**Design and preparation of a novel fluorescent naphthalimide derivative supramolecular self-assembly system and its bioimaging application**

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**Experimental**

**Reagents and materials**

Octadecylamine, 4-bromo-1,8-naphthalimide and phenylsilane were all purchased from Sinopharm Chemical Reagent Co., Ltd. Methyl 2-(allyloxy)-4-hydroxybenzoate was purchased from Shanghai Qianglu Medicine Co., Ltd. All inorganic metallic salts were provided by Zhengzhou Alfachem Co., Ltd. All other reagents were analytically pure. Water used throughout was deionized and then triply distilled. MCF-7 cells (Michigan Cancer Foundation–7) was provided by the Institute of Biochemistry and Cell Biology (Chinese Academy of Sciences).

**Gelation test**

The gelator and solvent were put in a septum-capped test tube and heated (>80 °C) until the solid was dissolved. The sample vial was then cooled to 25 °C (room temperature). Qualitatively, gelation was considered successful if no sample flow was observed upon inversion of the container at room temperature (the inverse flow method)24. Xerogels were obtained by evaporation of solvent from the gel via freeze drying.

**Confocal imaging for living cells**

The MCF-7 cell lines (human cervical epitheloid carcinoma) were provided by the Institute of Biochemistry and Cell Biology (Chinese Academy of Sciences). MCF-7 cells were grown in culture media (RPMI 1640) at 37 °C under a humidified atmosphere containing 5% CO2 for 24 h. Cells were plated on 15 mm glass coverslips and allowed to adhere for 24 h. The cells were incubated for 24 h prior to the imaging experiments. The living cells

were stained with 10 μM probe **N-18** for 30 min at 37 °C under 5% CO2. The cells were imaged under an Olympus FV1000 confocal luminescence microscope. For **N-18**, excited at 405 nm, emission was collected by a range 430*–*530 nm equipped with a 40×-oil immersion objective lens.

**Instrumentation conditions**

1H NMR and 13C NMR spectra were recorded on a Bruker-Avance (Bruker, Ltd., Switzerland), at 400 and 100 MHz, respectively. Proton chemical shifts were reported in parts per million downfield from tetramethylsilane. HRMS was recorded on a LTQ-Orbitrap mass spectrometer (ThermoFisher, San Jose, CA, USA). Field emission scanning electron microscope (FESEM) images were obtained using a FE-SEM S-4800 instrument (Hitachi, Ltd., Tokyo, Japan). Samples were prepared by spinning the samples on glass slides and coating with Pt. Powder X-ray diffractions were generated by using a Philips PW3830 (Philips, Ltd., Eindhoven, Holland) with a power of 40 kV at 40 mA (Cu target, λ = 0.1542 nm). UV-vis absorption spectra were recorded on a UV-vis 2550 spectroscope (Shimadzu, Ltd., Tokyo, Japan). Fluorescent spectra were recorded on Edinburgh Instruments FLS 900 (Edinburgh Instruments, Ltd. Livingston, UK). Water contact angles were performed using the sessile drop method (Dataphysics, OCA 20). The water droplets were introduced using a microsyringe, and images were captured to measure the angle of the liquid-solid interface; each sample was recorded at three different points. Cell imaging was carried out after washing the cells with PBS buffer (2 mL×3 times). Fluorescent images of the MCF-7 cells were observed on an Olympus FV1000 confocal laser-scanning microscope with an objective lens (×40). The excitation wavelength was 405 nm, and the emission filter was 420–500 nm.

**Synthesis of gelator 1**



**Scheme S1** The synthesis route of **N-18**.

**Compound 4** was synthesized according to literature 1.

**Synthesis of 3**: Compound **4** (2.60 g, 4.79 mmol), methyl-2-(allyloxy)-4-hydroxybenzoate (1.0 g, 4.79 mmol) and K2CO3 (1.98 g, 14.37 mmol) were mixed in DMF (50 mL). The reaction mixture was stirred for 12 h at 120 ºC under nitrogen atmosphere. After the reaction was over, DMF was removed under reduced pressure and the residue was subjected to column chromatography (petroleum ether/dichloromethane: 1/1, v/v as eluent) on silica gel to give **3** as a yellow powder. Yield 60.6 %; 1HNMR (600 MHz, CDCl3): 8.66 (d, *J* = 7.8 Hz, 1H), 8.58 (d, *J* = 7.8 Hz, 1H), 8.50 (t, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 8.4 Hz, 1H), 6.05 (m, 1H), 5.49 (dd, *J* = 17.4 Hz, 1H), 5.31 (dd, *J* = 10.2 Hz, 1H), 4.58 (m, 2H), 4.17 (t, *J* = 7.8 Hz, 2H), 3.90 (s, 3H), 1.73 (m, 2H), 1.42 (m, 2H), 1.34 (m, 2H), 1.28-1.24 (m, 26H), 0.86 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3): 165.9, 164.2, 163.7, 160.3, 159.9, 158.2, 134.1, 132.5, 132.1, 128.4, 126.9, 124.3, 122.9, 118.0, 117.2, 112.6, 111.4, 105.4, 69.7, 52.2, 40.6, 32.0, 29.8, 29.5, 29.4, 28.2, 27.2, 22.8, 14.2. HRMS calculated for C41H54NO6 [M+H]+ 656.3951, found: 656.3948.





**Figure S1** 1HNMR and 13CNMR spectra of compound **3** in CDCl3.

**Synthesis of 2**: Compound **3** (0.62 g, 0.95 mmol), phiiienylsilane (0.20 g, 1.90 mmol) and Pd(PPh3)4 (1.0 g, 0.86 mmol) were mixed in CH2Cl2 (50 mL). The reaction mixture was stirred for at room temperature under nitrogen atmosphere. After the reaction was over, CH2Cl2 was removed under reduced pressure and the residue was subjected to column chromatography (petroleum ether/dichloromethane: 2/1, v/v as eluent) on silica gel to give **3** as a yellow powder. Yield 91 %; 1HNMR (600 MHz, CDCl3): 11.00 (s, 1H), 8.65 (d, *J* = 7.8 Hz, 1H), 8.53 (t, *J* = 7.8 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 1H), 6.65 (dd, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 7.8 Hz, 2H), 3.96 (s, 3H), 1.71 (m, 2H), 1.41 (m, 2H), 1.35-1.23 (m, 26H), 0.86 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3): 170.0, 164.2, 163.8, 163.6, 161.9, 157.4, 132.5, 132.2, 132.1, 129.8, 128.3, 127.0, 124.6, 122.8, 114.0, 110.6, 107.6, 52.5, 40.6, 32.0, 29.8, 29.7, 29.5, 29.4, 28.2, 27.2, 22.8, 14.2. HRMS calculated for C38H50NO6 [M+H]+ 616.3638, found: 616.3641.





**Figure S2** 1HNMR and 13CNMR spectra of compound **2** in CDCl3.

**Synthesis of N-18**: Compound **2** (0.60 g, 0.97 mmol) and lithium hydroxide monohydrate (1.23 g, 29.2 mmol) were mixed in THF/H2O (120 mL, 1/1, v/v). The reaction mixture was stirred for at room temperature for 48 hours. After the reaction was over, THF was removed under reduced pressure and the pH value of the residue was tuned to **3** with diluted HCl solution. The crude product was subjected to column chromatography (methanol/dichloromethane: 1/20, v/v as eluent) on silica gel to give **N-18** as a yellow powder. Yield 95 %; 1HNMR (600 MHz, CDCl3): 10.70 (s, 1H), 8.66 (d, *J* = 6.6 Hz, 1H), 8.56 (d, *J* = 7.8 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 9.0 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 6.67 (m, 2H), 4.17 (t, *J* = 7.8 Hz, 2H), 1.73 (m, 2H), 1.41 (m, 2H), 1.37-1.24 (m, 28H), 0.86 (t, *J* = 7.2 Hz, 3H); 13CNMR (100 MHz, CDCl3): 172.7, 164.4, 164.3, 163.7, 163.0, 157.0, 133.2, 132.5, 132.1, 129.9, 128.3, 127.2, 124.7, 123.0, 118.8, 114.5, 110.8, 107.9, 107.3, 40.6, 32.0, 29.8, 29.7, 29.5, 29.4, 28.2, 27.2, 22.8, 14.2. HRMS calculated for C37H48NO6 [M+H]+ 602.3482, found: 602.3480.





**Figure S3** 1HNMR and 13CNMR spectra of compound **N-18** in CDCl3.

**Reference**

1. X. H. Cao, N. Zhao, H. T. Lv, Q. Q. Ding, A. P. Gao, Q. S. Jing and T. Yi, Strong Blue Emissive Supramolecular Self-Assembly System Based on Naphthalimide Derivatives and Its Ability of Detection and Removal of 2,4,6-Trinitrophenol. Langmuir, 2017, 33, 7788-7798.