# **Electronic Supplementary Information**

# A Fluorescent Sensor with High Selectivity for Ca<sup>2+</sup> against Mg<sup>2+</sup> in

## Seawater

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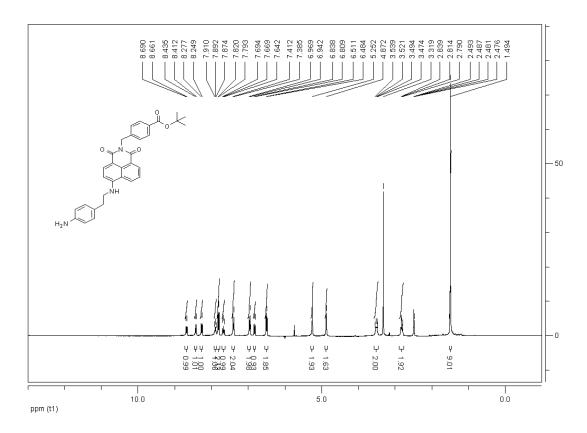
#### 1. Materials, Measurement and Methods

Unless otherwise noted, all materials including Aminocellulose and hydrogel D4 were obtained from Heowns Biochem Technologies LLC and were used without further purification. Flash chromatography was carried out on silica gel (300-400 mesh). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using Varian 300 MHz. MS spectra were recorded using Thermo Fisher Scientific Finnigan Lcqadvantage. Absorption spectra and fluorescence spectra were measured on the Gangdong A-230 photometer and F-280 fluorometer, respectively.

## 2. Synthesis

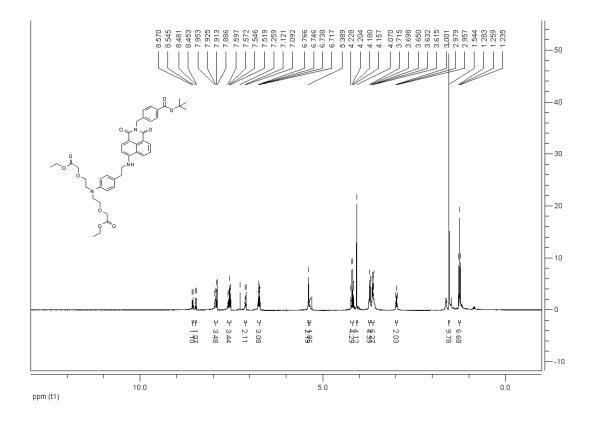
The compounds 1, 4 and 8 were synthesized according to a previously reported procedure. [1]

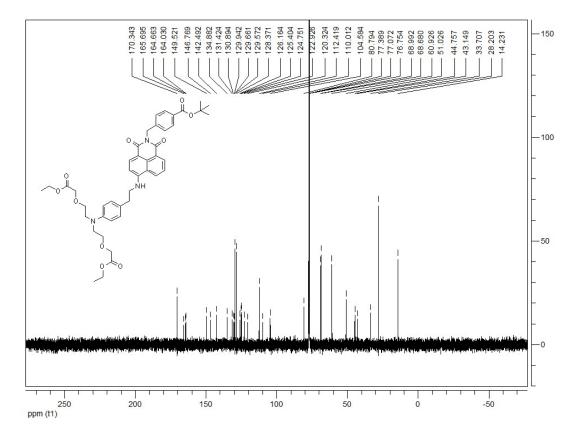
Synthesis of 5 A suspension of 1.94 g (14.22 mmol) compound 4, 4.0 g (9.48 mmol) t-butyl 4-chloro-1,8-naphthalimidylmethyl benzoate 1 and 2.36 mL (14.22 mmol) N,N-diisopropylethylamine in 5 mL Nmethylpyrolidinone (NMP) was heated at 95°C for 18 h. The progress was monitored by TLC (PE: EA=1:1). After the reaction was completed, the mixture was cooled and poured into 100 ml water. The resultant precipitate was filtered, dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with water (3 x 100 ml). The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to get 5.55 g crude product, which was purified by flash column chromatography, to obtain product 2.00 g. <sup>1</sup>H NMR (DMSO)  $\delta$  1.49(s, 9H), 2.79 (t, 2H), 3.32 (s, 2H), 3.47 (m, 2H), 5.25 (s, 2H), 6.48-8.69(m, 14H).

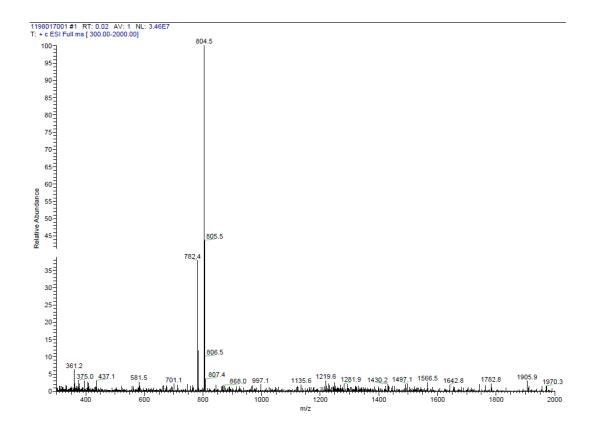


Synthesis of 9: A suspension of 0.5 g (0.96 mmol) of compound 5, 0.64 g (3.83 mmol) of compound 8, 0.64 mL (3.83 mmol) N, N-diisopropylethylamine and 0.64 g

(3.83 mmol) of KI in NMP (5 mL) was heated at 100°C for 20h under nitrogen atmosphere. The progress was monitored by TLC (PE: EA=1:1). After the reaction was complete, the mixture was cooled and poured into water. The resultant precipitate was filtered, dissolved in  $CH_2Cl_2$  and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated to get 0.55 g crude product, which was purified by flash column chromatography, to afford product 240 mg. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.29 (t, 6H), 1.48(s, 9H), 2.81 (t, 2H), 3.52 (t, 4H), 3.61 (t, 4H), 3.71 (t, 2H), 4.17 (t, 4H), 4.33 (s, 4H), 5.09 (s, 2H), 6.51-7.87 (m, 13H) <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  170.343, 165.695, 164.663, 164.029, 149.521, 146.769, 142.491, 134.882, 131.423, 130.893, 129.941, 129.661, 129.571, 128.371, 126.164, 125.404, 124.751, 122.926, 120.323, 112.418, 110.012, 104.583, 80.793, 77.389, 77.071, 76.753, 68.991, 68.679, 60.926, 51.025, 44.756, 43.149, 33.706, 28.203, 14.230. MS (+ESI): Calc. for MH<sup>+</sup>, 782.36; MNa<sup>+</sup>, 804.36; Found, 782.4; 804.5;

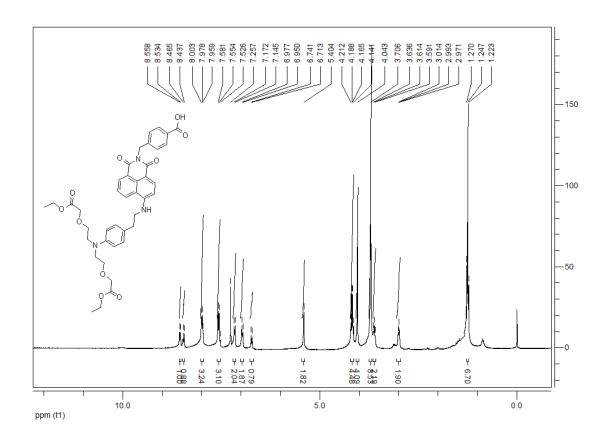


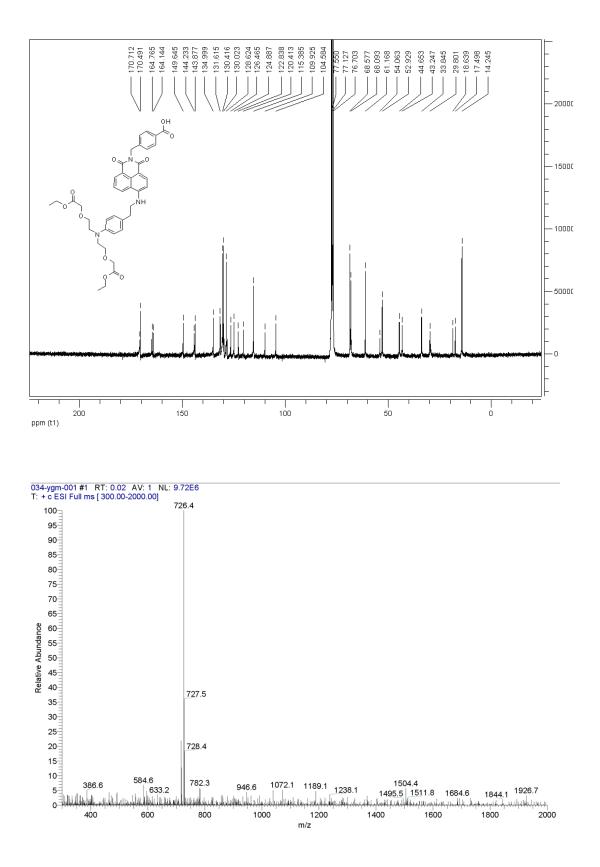




**Synthesis of 10:** 2mL of trifluoroacetic acid (TFA) was added into a solution of 0.15 g (0.19 mmol) of compound **9** in CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The resulting solution was stirred at room temperature for about 30 min when the TLC indicated that most of compound **7** were gone. The mixture was then diluted with 1:1 CH<sub>2</sub>Cl<sub>2</sub>:MeOH (20 mL) and the solvent was evaporated. The residue was dissolved in 20 ml methanol and evaporated again. This process was repeated for 6 times to remove TFA thoroughly, then placed on oil pump for 30 min to dry the product completely, afforded 144 mg yellow solid, which was used directly on to the next step without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  8.55 (d, *J* = 7.1 Hz, 1H), 8.45 (d, *J* = 8.4 Hz, 1H), 8.02 – 7.95 (m, 3H), 7.55 (t, *J* = 8.2 Hz, 3H), 7.16 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 5.40 (s, 2H), 4.18 (dd, *J* = 14.2, 7.1 Hz, 4H), 4.04 (s, 4H), 3.71 (s, 8H), 3.61 (t, *J* = 6.7 Hz, 2H), 2.99 (t, *J* = 6.5 Hz, 2H), 1.26 (d, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR

(CDCl<sub>3</sub>) & 170.712, 170.490, 164.765, 164.144, 149.644, 144.232, 143.877, 134.998, 131.615, 130.416, 130.023, 128.623, 126.464, 124.886, 122.837, 120.413, 115.385, 109.924, 104.584, 77.550, 77.126, 76.703, 68.577, 68.092, 61.168, 54.063, 52.928, 44.653, 43.247, 33.844, 29.801, 18.639, 17.498, 14.244. MS (+ESI): Calc. for MH<sup>+</sup>, 725.29; Found, 726.4.





Synthesis of 11: Hydrolysis of 10: 15 mg (20.5  $\mu$ mol) of compound 10 were dissolved in methanol (1 mL) and a solution of NaOH 33 mg (0.82 mmol) in water (3

ml). The resultant solution was stirred at 40 °C for 8h. The progress was monitored by TLC (DCM: MeOH=5:1). After the reaction was complete, it was used directly on to the fluorescence response without further purification.

Synthesis of 12: Immobilization of calcium fluoroionophore (10) onto aminocellulose: Aminocellulose (10.5 g) [2] was suspended in 100 mL 2.5% aqueous sodium carbonate for 30 min, filtered, re-suspended in 100mL DMF for 30 min, filtered, washed twice more with DMF in order to replace trapped water. The washed cellulose was then transferred into a flask containing 10 (0.144 g, 0.19 mmol), N, Ndicyclohexyl-1,3-carbodiimide (DCC, 0.196 g, 0.95 mmol) and N-hydroxysuccinimide (NHS, 0.11 g, 0.95mmol) in anhydrous DMF (20 mL). The suspension was stirred at room temperature for 20 h. The yellow cellulose fiber was filtered, washed with DMF ( $5 \times 30$  mL), CH<sub>2</sub>Cl<sub>2</sub> ( $3 \times 30$  mL), methanol ( $3 \times 30$  mL), water ( $3 \times 30$  mL), acetone ( $3 \times 30$  mL), ether ( $3 \times 30$  mL) and then dried at room temperature for 16 h, afforded 3.5g yellow powder.

Synthesis of 13: Hydrolysis of 12: 3.5g yellow powder 12 were suspended in a solution of NaOH 0.76 g (19 mmol) in water (15 ml), The resultant suspension was stirred at 40 °C for 5 h. Then the yellow cellulose fiber was filtered, washed with water until neutral, then washed with acetone ( $3 \times 30$  mL), ether ( $3 \times 30$  mL), dried at room temperature for 16 h, afforded 2.9g yellow powder.

**Preparation of sensor disk:** Sieved (25µm) indicator-immobilized amino-cellulose fiber(0.1 g) was stirred 16h into a hydrogel D4 dispersion (1.9g) containing 10% solids in 90% (w/w) ethanol/water. The resulting dispersion was knife-coated onto a 125µm polyester sheet such that the indicator layer dried to a thickness of 15µm. A second hydrogel layer consisting of 3% (w/w) carbon black (Degussa Corporation) in the same hydrogel dispersion was then knife-coated and allowed to dry overnight. A sensor disk 25mm in diameter was then punched out and soaked in buffer for at least 16h prior to use.

# **Reference:**

- Huarui He, Kenneth Jenkins, Chao Lin, analytica chimica acta, 2008, 611,197– 204
- (2) S.N. Zagrebel'nyi, S.M. Yasnetskaaya, L.A. Vasil'eva, Okrytica, Izobret.Prom. Obraztsu, Tovarnye Znaki, 1983, 26, 76.