Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

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

Bao Zha[ac], Jinxing Li,[b] Juntian Wu,[b] Xinrui Miao,, [b] and Min Zhang,*[a]*

[a] School of Electronic and Computer Engineering, Peking University, Shenzhen 518055, People's Republic of China.

[b] College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China.

[c] Shenzhen China Star Optoelectronics Technology Co., Ltd, Shenzhen 518132, People's Republic of China.

Corresponding authors：Xinrui Miao (msxrmiao@scut.edu.cn)

Min Zhang (zhangm@ece.pku.edu.cn)

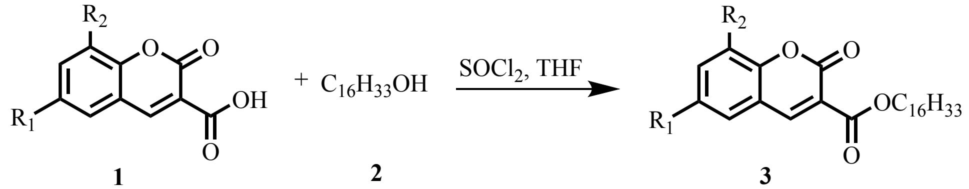
Experimental Section

1. General Information

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

2. Synthesis and Characterization of Co16 (3a), 6-Br-Co16(3b) and 6,8-Br-Co16 (3c)

2.1. Scheme S1.



1 2 3

a) R_1=R_2=H
b) R_1=Br; R_2=H
c) R_1=Br; R_2=Br

Compound 3a: hexadecyl ester coumarin-3-carboxylate (**Co16**)**; Compound 3b**: hexadecyl ester-6-bromo-coumarin-3-carboxylate (**6-Br-Co16**); **Compound 3c**: hexadecyl ester-6,8-dibromo-coumarin-3-carboxylate (**6,8-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 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 **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 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 **3b** as a solid.

Data for 3b. ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 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): δ 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

1. B. Zha, M. Q. Dong, X. R. Miao, S. Peng, Y. C. Wu, K. Miao, Y. Hu and W. L. Deng, *Nanoscale*, 2017, **9**, 237–250.

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

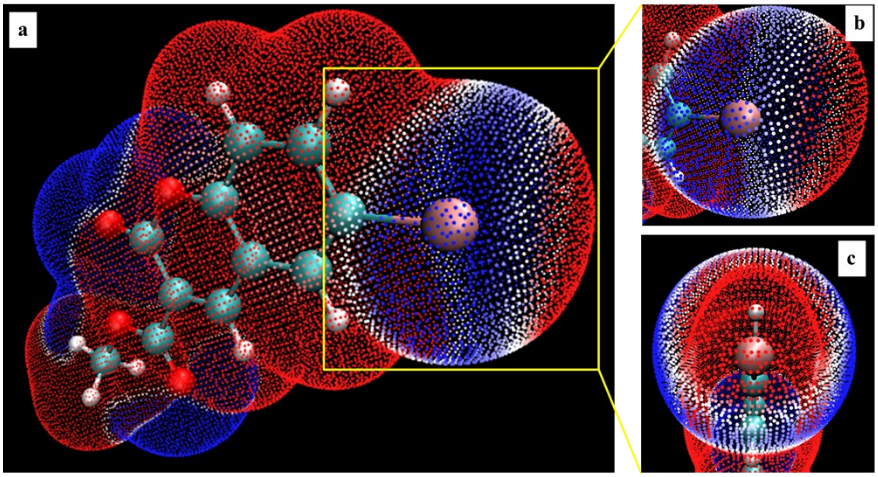


Fig. S1 (a) Electrostatic potential (ESP) maps of 6-Br-Co16 under vacuum, Inset iamges (b,c) show the ESP maps of Br atom. The map color scales from −4 (blue) to 4 (red) kcal/mol. The alkyl chains were replaced by methyl substituents.

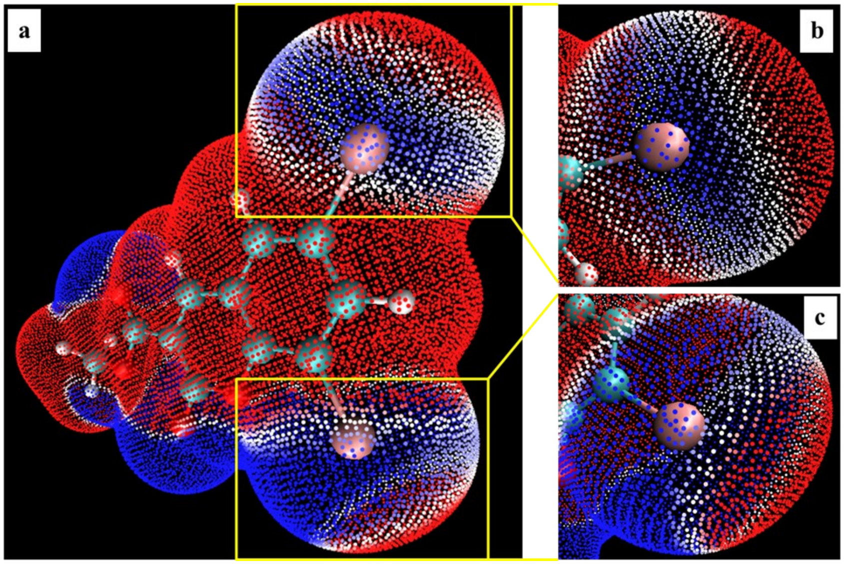


Fig. S2 (a) Electrostatic potential (ESP) maps of 6,8-Br-Co16 under vacuum, Inset iamges (b,c) show the ESP maps of Br atoms. The map color scales from −4 (blue) to 4 (red) kcal/mol. The alkyl chains were replaced by methyl substituents.