

## Supplementary Information

# Controlling Molecular Self-Assembly on an Insulating Surface by Rationally Designing an Efficient Anchor Functionality that Maintains Structural Flexibility

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## **Materials**

All reagents and solvents were purchased from Acros or Sigma-Aldrich and used without further purification. 2-Hydroxy-4-iodobenzoic acid was prepared according to literature.<sup>1</sup>

## **Characterization**

All <sup>1</sup>H NMR (360 MHz) and <sup>13</sup>C NMR (90 MHz) spectra were recorded on a Bruker Avance DPX (360 MHz) FT NMR spectrometer. All <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded on a Bruker Avance III (500 MHz) FT NMR spectrometer. Chemical shifts were given in ppm relative to the residual solvent peak (CDCl<sub>3</sub>: 7.26 for <sup>1</sup>H, 77.16 for <sup>13</sup>C; d<sup>6</sup>-DMSO: 2.50 for <sup>1</sup>H, 39.52 for <sup>13</sup>C). RP-UPLC-MS analysis was performed on a Waters ACQUITY UPLC equipped with a ACQUITY UPLC BEH column (C18, 1.7 μm, 50 x 2.1 mm). The samples were eluted with an acetonitrile/water gradient (buffered with 5 mM formic acid), starting from 5% acetonitrile and rising to 100% over a period of 4 min. UV detection was performed at 254 nm. MS (ES<sup>+</sup>) mass spectra were measured on a SQ Detector.

## Synthesis of OIB

### 2-Hydroxy-4-iodo-*N*-(4-iodophenyl)benzamide (OIB)

2-Hydroxy-4-iodobenzoic acid (0.38g, 1.44 mmol) was dissolved in 6 mL thionyl chloride and refluxed for 2 h. After removal of thionyl chloride under reduced pressure, the yellow solid was dissolved in 4 mL anhydrous THF. Then a solution of 4-iodaniline (0.31 g, 1.44 mmol) in a mixture of 4 mL anhydrous THF and 0.41 mL triethylamine was added. After stirring for 24 h at room temperature, the mixture was diluted with 20 mL water, filtered and washed with cold methanol. The resulting colorless solid was reprecipitated twice from DMSO in methanol to afford the product as colorless solid (0.27 g, 40%).

<sup>1</sup>H-NMR (500 MHz, d<sup>6</sup>-DMSO): δ (ppm) 11.83 (br-s, 1H), 10.46 (br-s, 1H), 7.71 (d, <sup>3</sup>J = 8.28 Hz, 2H), 7.62 (d, <sup>3</sup>J = 8.28 Hz, 1H), 7.55 (d, <sup>3</sup>J = 8.28 Hz, 2H), 7.37 (d, <sup>4</sup>J = 1.50, Hz 1H), 7.31 (dd, <sup>3</sup>J = 8.28 Hz, <sup>4</sup>J = 1.50, 1H).

<sup>13</sup>C-NMR (125 MHz, d<sup>6</sup>-DMSO): δ (ppm) 165.59, 158.25, 138.12, 137.43, 130.85, 127.89, 125.65, 122.72, 118.35, 100.29, 87.94.

## Synthesis of OIBal

### Hexyl 2-(hexyloxy)-4-iodobenzoate

2-Hydroxy-4-iodobenzoic acid (2.77 g, 10.49 mmol), 2-hexyl bromide (3.81 g, 23.08 mmol) and potassium carbonate (3.62 g, 26.23 mol) were refluxed in 30 mL anhydrous acetone for 3 days. After cooling to room temperature and evaporation of acetone, 50 mL water was added and the mixture was extracted with chloroform. The combined organic extracts were washed with water,

dried over  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. The residual colorless oil was used in the next step without further purification (3.95 g, 87%).

### **2-(Hexyloxy)-4-iodobenzoic acid**

Hexyl 2-(hexyloxy)-4-iodobenzoate (3.95 g, 9.14 mmol) was dissolved in a mixture of 40 mL ethanol and 25 mL 1N sodium hydroxide solution. After stirring at  $60^\circ\text{C}$  for 18 h, ethanol was evaporated. The remaining solution was acidified with 3 N hydrochloric acid, filtered, washed with water and dried in vacuum. The residual colorless solid was used in the next step without further purification (2.93 g, 92%).

$^1\text{H}$ -NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 10.75 (br-s, 1H), 7.85 (d,  $^3J = 8.28$  Hz, 1H), 7.49 (dd,  $^3J = 8.28$  Hz,  $^4J = 1.44$  Hz, 1H), 7.39 (d,  $^4J = 1.08$  Hz, 1H), 4.23 (t,  $^3J = 6.48$  Hz, 2H), 1.95 - 1.87 (m, 2H), 1.50 - 1.45 (m, 2H), 1.38 - 1.34 (m, 4H), 0.91 (t,  $^3J = 7.20$  Hz, 3H).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 164.97, 157.47, 134.81, 131.75, 122.21, 117.43, 101.81, 70.90, 31.42, 28.91, 25.60, 22.58, 14.07.

### **2-(Hexyloxy)-4-iodo-*N*-(4-iodophenyl)benzamide (OIBaI)**

2-(Hexyloxy)-4-iodobenzoic acid (2.93 g, 8.42 mmol) was dissolved in 10 mL thionyl chloride and refluxed for 3 h. After removal of thionyl chloride under reduced pressure, the yellow solid was dissolved in 6 mL anhydrous THF. Then a solution of 4-iodaniline (1.84 g, 8.42 mmol) in a mixture of 6 mL anhydrous THF and 1 mL pyridine was added. After stirring for 18 h at room temperature, the mixture was diluted with 20 mL water, filtered and washed with cold methanol. The resulting colorless solid was recrystallized twice from ethanol to afford the product as colorless crystals (3.76 g, 82%).

$^1\text{H}$ -NMR (360 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 9.90 (br-s, 1H), 7.97 (d,  $^3J = 8.64$  Hz, 1H), 7.65 (d,  $^3J = 8.64$  Hz, 2H), 7.47 (d,  $^3J = 8.64$  Hz, 1H), 7.42 (d,  $^3J = 8.64$  Hz, 2H), 7.34 (s, 1H), 4.18 (t,  $^3J = 6.48$  Hz, 2H), 2.01 - 1.93 (m, 2H), 1.57 - 1.51 (m, 2H), 1.42 - 1.32 (m, 4H), 0.91 (t,  $^3J = 6.84$  Hz, 3H).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 162.76, 156.78, 138.24, 138.11, 133.82, 131.17, 121.98, 121.91, 121.15, 99.89, 87.44, 70.09, 31.62, 29.36, 25.98, 22.71, 14.15.

RP-UPLC (min): 2.82.

MS (ES $^+$ ): (M+H) $^+$  549.98.

## Synthesis of OIBca

### 5-Cyanopentyl 2-((5-cyanopentyl)oxy)-4-iodobenzoate

2-Hydroxy-4-iodobenzoic acid (0.66 g, 2.50 mmol), 6-bromohexanenitrile (1.20 g, 6.82 mmol) and potassium carbonate (0.86 g, 26.23 mol) were heated at 100°C in 30 mL anhydrous dimethylformamide for 2 days. After cooling to room temperature water was added and the mixture was extracted with diethylether. The combined organic extracts were washed with water, dried over  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. The residual colorless oil was immediately used in the next step without further purification.

### 2-((5-Cyanopentyl)oxy)-4-iodobenzoic acid

5-Cyanopentyl 2-((5-cyanopentyl)oxy)-4-iodobenzoate was dissolved in a mixture of 30 mL ethanol and 10 mL 1N sodium hydroxide solution. After stirring at room temperature for 5 h, ethanol was evaporated. The remaining solution was acidified with 3 N hydrochloric acid,

filtered, washed with water and dried in vacuum. The residual colorless solid was immediately used in the next step without further purification.

### **2-((5-Cyanopentyl)oxy)-4-iodo-*N*-(4-iodophenyl)benzamide**

2-((5-Cyanopentyl)oxy)-4-iodobenzoic acid was dissolved in 5 mL thionyl chloride and refluxed for 2 h. After removal of thionyl chloride under reduced pressure, the yellow solid was dissolved in 6 mL anhydrous NMP. Then a solution of 4-iodaniline (0.50 g, 2.28 mmol) in a mixture of 6 mL anhydrous NMP was added. After stirring for 18 h at room temperature, the mixture was extracted with dichloromethane. The combined organic extracts were washed with water, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The residual yellow solid was purified by silica gel column chromatography eluted by hexane/ethyl acetate (4:1) to afford the product as colorless solid (0.78 g, 56% over three steps).

<sup>1</sup>H-NMR (500 MHz, d<sup>6</sup>-DMSO): δ (ppm) 10.17 (br-s, 1H), 7.68 (d, <sup>3</sup>J = 8.64 Hz, 2H), 7.53 (d, <sup>3</sup>J = 8.50 Hz, 2H), 7.52 (d, <sup>4</sup>J = 1.50 Hz, 1H), 7.43 (dd, <sup>3</sup>J = 7.92 Hz, <sup>4</sup>J = 1.50 Hz, 1H), 7.35 (d, <sup>3</sup>J = 7.92 Hz, 1H), 4.10 (t, <sup>3</sup>J = 6.12 Hz, 2H), 2.40 (t, <sup>3</sup>J = 6.84 Hz, 2H), 1.78 - 1.73 (m, 2H), 1.60 - 1.56 (m, 2H), 1.49 - 1.43 (m, 2H).

<sup>13</sup>C-NMR (125 MHz, d<sup>6</sup>-DMSO): δ (ppm) 164.10, 156.23, 138.75, 137.46, 131.12, 129.48, 124.80, 121.66, 121.52, 120.61, 98.54, 87.11, 68.44, 27.64, 24.60, 24.34, 16.08.

RP-UPLC (min): 2.36.

MS (ES<sup>+</sup>): (M+H)<sup>+</sup> 560.94.

### **6-(5-Iodo-2-((4-iodophenyl)carbamoyl)phenoxy)hexanoic acid (OIBca)**

2-((5-Cyanopentyl)oxy)-4-iodo-*N*-(4-iodophenyl)benzamide (200 mg, 0.36 mmol) was refluxed for 3 days in a solution of potassium hydroxide (100 mg, 1.80 mmol) in 5 mL water and 20 mL ethanol. After evaporation of ethanol, water was added and the remaining solution was acidified with 3 N hydrochloric acid, filtered, washed with water and dried in vacuum. The colorless solid was purified by preparative reversed-phase high-performance liquid chromatography eluted by acetonitrile/water (3:1) to afford the product as colorless solid (0.12 g, 59%).

<sup>1</sup>H-NMR (500 MHz, d<sup>6</sup>-DMSO):  $\delta$  (ppm) 12.11 (br-s, 1H), 10.15 (br-s, 1H), 7.66 (d, <sup>3</sup>J = 8.00 Hz, 2H), 7.53 - 7.50 (m, 3H), 7.42 (dd, <sup>4</sup>J = 1.50 Hz, <sup>3</sup>J = 8.00 Hz, 1H), 7.36 (d, <sup>3</sup>J = 8.00 Hz, 1H), 4.08 (t, <sup>3</sup>J = 6.50 Hz, 2H), 2.11 (t, <sup>3</sup>J = 7.00 Hz, 2H), 1.75 - 1.70 (m, 2H), 1.53 - 1.47 (m, 2H), 1.40 - 1.34 (m, 2H).

<sup>13</sup>C-NMR (125 MHz, d<sup>6</sup>-DMSO):  $\delta$  (ppm) 174.50, 163.97, 156.28, 138.69, 137.42, 131.21, 129.46, 124.57, 121.65, 121.55, 98.60, 87.08, 68.65, 33.84, 28.20, 24.94, 24.19.

RP-UPLC (min): 2.26.

MS (ES<sup>+</sup>): (M+H)<sup>+</sup> 579.96.

## References

1. Hwang, S. G.; Takasugi, J.; Ren, H.; Wilde, R. G.; Turpoff, A.; Arefolov, A.; Karp, G. M.; Chen, G.; Campbell, J.A., International Publication Number WO 2006/19831 A1, Feb 23, **2006**.