7.18 (d, J = 7.5 Hz, 2H), 7.13 – 7.09 (m, 4H), 6.65 – 6.60 (m, 2H), 3.25 (t, J = 6.8 Hz, 8H), 1.91 – 1.78 (m, 8H), 1.62 (p, J = 7.1 Hz, 8H), 1.21 – 1.08 (m, 8H), 0.99 (p, J = 7.4 Hz, 8H), 0.62 – 0.48 (m, 8H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.51, 150.48, 142.56, 140.75, 139.77, 139.57, 129.03, 128.55, 127.95, 127.10, 126.93, 125.01, 124.82, 124.12, 122.67, 122.29, 120.01, 119.73, 116.39, 54.85, 40.17, 33.93, 32.66, 29.07, 27.79, 26.92, 23.50. MALDI-TOF-MS calcd. for $C_{64}H_{70}Br_4O$: 1174.88; found: [M+] 1174.76.

The synthesis of OF$^+$



In a 25 ml flask, **OF** (100 mg) was dissolved into THF (10 mL). trimethylamine (TMA) solution in ethanol (33%, 5 mL) was then added at -78 °C. After stirred at room temperature for 24 h, some solid precipitated. Then trimethylamine (TMA) solution in ethanol (33%) was added to the mixture until the solid was completely dissolved. After stirring for another 24 h, the solvent was evaporated under vacuum. The resulting solid mixture was washed with THF twice, collected by centrifugation and dried at 45 °C overnight in vacuum to afford **OF$^+$** (110 mg, 92%) as a light-yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.83 – 7.74 (m, 4H), 7.48 – 7.40 (m, 4H), 7.35 – 7.30 (m, 4H), 7.29 – 7.21 (m, 6H), 7.01 (d, J = 8.0 Hz, 2H), 6.66 (t, J = 7.4 Hz, 2H), 3.25 – 3.15 (m, 8H), 3.00 (s, 36H), 2.00 – 1.84 (m, 8H), 1.46 (t, J = 7.6 Hz, 8H), 1.08 – 0.94 (m, 16H), 0.60 – 0.39 (m, 8H). ^{13}C NMR (151 MHz, DMSO) δ 153.41, 150.67, 142.47, 140.62, 140.50, 139.73, 129.02, 128.93, 128.23, 127.80, 127.48, 124.62, 124.35, 123.30, 122.84, 120.88, 120.50, 116.85, 65.49, 54.98, 52.51, 29.25, 25.92, 23.79, 22.52.

(c) SUPER-RESOLUTION IMAGING.

The samples for the optical imaging were dispersed on a clean coverslip by a simple drop-coating method. The coverslips with bacterial nanocelluloses were then exposed in atmosphere until the water evaporates completely, the difference was the coverslips with silver nanowires and block copolymer micelles were spun a minute at 3000 rpm. At the time of super-resolution imaging experiments, the 405 nm laser needed to be on all the time, and we dropped 50 μL OF$^+$ water solution on the sample. Usually 5000 frames were recorded with a speed of 20 ms per frame to get a good super-resolution image. The size of individual pixel of the pictures from conventional optical imaging is 100 nm while it is 10 nm for the reconstructed.

The super-resolution microscopy imaging was obtained by the home-built system consisting of an Olympus IX 73P2F inverted optical microscope, a 100x/NA1.49 oil immersion TIRF objective (UAPON 100XOTIRF, Olympus), a 405-nm laser (OBIS 405 LX, Coherent, 50 mW), and an sCMOS camera (ORCA-flash4.0 C11440). A dichroic mirror (DM: ZTUV-405/488/561rpc, Chroma) and a single band filter (EM: ET525/50m, Chroma) were used to separate the collected fluorescence from scattering laser and impurity fluorescence. ImageJ plugin written in Java was used to analyze the image.

The Image J plugins written in Java was used to analyze the images. An ultra-fast and high-precision image analysis method, termed MaLiang[3] (maximum likelihood algorithm encoded on a Graphics Processing Unit (GPU)), was established. Briefly, Gaussian fitting with the following equation was used to localize the single molecules in the conventional fluorescence microscopy images.

$$I = I_{sig} \times exp\left(- \frac{(i - x_0)^2 + (j - y_0)^2}{2s^2} \right) + I_{bkg}$$

Here (x_0, y_0) was the position of fluorescent molecule, s was the width of Gaussian kernel, and I_{sig} and I_{bkg} denoted the peak value of signal and the intensity of background photon (including background fluorescence, remnant laser scattering and average readout noise), respectively. The localization precision for individual fluorescent molecule imaged by sCMOS camera could be calculated by:

$$< \Delta x^2 >= \frac{2s^2 + a^2/12}{\emptyset N} + \frac{16\pi s^4(\emptyset I_b)}{a^2(\emptyset N)^2}$$

where s was the width of Gaussian kernel, a was the pixel size, I b was the background photon $(I_b = I_{bkg} - N_r^2)$, N_r was the readout noise, Φ was the quantum efficiency, and N was the number of the photons collected.

2. ADDITIONAL DATA

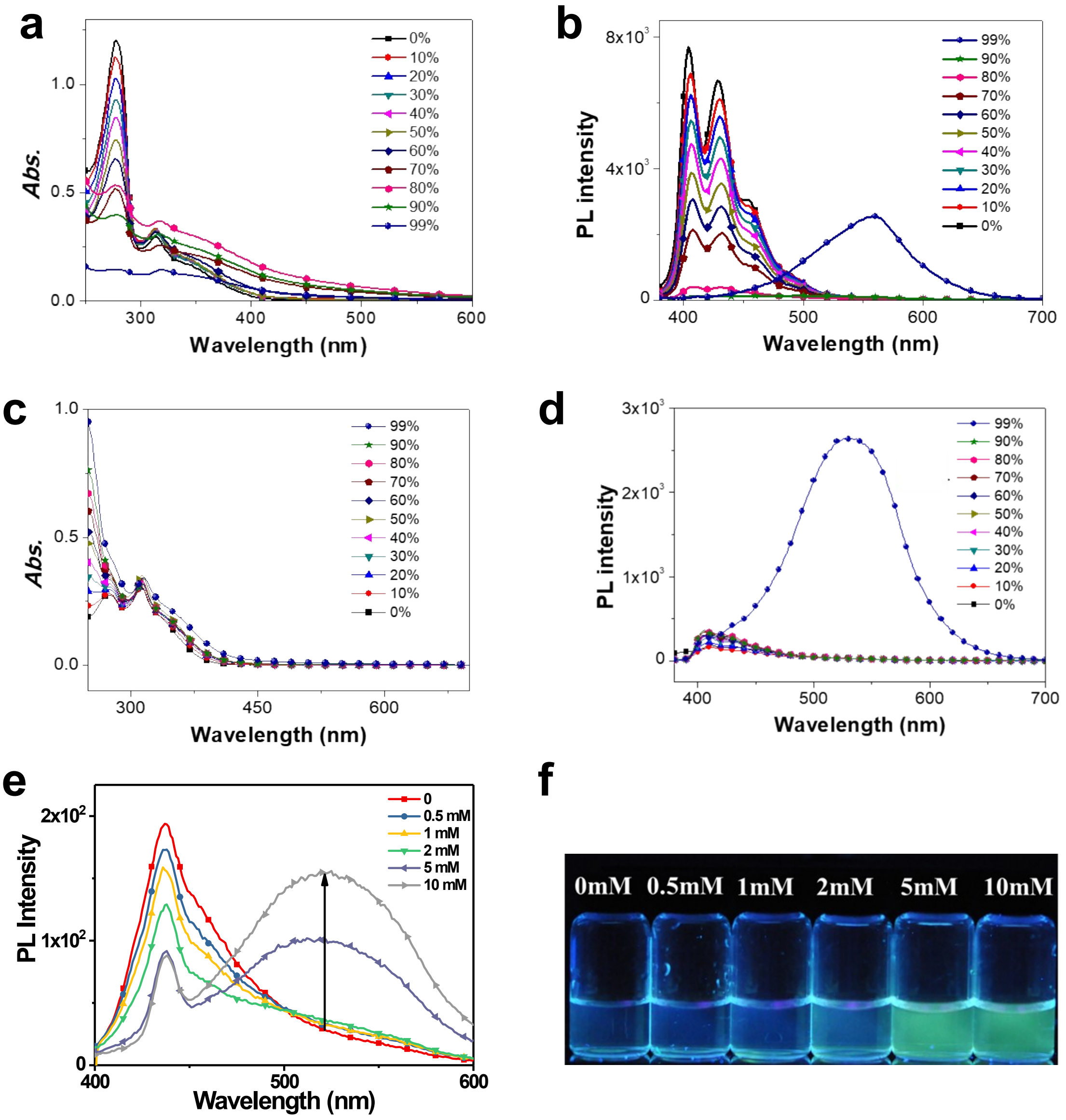


Fig. S1 (a) UV−vis absorption of OF in different water/THF mixture. (b) PL spectra of OF in in water/THF ([OF] = 1.0 μM, excitation at 380 nm). (c) UV−vis absorption of OF^+ in different water/THF mixture. (d) PL spectra of OF^+ in in water/THF ($[OF^+]$ = 1.0 μM, excitation at 380 nm). (e) The fluorescence emission spectra of OF^+ with different concentration of PMDETA. The concentration of OF^+ is kept at 1 μM. (f) Fluorescence pictures of OF^+ with different concentration of PMDETA under 365 nm irradiation. The concentration of OF^+ is kept at 1 μM.

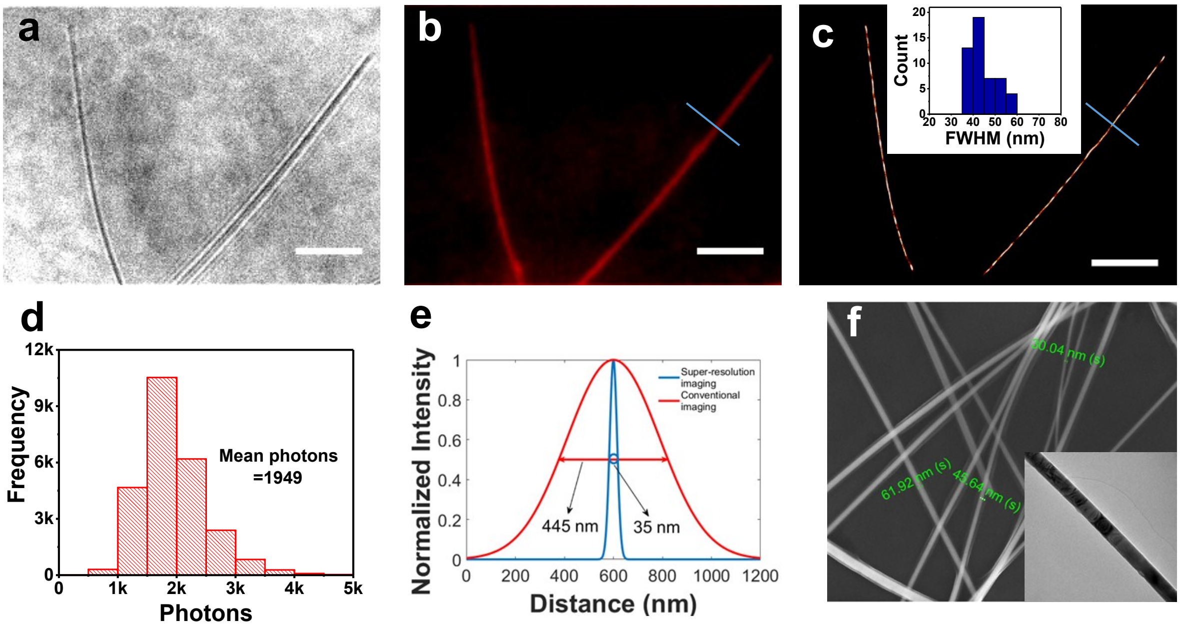
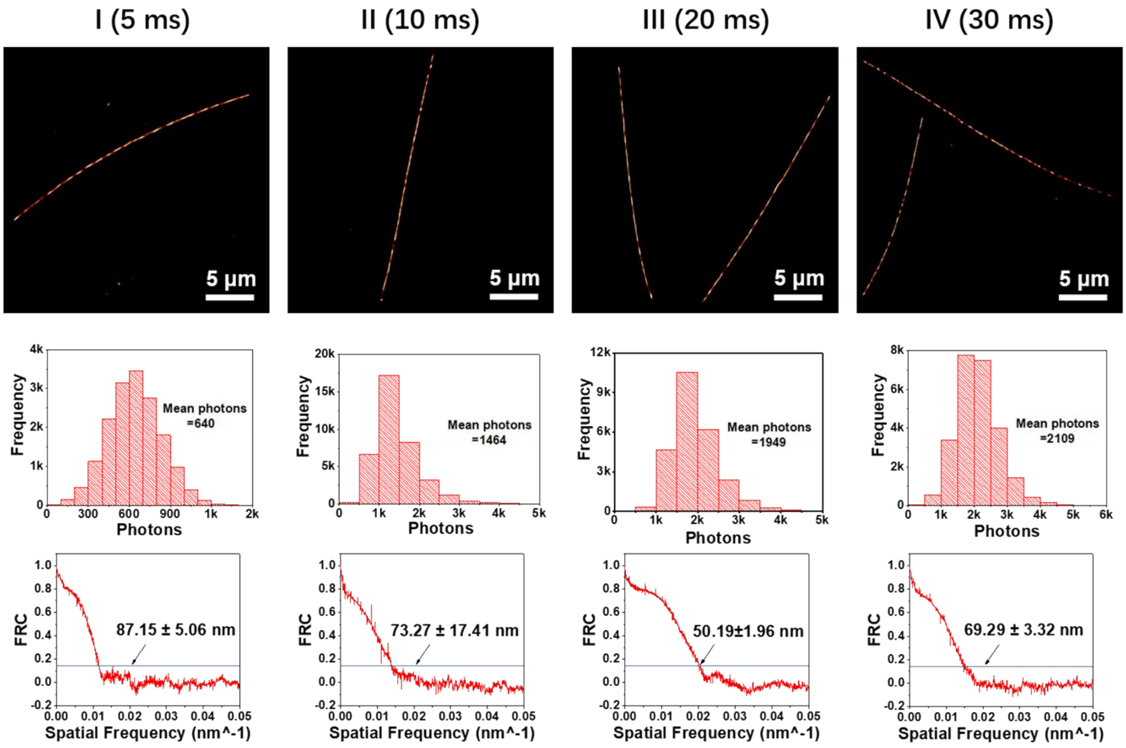
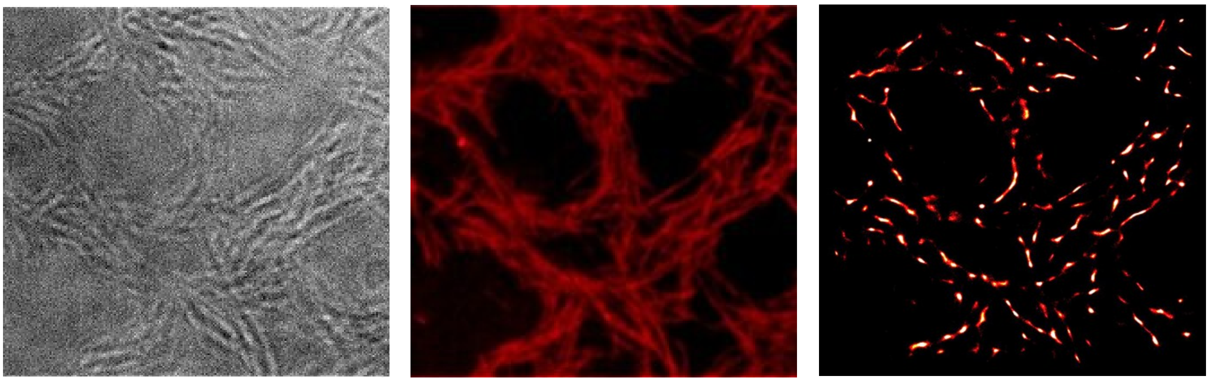


Fig. S2 Super-resolution imaging of silver nanowires. (a) Bright field image. (b) Conventional fluorescence image. (c) Super-resolution image corresponding to the same field of fluorescence image. (d) The photon count distribution each event. (e) Conventional fluorescence and super-resolution imaging cross-sectional profiles of single silver nanowire. (f) SEM image of silver nanowires. Inset: TEM image of single silver nanowires.



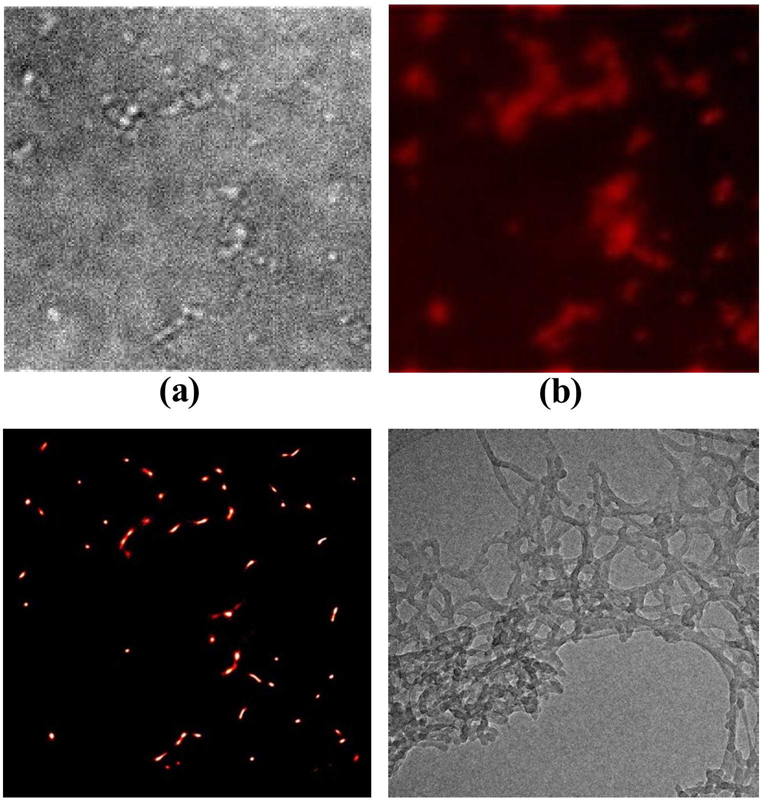
(a) (b) (c) (d)

Fig. S3 Super-resolution imaging at various exposure times. (a) 5 ms. (b) 10 ms. (c) 20 ms. (d) 30 ms.



(a) (b) (c)

Fig. S4 Super-resolution imaging of bacterial nanocelluloses. (a) Bright field image. (b) Conventional fluorescence image. (c) Super-resolution image corresponding to the same field of fluorescence image.

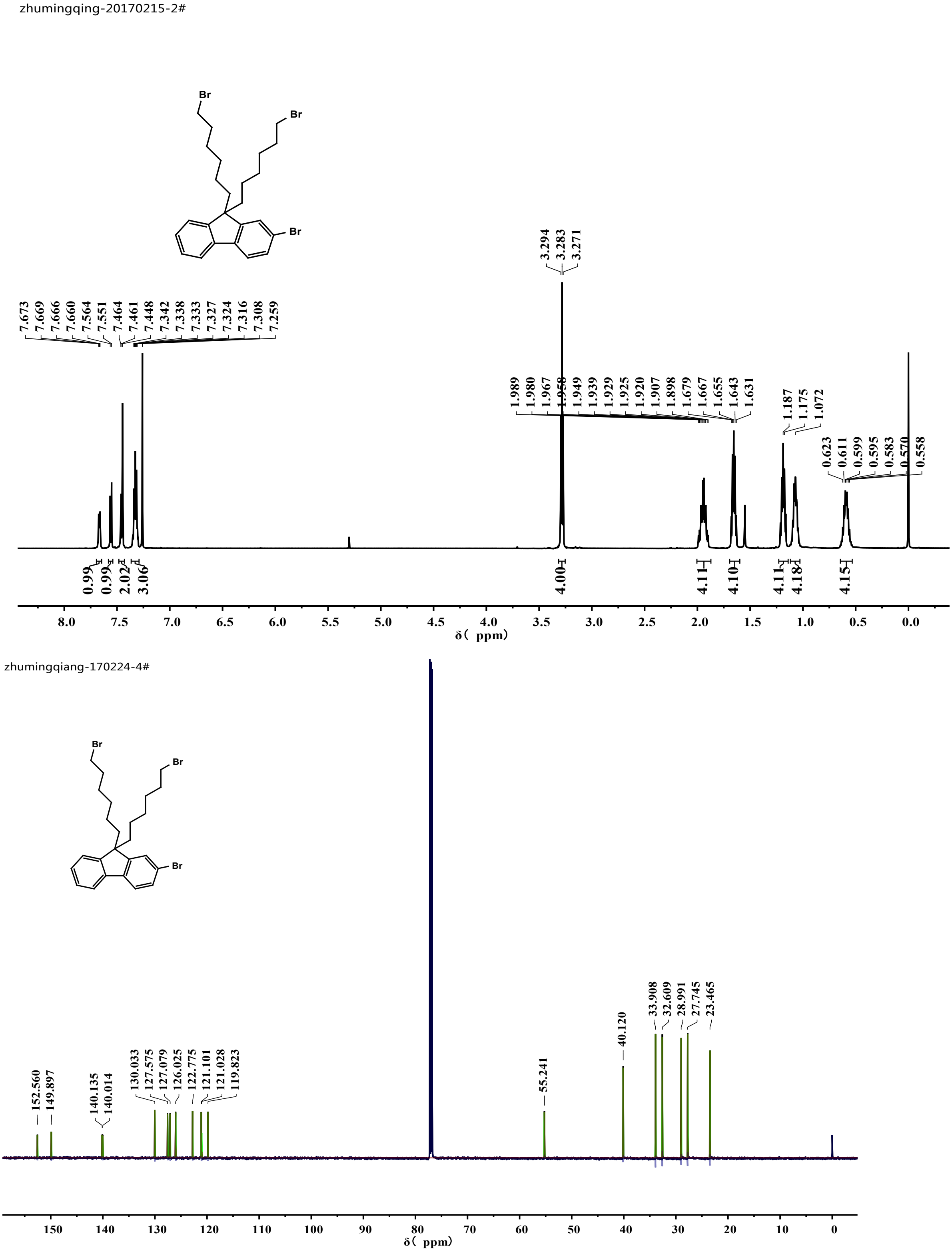


(a) (b)

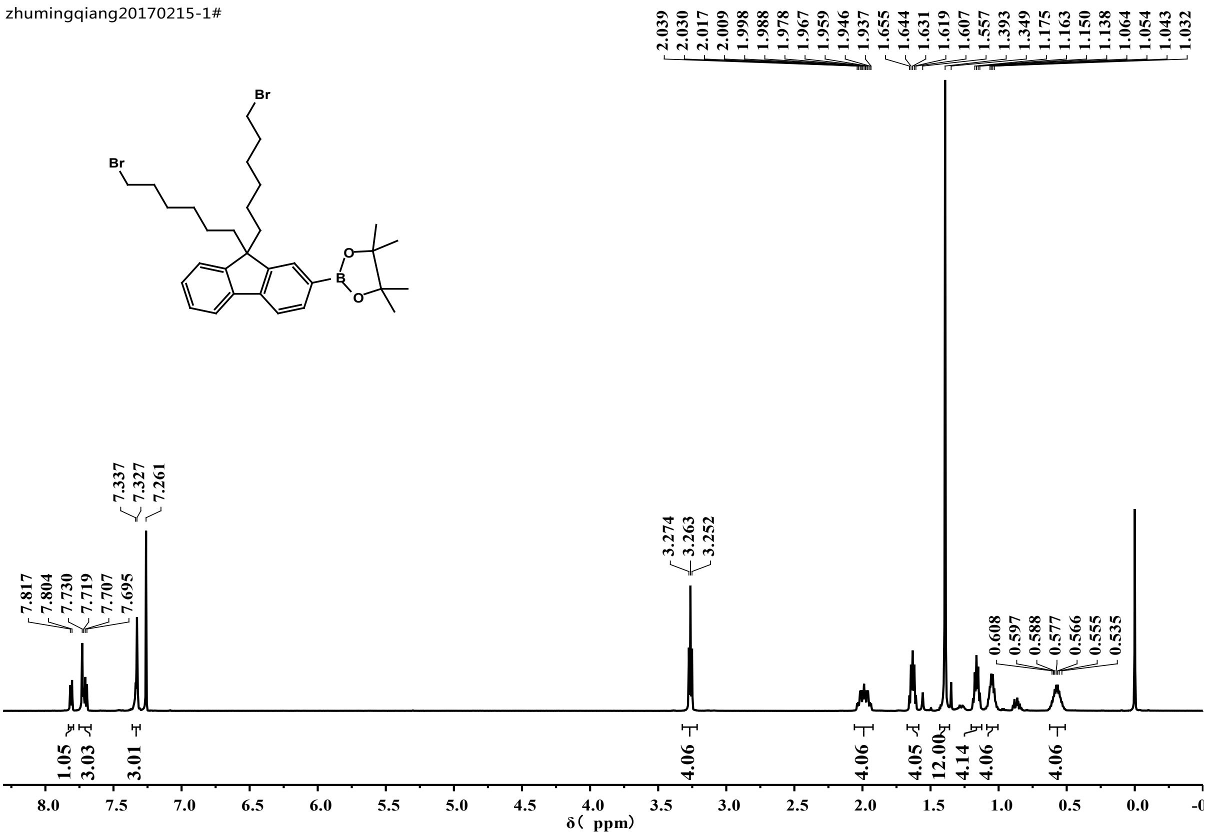
(c) (d)

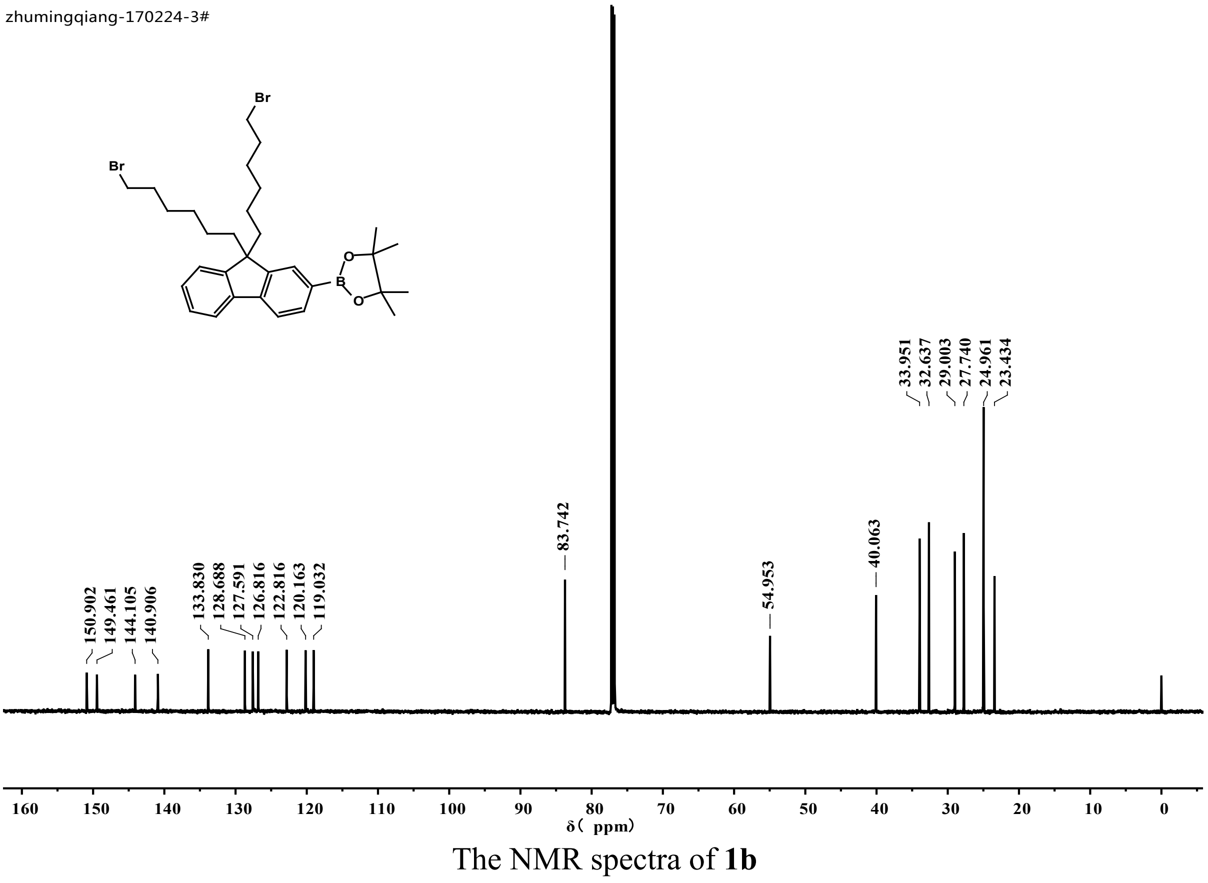
Fig. S5 Super-resolution imaging of block copolymer micelles of PSt-b-PAA. (a) Bright field image. (b) Conventional fluorescence image. (c) Super-resolution image corresponding to the same field of fluorescence image. (d) TEM image of block copolymer micelles of PSt-b-PAA.

3. NMR SPECTRA.

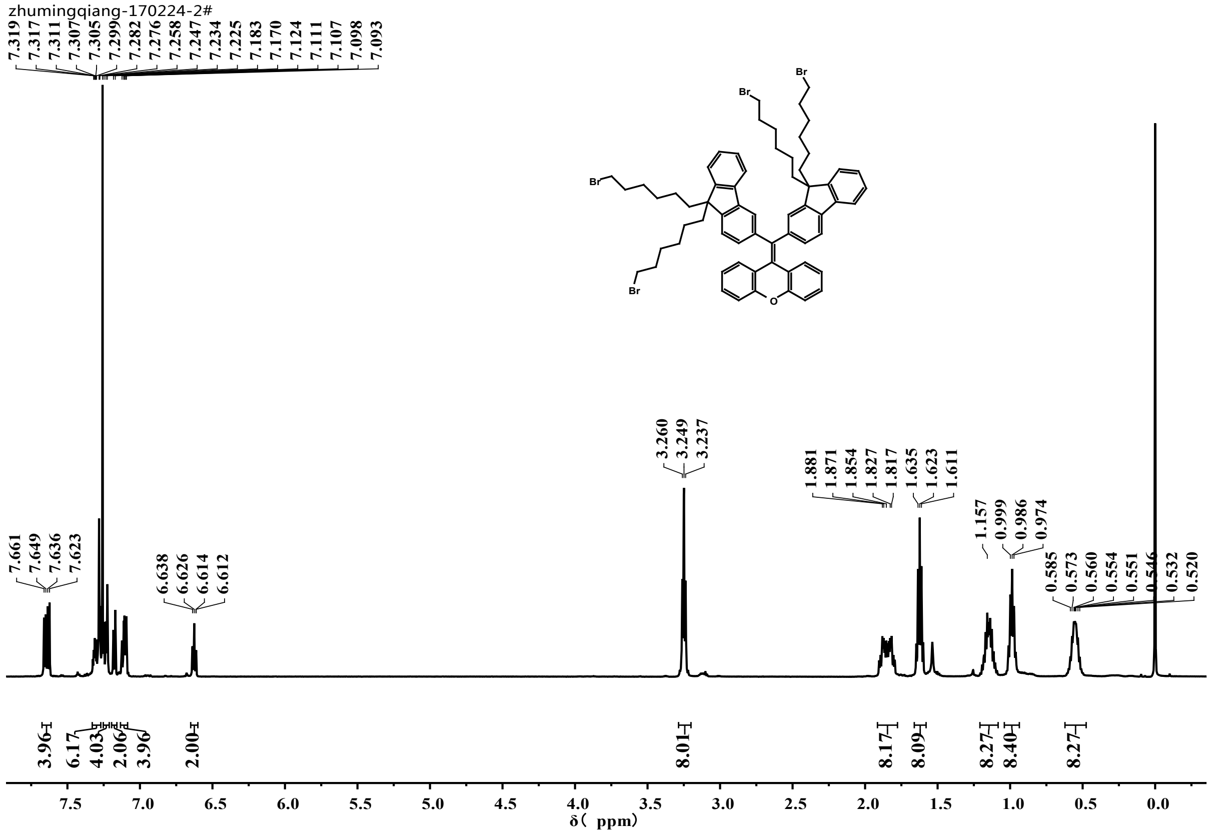


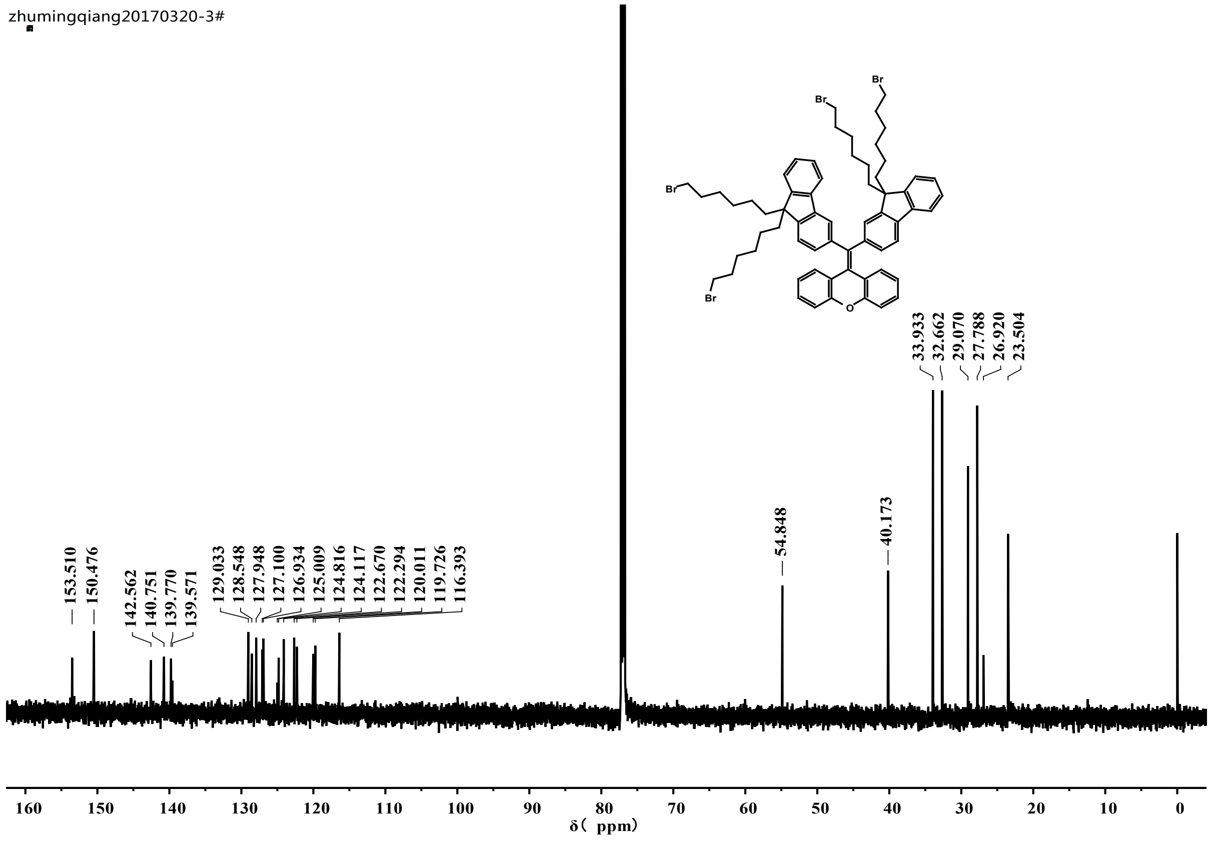
The NMR spectra of **1a**



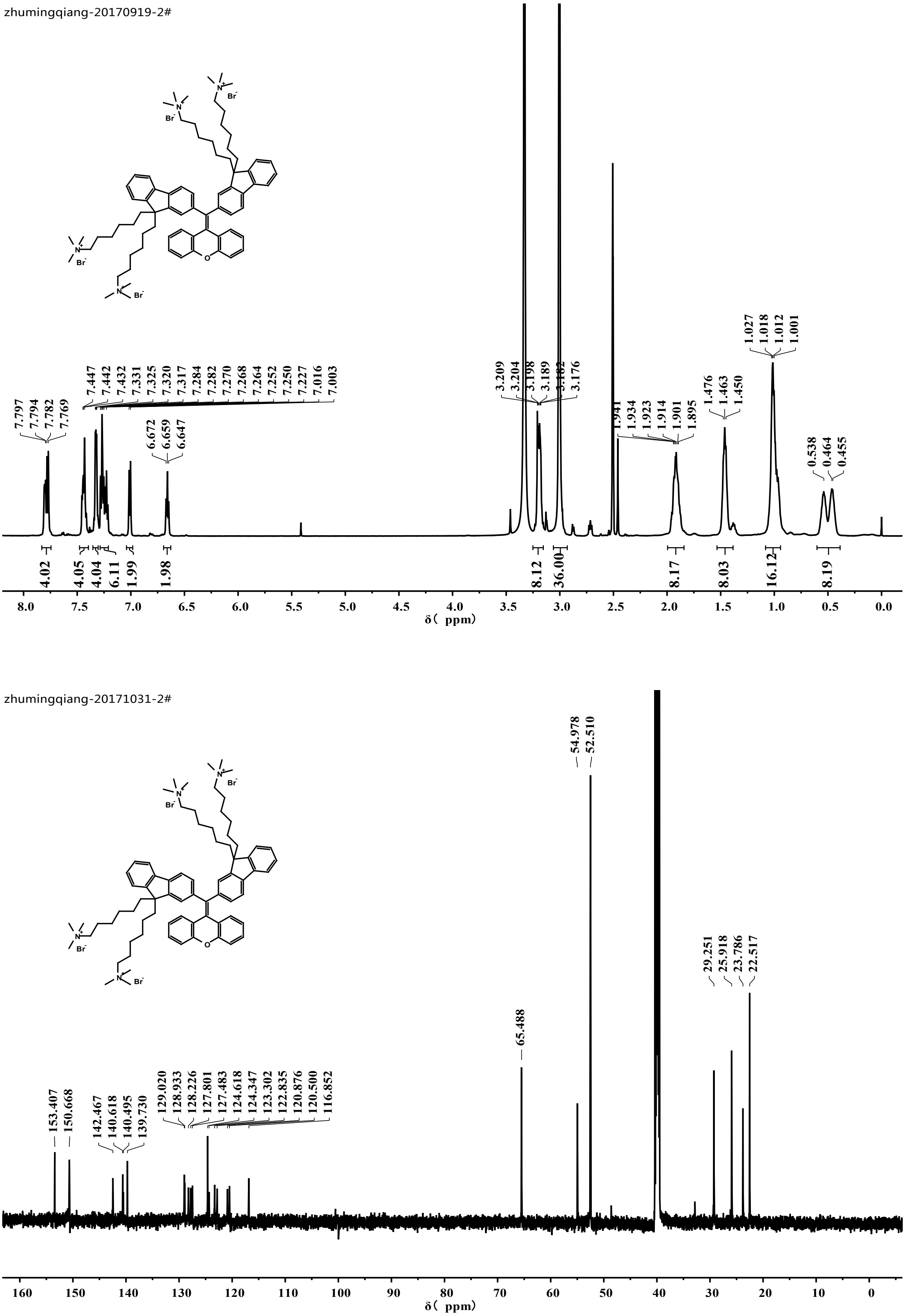


The NMR spectra of **1b**





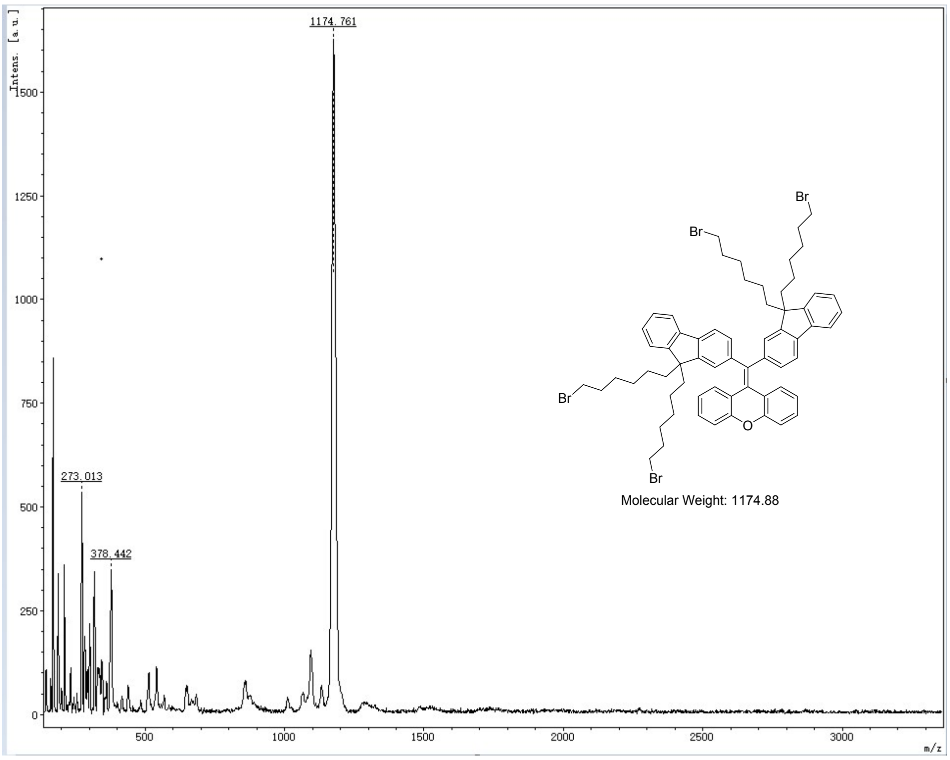
The NMR spectra of **OF**



The NMR spectra of **OF**$^+$

4. MASS SPECTRA.

OF



5. REFERENCES.

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