## **Electronic Supplementary Information**

**Chemicals:** Dansyl chloride (>98.0%), 1-naphthalenesulfonyl chloride (>99.0%), and N-(3-Aminopropyl)imidazole (>99%), were purchased from Aldrich. 1,1,2,2,3,3-Hexafluoropropane-1,3-disulfonimide potassium Salt (K[HFPSI], >98.0%), and potassium perfluorooctanesulfonate (K[PFOS]) were purchased from TCI. Other commercially available regents were purchased from Tianjin Chemical Reagent Corporation Ltd., or Nanjing Chemlin Chemical Industrial Co., and used in this work were of analytical grade.

**Synthetic procedures:** All fluorescent low melting salts (FLMSs) could be easily obtained according to the synthetic routes shown in Figure S1.



Figure S1. Synthetic routes.

### Synthetic details of the FLMSs:

### (1) Synthesis of FLMSs 1-7

### (a) N-(3-(1H-imidazol-1-yl)propyl)-6-(dimethylamino)naphthalene-2-sulfonamide

To a solution of dansyl chloride (270 mg, 1 mmol) and triethylamine (1.4 mL, 10 mmol) in methanol (20 mL) solution at 0 °C was added a solution of N-(3-Aminopropyl)imidazole (125 mg, 1 mmol) in methanol (10 mL) solution over a period of 15 min. After addition, the mixture was stirred at room temperature for 48 h. After removal of the volatile components, 50 mL cold water was poured into the mixture and then extracted with ethyl acetate (3×20mL). The combined organic extracts were washed with brine (3×20mL), the solvent evaporated under reduced pressure and the residue purified by flash column chromatography (silica, 1% NH<sub>3</sub> aq (880)/10% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) to give the desired sulfinamide (258 mg, *ca.* 72% yield).

#### (b) The quaternization reaction and anion exchange to yield the desired FLMSs

A mixture of above obtained sulfinamide (258 mg, 0.72 mmol) and bromoethane (11g, 0.1 mol) in toluene (50 mL) was stirred at 50 °C for 2 days. After removal of the volatile components, the mixtures were washed with the absolute ethyl ether for three times to remove the unreacted reagents, and the resulting FLMS 1 (317 mg) could be obtained as a laurel-green solid with the yield of ca. 68%. Then, to a solution of the obtained FLMS 1 (317 mg) in distilled water (100 mL), 10 mL aqueous solution containing  $NaBF_4$  (0.1 mmol) was added under vigorous stirring at room temperature, and the reaction mixture was stirred for 12 h. The crude products was extracted by  $CH_2Cl_2$  (3×20mL), and washed with the deionized water until no residual bromide ion in the washed water was detected with use of the aqueous solution containing AgNO<sub>3</sub>. The final product was dried in a vacuum (pressure  $10^{-2}$ - $10^{-3}$  mbar) for more than 12 hours at 90 °C, and 289 mg FLMS 2 (ca. 61% yield from dansyl chloride) was obtained as a laurel-green liquid. The product was analytically pure as determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy; spectra are provided below. The same procedure as that described above for the synthesis of FLMSs 3-7 was followed, except the aqueous solution containing NaBF4was used instead of the same amount of aqueous solution containing KPF<sub>6</sub> NaDCA, LiTFSI, K[HFPSI], and K[PFOS], respectively. The desired FLMSs 3-7 were obtained as waxy solids or highly viscous liquids. The yields of FLMSs 3-7 are 63%, 57%, 62%, 60%, and 55%, respectively.

#### (2) Synthesis of FLMS 8

The same procedure as that described above for synthesis of the was N-(3-(1H-imidazol-1-yl)propyl)-6-(dimethylamino)naphthalene-2-sulfonamide followed. except 1-naphthalenesulfonyl chloride (226 mg, 1 mmol) was used instead of dansyl chloride (270 mg, 1 mmol). And then, the same quaternization procedure of the obtained sulfinamide containing a naphthyl unit and subsequent anion exchange as described above for the synthesis of FLMS 5 were used to yield the FLMS 8 with a yield of 66%.

**Note:** To ensure that the effect of the water on the properties of these FLMS materials was reduced as low as possible, each FLMS was further treated in a vacuum (pressure  $10^{-2}$ - $10^{-3}$  mbar) at 60 °C for 12 hour before every test.

<sup>1</sup>H-NMR and FT-IR: <sup>1</sup>H-NMR spectra (ppm,  $\delta$ ) were recorded in CDCl<sub>3</sub> with tetramethylsilane as internal standard on a Bruker AMX FT 400-MHz NMR spectrometer. IR spectra (cm<sup>-1</sup>) were obtained in KBr disc using a Thermo Nicolet 5700 FT-IR spectrophotometer.

**Phase transitions and thermal stability:** The DSC data were evaluated by using the Mettler–Toledo STARe software version 7.01. The samples were sealed in 40  $\mu$ L aluminum pan and a pinhole at the top of the pan for the sake of the sample exposing to a flowing N<sub>2</sub> (50 mL min<sup>-1</sup>) atmosphere using an empty pan as the reference. DSC traces were typically scanned from 100 to -100 °C at speed of 10 °C min<sup>-1</sup>, and then followed the heating process at the same speed. The decomposition temperature (T<sub>d</sub>) was recorded with 5% of mass loss by Pyris Diamond Perkin-Elmer TG/DTA at scan rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere (flow rate = 100 mL min<sup>-1</sup>) and each IL was heated from room temperature to 800 °C.

#### Analytical data:

*N-(3-(1H-imidazol-1-yl)propyl)-6-(dimethylamino)naphthalene-2-sulfonamide:* 



Laurel-green solid, mp = 56.5°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.543-8.523 (1H, d), 8.353-8.331 (1H, d), 8.225-8.207 (1H, d), 7.522-7.473 (2H, m), 7.169-7.151

(1H, d), 6.965 (1H, s), 6.819 (1H, s), 6.708 (1H, s), 3.919-3.886 (1H, t), 2.874 (6H, d), 1.865-1.835 (2H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.999, 137.151, 134.637, 130.495, 129.843, 129.516, 129.157, 128.346, 123.183, 118.706, 115.205, 45.341, 43.589, 39.615, 30.908.

**FLMS 1:** 



Laurel-green solid, mp =  $18.9^{\circ}$ C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.820 (1H, s), 8.485-8.454 (2H, m), 8.151-8.134 (1H, d), 7.803-7.778 (1H,

t), 7.585-7.545 (1H, t), 7.488-7.449 (1H, t), 7.377 (1H, s), 7.182-7.129 (1H, d), 4.452-4.422 (2H, t), 4.260-4.205 (2H, m), 2.925-2.842 (8H, m), 2.111 (2H, m), 1.477-1.441 (3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 151.500, 136.313, 134.880, 130.057, 129.645, 129.420, 128.834, 128.460, 123.176, 122.814, 121.613, 119.510, 115.319, 46.995, 45.341, 45.116, 39.226, 29.758, 15.195.

**FLMS 2:** 



d), 7.521-7.423 (2H, m), 7.336 (1H, s), 7.117-7.097 (1H, d), 6.205 (1H, s), 4.265-4.233 (2H, t), 4.154-4.100 (2H, m), 2.856-2.817 (8H, m), 2.111 (2H, m), 2.023-2.009 (2H, m), 1.436-1.400 (3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.805, 135.421, 134.423, 130.377, 129.706, 129.382, 129.169, 128.674, 123.202, 122.535, 121.865, 118.775, 115.365, 46.987, 45.330, 45.097, 39.702, 29.373, 14.837.

FLMS 3:



8.094-8.051 (2H, m), 7.778 (1H, s), 7.656-7.601 (2H, m), 7.282 (1H, s), 4.194-4.139 (4H, m), 2.834-2.751 (8H, m), 1.929-1.895 (2H, t), 1.429-1.391 (3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.443, 135.836, 135.493, 129.584, 128.978, 128.365, 127.984, 123.594, 122.230, 122.166, 118.832, 115.186, 46.240, 45.036, 44.217, 29.567, 14.924.

**FLMS 4:** 



Laurel-green liquid,  $T_g = -1.8^{\circ}C.$  <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 9.041$  (1H, s), 8.501-8.479 (1H, d), 8.309-8.289 (1H, d),

8.129-8.112 (1H, d), 7.606-7.566 (1H, t), 7.505-7.280 (3H, m), 7.162-7.144 (1H, d), 4.331-4.298 (2H, t), 4.205-4.150 (2H, t), 2.847-2.819 (8H, m), 2.044-2.017 (2H, t), 1.500-1.493 (3H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.828, 135.703, 134.560, 130.346, 129.714, 129.352, 129.100, 128.594, 123.198, 122.608, 121.911, 118.836, 115.380, 47.128, 45.315, 45.280, 39.352, 29.487, 14.970.

FLMS 5:



8.123-8.105 (1H, d), 7.546-7.457 (2H, m), 7.307 (1H, s), 7.238 (1H, s), 7.158-7.140 (1H, d), 4.269-4.235 (2H, t), 4.165-4.110 (2H, m), 2.875-2.847 (8H, m), 2.025-1.995 (2H, t), 1.478-1.440 (3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.992, 135.185, 134.008, 130.674, 129.763, 129.382, 129.321, 128.757, 123.187, 122.676, 121.884, 119.708, 118.375, 115.410, 47.079, 45.311, 45.227, 39.698, 29.342, 14.791.

**FLMS 6:** 



Laurel-green waxy solid,  $T_g = -9.2^{\circ}C$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 8.734$  (1H, s), 8.522-8.500 (1H, d), 8.246-8.224 (1H, d),

8.137-8.120 (1H, d), 7.567-7.467 (2H, m), 7.314 (1H, s), 7.220 (1H, s), 7.166-7.147 (1H, d), 4.292-4.259 (2H, t), 4.171-4.118 (2H, m), 2.854 (8H, m), 2.033-2.003 (2H, t), 1.483-1.446 (3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 152.012, 135.374, 134.193, 130.632, 129.828, 129.372, 128.733, 123.195, 122.683, 121.825, 118.516, 115.420, 47. 167, 45.292, 39.707, 30.820, 29.450, 14.813.

FLMS 7:



8.117-8.100 (1H, d), 7.562-7.442(3H, m), 7.267-7.250 (1H, d), 7.162-7.143 (1H, d), 4.378-4.346 (2H, t), 4.222-4.167 (2H, m), 2.913-2.854 (8H, m), 2.108-2.079 (2H, m), 1.511-1.474 (3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 151.807, 136.178, 134.539, 130.317, 129.844, 129.064, 128.599, 123.077, 122.794, 121.525, 118.973, 115.428, 47.427, 45.339, 45.229, 39.904, 30.860, 29.339, 14.810.

**FLMS 8:** 



Laurel-yellow liquid,  $T_g = -22.9^{\circ}C$ . <sup>1</sup>H NMR (400 MHz, d-DMSO):  $\delta = 9.125$  (1H, s), 8.431 (1H, s), 8.180-8.150 (2H, m), 8.074-8.055 (1H, d),

7.877-7.689 (6H, m), 4.215-4.138 (4H, m), 2.807-2.758 (2H, m), 1.974-1.940 (2H, t), 1.422-1.385 (3H, t). <sup>13</sup>C NMR (100 MHz, d-DMSO):  $\delta$  = 136.979, 135.844, 134.156, 131.687, 129.470, 129.119, 128.769, 127.812, 127.625, 127.397, 122.291, 122.162, 122.108, 119.470, 46.290, 44.198, 29.361, 14.882.



Figure S2 Different emissions for different FLMSs at maximum excited wavelength



**Figure S3** Emission spectra of FLMS 4 in methanol solution (10<sup>-5</sup> M) under varied excitation wavelengths

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