Supplementary Information

Cooperation and competition of hydrogen and halogen bonds in 2D self-assembled nanostructures based on bromine substituted coumarins

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Experimental Section

1. General Information

$^1$H spectra were recorded out on a Bruker AV-600 MHz NMR spectrometer.

2. Synthesis and Characterization of $\text{Co16 (3a)}$, 6-Br-$\text{Co16 (3b)}$ and 6,8-Br-$\text{Co16 (3c)}$

2.1. Scheme S1.

![Chemical Structure](image)

**Compound 3a**: hexadecyl ester coumarin-3-carboxylate ($\text{Co16}$); **Compound 3b**: hexadecyl ester-6-bromo-coumarin-3-carboxylate ($6$-$\text{Br-Co16}$); **Compound 3c**: hexadecyl ester-6,8-dibromo-coumarin-3-carboxylate ($6,8$-$\text{Br-Co16}$) were synthesized as previously reported in the literature.$^1$

**Compound 3a** The coumarin-3-carboxylic acid (1.90 g 10 mmol) was dissolved in SOCl$_2$ (20 mL) and the reaction mixture was stirred at 80 °C for 6 h. The SOCl$_2$ was removed under reduced pressure. $n$-Hexadecanol (4.85 g, 20 mmol) and THF (30 mL) were added to the mixture, which was stirred at 100 °C for another 2 h. The solvent was removed by vacuum. The crude product was subjected to column chromatography (Silical gel 10% EA/PE) to give 3a as a solid.

**Data for 3a.** $^1$H NMR (600 MHz, CDCl$_3$, ppm): δ 8.51 (1H, m), 7.61 (2H, m), 7.35 (2H, m), 4.35 (2H, m), 1.78 (2H, m), 1.26 (26H, m), 0.88 (3H, m).

**Compound 3b** The 6-bromo coumarin-3-carboxylic acid (2.69 g 10 mmol) was dissolved in SOCl$_2$ (20 mL) and the reaction mixture was stirred at 80 °C for 6 h. The SOCl$_2$ was removed under reduced pressure. $n$-Hexadecanol (4.85 g, 20 mmol) and THF (30 mL)
were added to the mixture, which was stirred at 100 ºC for another 2 h. The solvent was removed by vacuum. The crude product was subjected to column chromatography (Silical gel 10% EA/PE) to give 3b as a solid.

**Data for 3b.** $^1$H NMR (600 MHz, CDCl$_3$, ppm): $\delta$ 8.41 (1H, m), 7.75 (1H, m), 7.71 (1H, m), 7.21 (1H, m), 4.35 (2H, m), 1.77 (2H, m), 1.26 (26H, m), 0.88 (3H, m).

**Compound 3c** The 6,8-dibromo coumarin-3-carboxylic acid (3.47 g 10 mmol) was dissolved in SOCl$_2$ (20 mL) and the reaction mixture was stirred at 80 ºC for 6 h. The SOCl$_2$ was removed under reduced pressure. $n$-Hexadecanol (4.85 g, 20 mmol) and THF (30 mL) were added to the mixture, which was stirred at 100 ºC for another 2 h. The solvent was removed by vacuum. The crude product was subjected to column chromatography (Silical gel 10% EA/PE) to give 3c as a solid.

**Data for 3c.** $^1$H NMR (600 MHz, CDCl$_3$, ppm): $\delta$ 8.36 (1H, m), 7.98 (1H, m), 7.69 (1H, m), 4.35 (2H, m), 1.76 (2H, m), 1.25 (26H, m), 0.88 (3H, m).

**Notes and references**

3. Electrostatic potential (ESP) maps of 6-Br-Co16 and 6,8-Br-Co16.

**Fig. S1** (a) Electrostatic potential (ESP) maps of 6-Br-Co16 under vacuum, Inset images (b,c) show the ESP maps of Br atom. The map color scales from −4 (blue) to 4 (red) kcal/mol. The alkyl chains were replaced by methyl substituents.

**Fig. S2** (a) Electrostatic potential (ESP) maps of 6,8-Br-Co16 under vacuum, Inset images (b,c) show the ESP maps of Br atoms. The map color scales from −4 (blue) to 4 (red) kcal/mol. The alkyl chains were replaced by methyl substituents.