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(a)





Fig. 1. Synthetic scheme of (a) Asymmetric HRM2, (b) symmetric HRM3.

# 1-(4-((6-(Acryloyloxy)hexyl)oxy)phenyl)4-(3-formyl-4-hydroxyphenyl)(1s,4s)-cyclohexane-1,4-dicarboxylate (1)

To a solution of 4-((6-(acryloyloxy)hexyl)oxy) phenyl hydrogen *trans*-cyclohexane-1,4-dicarboxylate (3.33 g, 7.96 mmol) in THF (20 mL) was added triethylamine (3.53 mL, 25.34 mmol), and methanesulfonyl chloride (0.84 mL, 10.86 mmol) at 0 °C. The reaction mixture was stirred for 3h under nitrogen atmosphere. To the reaction mixture was added 2,5-dihydroxybenzaldehyde (0.50 g, 3.62 mmol), 4-(*N*,*N*-dimethylamino)pyridine (0.18 g, 1.45 mmol) in THF (10 mL). The reaction mixture was further stirred for 18 h at 60 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure. The mixture was purified by column chromatography (hexane/ethyl acetate = 7/3) to yield 1.00 g (30%) of white solid. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  10.94 (s, 1H), 9.92 – 9.90 (m, 1H), 7.38 (d, *J* = 2.8 Hz, 1H), 7.30 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 7.02 – 6.99 (m, 2H), 6.94 – 6.90 (m, 2H), 6.40 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.16 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.84 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.20 – 4.17 (t, *J* = 6.7 Hz, 2H), 4.01 – 3.97 (t, *J* = 6.5 Hz, 2H), 2.67 – 2.58 (ddd, *J* = 12.1, 6.2, 3.2 Hz, 2H), 2.34 – 2.27 (d, *J* = 6.5 Hz, 4H), 1.86 – 1.79 (m, 2H), 1.76 – 1.67 (m, 6H), 1.56 – 1.47 (m, 4H).

# 1-(4-((4-((6-(Acryloyloxy)hexyl)oxy)benzoyl)oxy)-3-formylphenyl)4-(4-((6-(acryloyloxy) hexyl)oxy)phenyl) (1s,4s)-cyclohexane-1,4-dicarboxylate (2)

To a solution of 4-(6-acryloyloxyhexyloxy)benzoic acid (0.60 g, 2.04 mmol) in THF (20 mL) was added triethylamine (1.29 mL, 9.28 mmol), and methanesulfonyl chloride (0.29 mL, 3.71 mmol) at 0 °C. The reaction mixture was stirred for 3 h under a nitrogen atmosphere. To the reaction mixture was added compound **1** (1.00 g, 1.86 mmol) in THF (10 mL). The reaction mixture was further stirred for 18 h at 60 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give a white solid (1.19 g, 79 %). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  10.17 (s, 1H), 8.19 – 8.13 (m, 2H), 7.65 (d, *J* = 2.8 Hz, 1H), 7.42 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.05 – 7.01 (m, 2H), 7.00 – 6.95 (m, 2H), 6.91 – 6.85 (m, 2H), 6.40 – 6.33 (ddd, *J* = 17.3, 2.5, 1.6 Hz, 2H), 6.16 – 6.08 (ddd, *J* = 17.3, 10.4, 2.1 Hz, 2H), 5.83 – 5.79 (ddd, *J* = 10.4, 2.4, 1.6 Hz, 2H), 4.17 – 4.13 (m, 4H),

4.11 – 4.05 (t, *J* = 6.5 Hz, 2H), 3.98 – 3.93 (t, *J* = 6.5 Hz, 2H), 2.66 – 2.57 (dd, *J* = 15.4, 11.8 Hz, 2H), 2.33 – 2.24 (m, 4H), 1.88 – 1.77 (m, 4H), 1.73 – 1.64 (m, 8H), 1.52 – 1.44 (m, 8H); UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 254 nm.

#### HRM2

To a solution of compound **2** (1.00 g, 1.23 mmol) in ethanol (40 mL) was added *p*-phenylenediamine (66 mg, 0.61 mmol). The reaction mixture was stirred for 4 h at 60 °C. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.50 g, 96 %). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.59 (s, 2H), 8.17 – 8.14 (m, 4H), 7.94 (d, *J* = 2.7 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 8.8, 2.7 Hz, 2H), 7.13 (s, 4H), 7.01 – 6.97 (m, 8H), 6.90 – 6.88 (m, 4H), 6.38 – 6.33 (m, 4H), 6.15 – 6.09 (ddd, *J* = 17.3, 10.4, 2.3 Hz, 4H), 5.82 – 5.79 (ddd, *J* = 10.4, 3.1, 1.5 Hz, 4H), 4.17 – 4.14 (dt, *J* = 6.7, 3.3 Hz, 8H), 4.08 – 4.05 (t, *J* = 6.5 Hz, 4H), 3.97 – 3.94 (t, *J* = 6.5 Hz, 4H), 2.66 – 2.57 (m, 4H), 2.32 – 2.27 (m, 8H), 1.85 – 1.78 (m, 8H), 1.73 – 1.66 (m, 16H), 1.54 – 1.46 (m, 16H); FAB-MS m/z: calcd for C<sub>98</sub>H<sub>108</sub>N<sub>2</sub>O<sub>24</sub> 1697.74, found: 1699 [M+H]<sup>+</sup>; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 268 nm, 364 nm.

### 1-(4-(((1s,4s)-4-((4-((6-(Acryloyloxy)hexyl)oxy)phenoxy)carbonyl)cyclohexane-1-carbonyl)oxy)-2-formylphenyl)4-(4-((6-(acryloyloxy)hexyl)oxy)phenyl)(1r,4r)-cyclohexane-1,4-dicarboxylate (3)

To a solution of 4-((6-(acryloyloxy)hexyl)oxy) phenyl hydrogen *trans*-cyclohexane-1,4-dicarboxylate (3.33 g, 7.96 mmol) in THF (20 mL) was added triethylamine (3.53 mL, 25.34 mmol), and methanesulfonyl chloride (0.84 mL, 10.86 mmol) at 0 °C. The reaction mixture was stirred for 3 h under a nitrogen atmosphere. To the reaction mixture was added 2,5-dihydroxybenzaldehyde (0.50 g, 3.62 mmol) in THF (10 mL). The reaction mixture was further stirred for 18 h at 60 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give the white solid (1.38 g, 40%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  10.09 (s, 1H), 7.61 (d, *J* = 2.9 Hz, 1H), 7.38 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.99 – 6.96 (m, 4H), 6.90 – 6.87 (m, 4H), 6.36 (dd, *J* = 17.3, 1.5)

Hz, 2H), 6.12 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.81 (dd, *J* = 10.4, 1.5 Hz, 2H), 4.15 (t, *J* = 6.7 Hz, 4H), 3.95 (t, *J* = 6.5 Hz, 4H), 2.71 (td, *J* = 11.6, 3.6 Hz, 1H), 2.66 – 2.55 (m, 3H), 2.35 – 2.26 (m, 8H), 1.79 (p, *J* = 6.5 Hz, 4H), 1.73 – 1.63 (m, 12H), 1.53 – 1.44 (m, 8H); UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 278 nm.

#### HRM3

To a solution of compound **3** (0.50 g, 0.53 mmol) in ethanol (40 mL) was added *p*-phenylenediamine (29 mg, 0.27 mmol). The reaction mixture was stirred for 3 h at 60 °C. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.42 g, 81%). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.56 (s, 2H), 7.91 (d, J = 2.8 Hz, 2H), 7.27 (s, 4H), 7.24 (dd, J = 8.8, 2.8 Hz, 2H), 7.18 (d, J = 8.8 Hz, 2H), 6.98 – 6.94 (m, 8H), 6.90 – 6.86 (m, 8H), 6.36 (ddd, J = 17.3, 2.5, 1.6 Hz, 4H), 6.12 (ddd, J = 17.3, 10.4, 2.7 Hz, 4H), 5.80 (ddd, J = 10.4, 2.8, 1.5 Hz, 4H), 4.14 (td, J = 6.7, 3.5 Hz, 8H), 3.97 – 3.93 (m, 8H), 2.71 (s, 2H), 2.66 – 2.57 (m, 6H), 2.33 – 2.25 (m, 16H), 1.80 – 1.75 (dd, J = 13.5, 7.1 Hz, 8H), 1.73 – 1.65 (m, 24H), 1.52 – 1.44 (m, 16H); FAB-MS m/z: calcd for C<sub>112</sub>H<sub>128</sub>N<sub>2</sub>O<sub>28</sub> 1949.87, found: 1951 [M+H]<sup>+</sup>; UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 278 nm, 365 nm.