*Supporting Information*

# Systematical Investigation of Chain Length Effect on the Melting Point of a Series of Bifunctional Anthraquinone Derivatives via X-Ray Diffraction and Scanning Tunneling Microscopy

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## 1. Crystal structure analysis

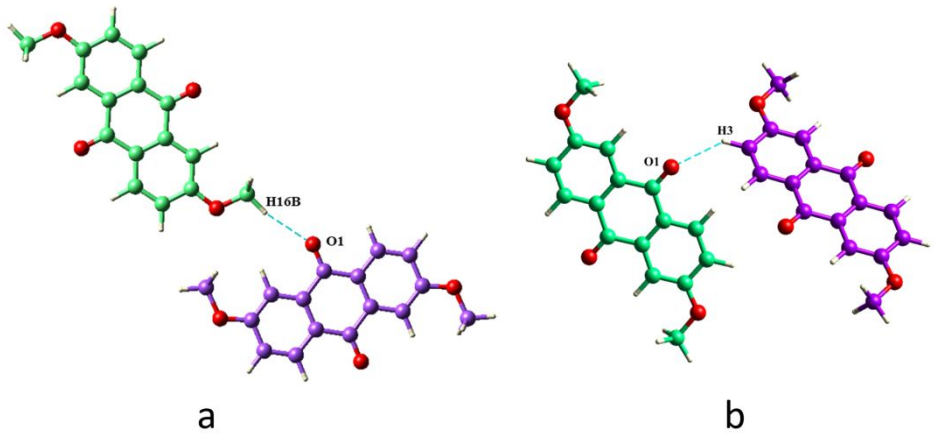


**Figure S1.** Hydrogen bonds presented in A-$OC_1$ (a)$C(sp^3)$–H···$O(sp^2)$=C(2.473 Å,138.12°). (b)$C(sp^3)$–H···$O(sp^2)$=C(2.565 Å，161.78°).

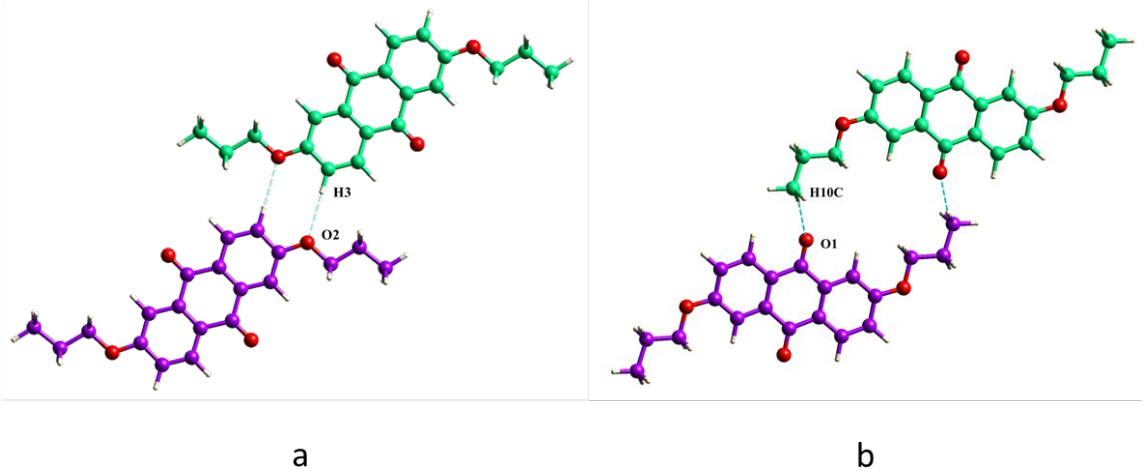


**Figure S2.** Hydrogen bonds presented in A-$OC_3$ (a) $C(sp^2)$–H···$O(sp^3)$(2.438 Å,174.01°). (b) $C(sp^3)$–H···$O(sp^2)$=C (2.545Å,161.61°).

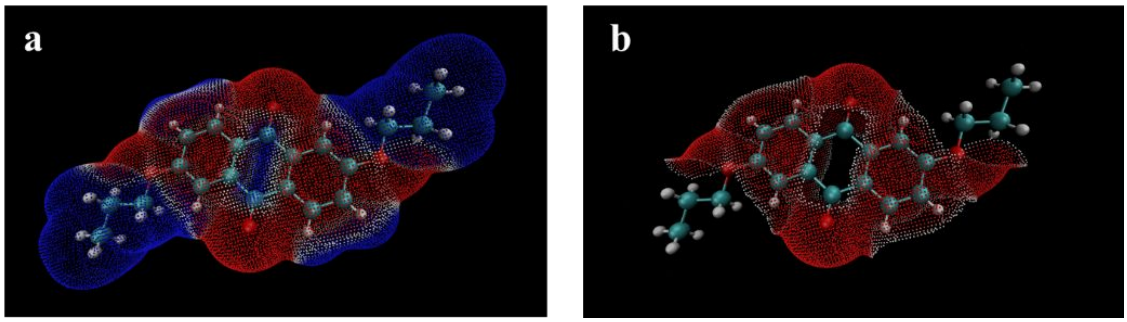


**Figure S3.** (a) Calculated the electrostatic potential of A-$OC_3$ molecule. (b) Molecular electrostatic potential less than 0. The color scales from −5 (red) to 5 kcal $mol^{-1}$ (blue).

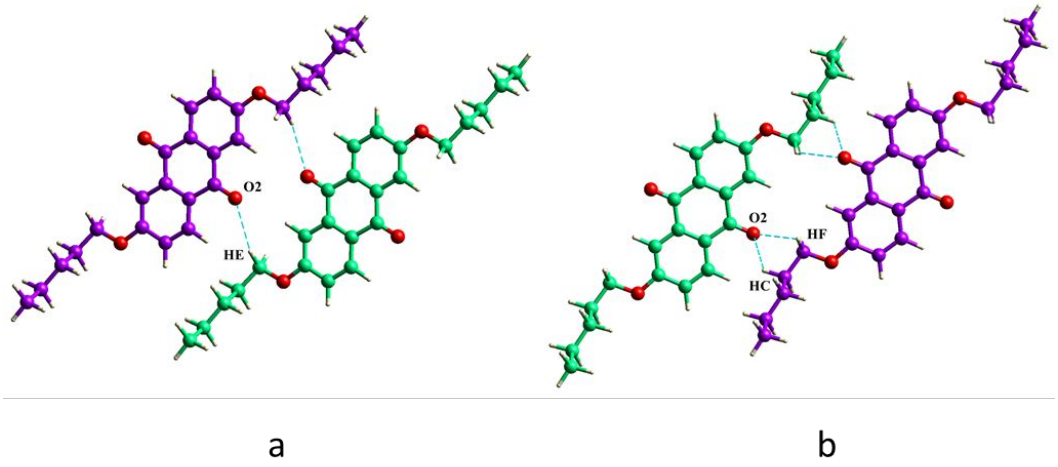


**Figure S4.** Hydrogen bonds presented in A-$OC_5$ (a)$C(sp^3)$–H···$O(sp^2)$=C(2.657 Å,147.38°). (b) $C(sp^3)$–H···$O(sp^2)$=C(2.602 Å,124.17° and 2.647 Å,122.96°).

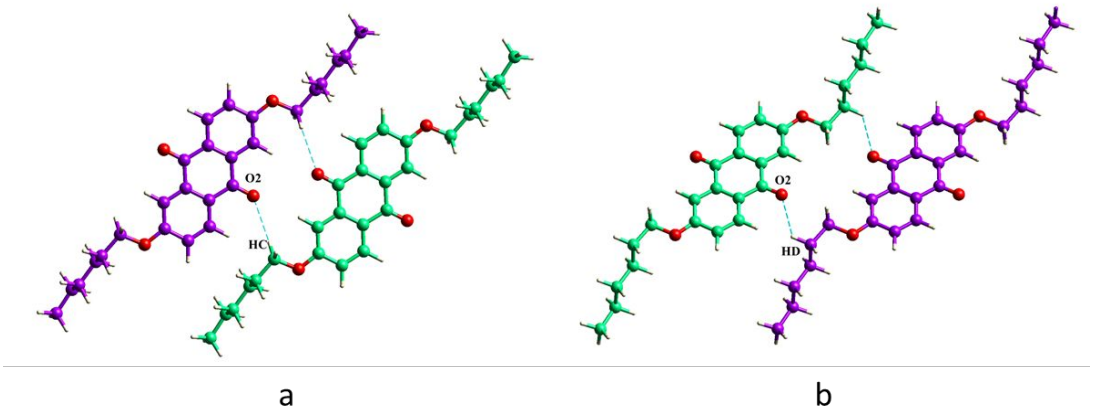


**Figure S5.** Hydrogen bonds presented in A-$OC_5$ (a)$C(sp^3)$–H···$O(sp^2)$=C(2.625 Å,146.84°). (b) $C(sp^3)$–H···$O(sp^2)$=C(2.607 Å,125.80°).

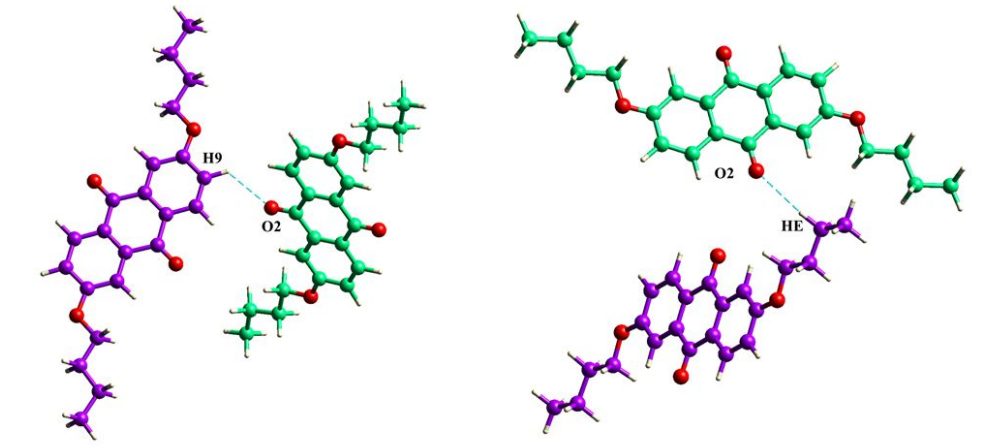


**Figure S6.** Hydrogen bonds presented in A-$OC_4$ (a) $C(sp^2)$–H···$O(sp^2)$=C(2.603 Å,124.49°). (b) $C(sp^3)$–H···$O(sp^2)$=C(2.675 Å,174.60°).

## 2. Hirshfeld Surface and fingerplots analysis

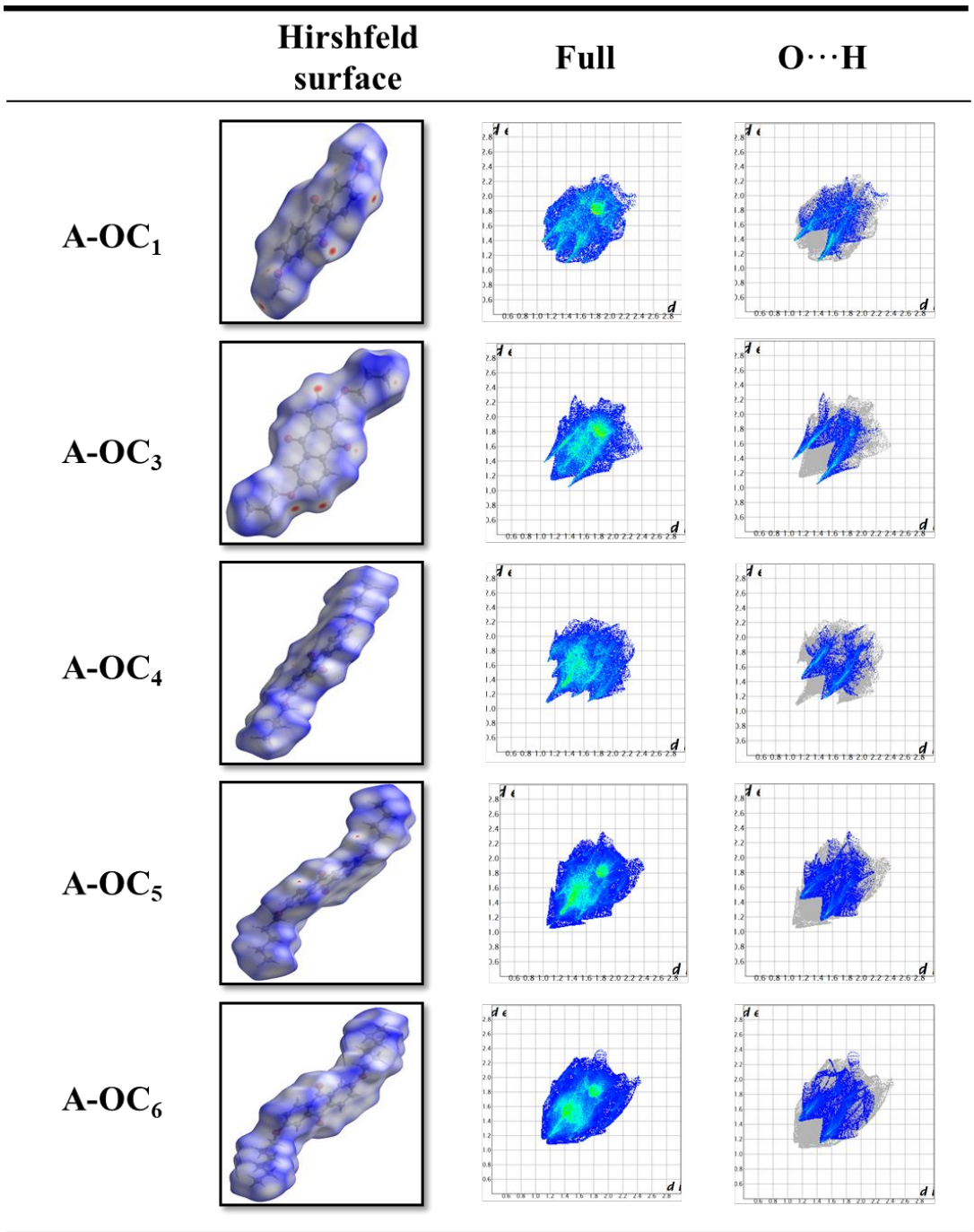


**Figure S7.** Hirshfeld surface and Fingerprint Plots for A-$OC_n$ (n = 1, 3, 4, 5, 6).

## 3. The decomposition of interactions energy

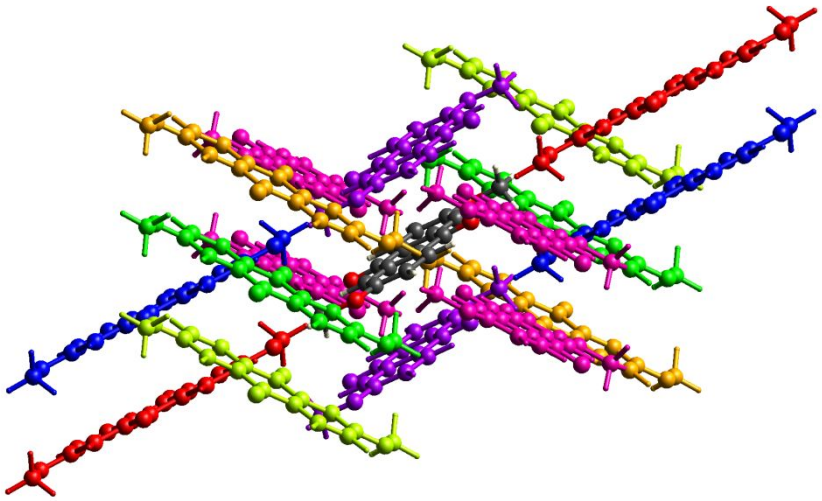

**Figure S8.** Colour coding based on the interactions energy with the central molecule for A-$OC_1$.

**Table S1. Molecular pairs and the stabilization energies (kJ $mol^{-1}$) obtained from decomposition of interactions energy calculation for A-$OC_1$**

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot | ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | - | 11.59 | B3LYP/6-31G(d,p) | -9.7 | -2.4 | -12.2 | 8.3 | -17.5 | 0.795 |
| | 2 | - | 11.27 | B3LYP/6-31G(d,p) | -0.6 | -0.4 | -6.1 | 2.3 | -4.8 | 0.098 |
| | 2 | - | 11.27 | B3LYP/6-31G(d,p) | -7.1 | -1.4 | -5.6 | 5.4 | -10.0 | 1.268 |
| | 2 | - | 10.56 | B3LYP/6-31G(d,p) | -7.1 | -2.5 | -15.5 | 9.6 | -16.9 | 0.458 |
| | 2 | - | 10.17 | B3LYP/6-31G(d,p) | -7.3 | -1.7 | -17.4 | 10.6 | -17.6 | 0.420 |
| | 2 | x, y, z | 3.94 | B3LYP/6-31G(d,p) | -4.0 | -2.4 | -83.5 | 48.8 | -48.6 | 0.048 |
| | 4 | -x+1/2, y+1/2, -z | 8.37 | B3LYP/6-31G(d,p) | -6.9 | -1.7 | -12.9 | 11.4 | -12.7 | 0.535 |

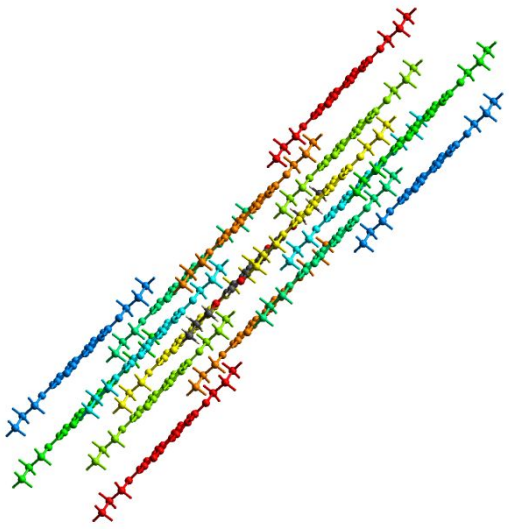

**Figure S9.** Colour coding based on the interactions energy with the central molecule for A-$OC_3$.

**Table S2. Molecular pairs and the stabilization energies (kJ $mol^{-1}$) obtained from decomposition of interactions energy calculation for A-$OC_3$**

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot | ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | x, y, z | 16.42 | B3LYP/6-31G(d,p) | 0.2 | -0.1 | -3.4 | 0.8 | -2.3 | -0.059 |
| | 2 | x, y, z | 4.91 | B3LYP/6-31G(d,p) | -13.7 | -2.6 | -99.3 | 58.1 | -67.1 | 0.138 |
| | 2 | x, y, z | 11.69 | B3LYP/6-31G(d,p) | -12.1 | -1.5 | -24.1 | 22.0 | -21.3 | 0.502 |
| | 2 | x, y, z | 13.14 | B3LYP/6-31G(d,p) | -3.1 | -3.0 | -20.3 | 11.4 | -16.1 | 0.153 |
| | 2 | x, y, z | 18.87 | B3LYP/6-31G(d,p) | -0.2 | -0.2 | -7.4 | 4.2 | -4.2 | 0.027 |
| | 2 | x, y, z | 8.80 | B3LYP/6-31G(d,p) | -5.8 | -1.4 | -31.7 | 17.3 | -24.1 | 0.183 |
| | 2 | x, y, z | 11.14 | B3LYP/6-31G(d,p) | -8.8 | -2.4 | -12.3 | 9.7 | -15.8 | 0.715 |
| | 2 | x, y, z | 16.51 | B3LYP/6-31G(d,p) | 0.3 | -0.1 | -2.5 | 0.0 | -1.9 | -0.120 |

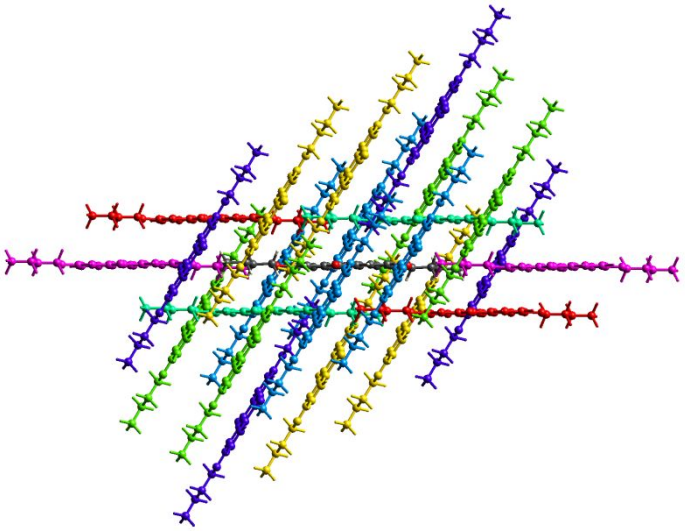

**Figure S10.** Colour coding based on the interactions energy with the central molecule for A-$OC_4$.

**Table S3. Molecular pairs and the stabilization energies (kJ $mol^{-1}$) obtained from decomposition of interactions energy calculation for A-$OC_4$**

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot | ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | x, y, z | 10.98 | B3LYP/6-31G(d,p) | -8.6 | -1.1 | -52.8 | 31.1 | -36.6 | 0.163 |
| | 4 | -x+1/2, y+1/2, -z+1/2 | 10.04 | B3LYP/6-31G(d,p) | -4.6 | -2.0 | -19.6 | 13.7 | -15.0 | 0.235 |
| | 4 | -x+1/2, y+1/2, -z+1/2 | 13.40 | B3LYP/6-31G(d,p) | -0.1 | -0.1 | -1.9 | 0.0 | -1.8 | 0.053 |
| | 2 | x, y, z | 7.23 | B3LYP/6-31G(d,p) | -13.9 | -2.2 | -83.9 | 48.3 | -59.5 | 0.166 |
| | 4 | -x+1/2, y+1/2, -z+1/2 | 8.67 | B3LYP/6-31G(d,p) | -5.2 | -2.1 | -9.7 | 6.1 | -11.7 | 0.536 |
| | 4 | -x+1/2, y+1/2, -z+1/2 | 14.33 | B3LYP/6-31G(d,p) | -1.1 | -0.2 | -6.4 | 2.8 | -5.1 | 0.172 |
| | 2 | x, y, z | 16.65 | B3LYP/6-31G(d,p) | -3.4 | -0.6 | -24.5 | 16.5 | -15.1 | 0.139 |

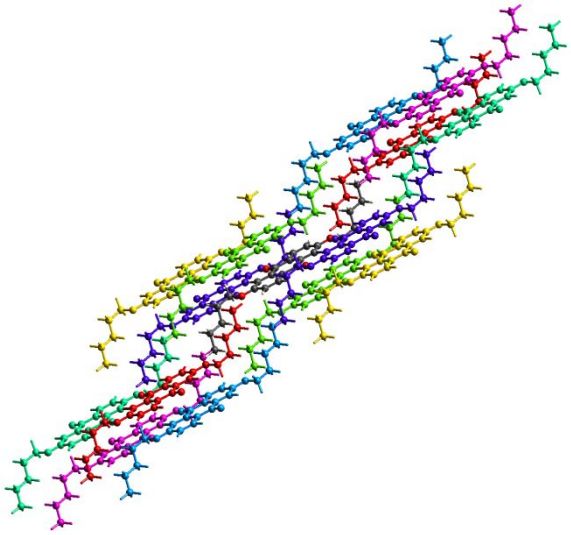

**Figure S11.** Colour coding based on the interactions energy with the central molecule for A-$OC_5$.

**Table S4. Molecular pairs and the stabilization energies (kJ $mol^{-1}$) obtained from decomposition of interactions energy calculation for A-$OC_5$**

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot | ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | x, y, z | 17.46 | B3LYP/6-31G(d,p) | -1.8 | -0.3 | -25.8 | 12.8 | -16.6 | 0.070 |
| | 2 | x, y, z | 9.91 | B3LYP/6-31G(d,p) | -13.2 | -4.5 | -24.3 | 17.1 | -27.8 | 0.543 |
| | 2 | x, y, z | 4.63 | B3LYP/6-31G(d,p) | -14.1 | -2.0 | -116.0 | 64.7 | -77.4 | 0.122 |
| | 2 | x, y, z | 22.26 | B3LYP/6-31G(d,p) | -0.2 | -0.0 | -5.7 | 1.7 | -4.1 | 0.035 |
| | 2 | x, y, z | 15.50 | B3LYP/6-31G(d,p) | -2.3 | -0.2 | -22.8 | 11.8 | -15.1 | 0.101 |
| | 2 | x, y, z | 8.12 | B3LYP/6-31G(d,p) | -11.7 | -5.6 | -44.5 | 33.7 | -34.4 | 0.263 |
| | 2 | x, y, z | 20.49 | B3LYP/6-31G(d,p) | -0.8 | -0.1 | -6.8 | 3.2 | -4.9 | 0.118 |

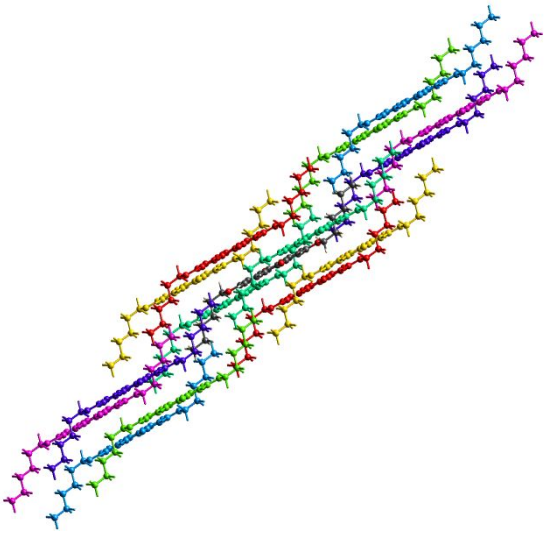

**Figure S12.** Colour coding based on the interactions energy with the central molecule for A-$OC_6$.

**Table S5. Molecular pairs and the stabilization energies (kJ $mol^{-1}$) obtained from decomposition of interactions energy calculation for A-$OC_6$**

| | N | Symop | R | Electron Density | E_ele | E_pol | E_dis | E_rep | E_tot | ratio |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2 | x, y, z | 4.63 | B3LYP/6-31G(d,p) | -14.5 | -2.2 | -123.2 | 68.2 | -82.1 | 0.118 |
| | 2 | x, y, z | 9.98 | B3LYP/6-31G(d,p) | -12.1 | -4.3 | -23.5 | 14.8 | -27.3 | 0.515 |
| | 2 | x, y, z | 16.83 | B3LYP/6-31G(d,p) | -3.4 | -0.2 | -23.3 | 15.3 | -14.6 | 0.146 |
| | 2 | x, y, z | 8.24 | B3LYP/6-31G(d,p) | -12.4 | -5.4 | -43.5 | 31.2 | -35.8 | 0.285 |
| | 2 | x, y, z | 21.89 | B3LYP/6-31G(d,p) | -0.6 | -0.1 | -8.5 | 2.7 | -6.4 | 0.071 |
| | 2 | x, y, z | 18.67 | B3LYP/6-31G(d,p) | -4.0 | -0.4 | -32.2 | 17.5 | -21.7 | 0.124 |
| | 2 | x, y, z | 23.56 | B3LYP/6-31G(d,p) | -2.1 | -0.1 | -10.7 | 9.0 | -6.0 | 0.196 |

## 4. 2D self-assembly analysis

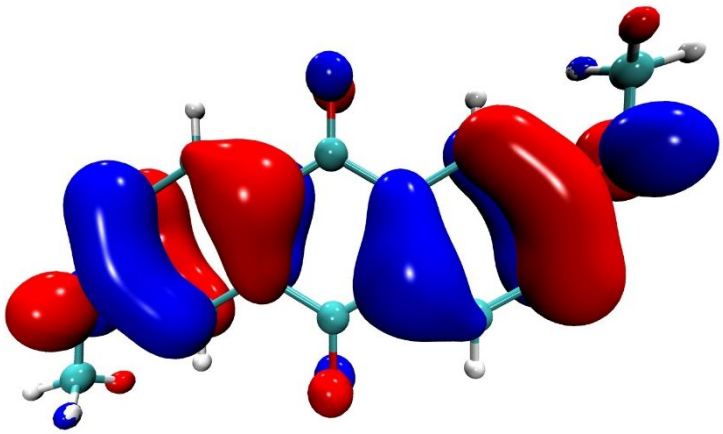

**Figure S13.** The image of the highest occupied molecular orbital (HOMO).

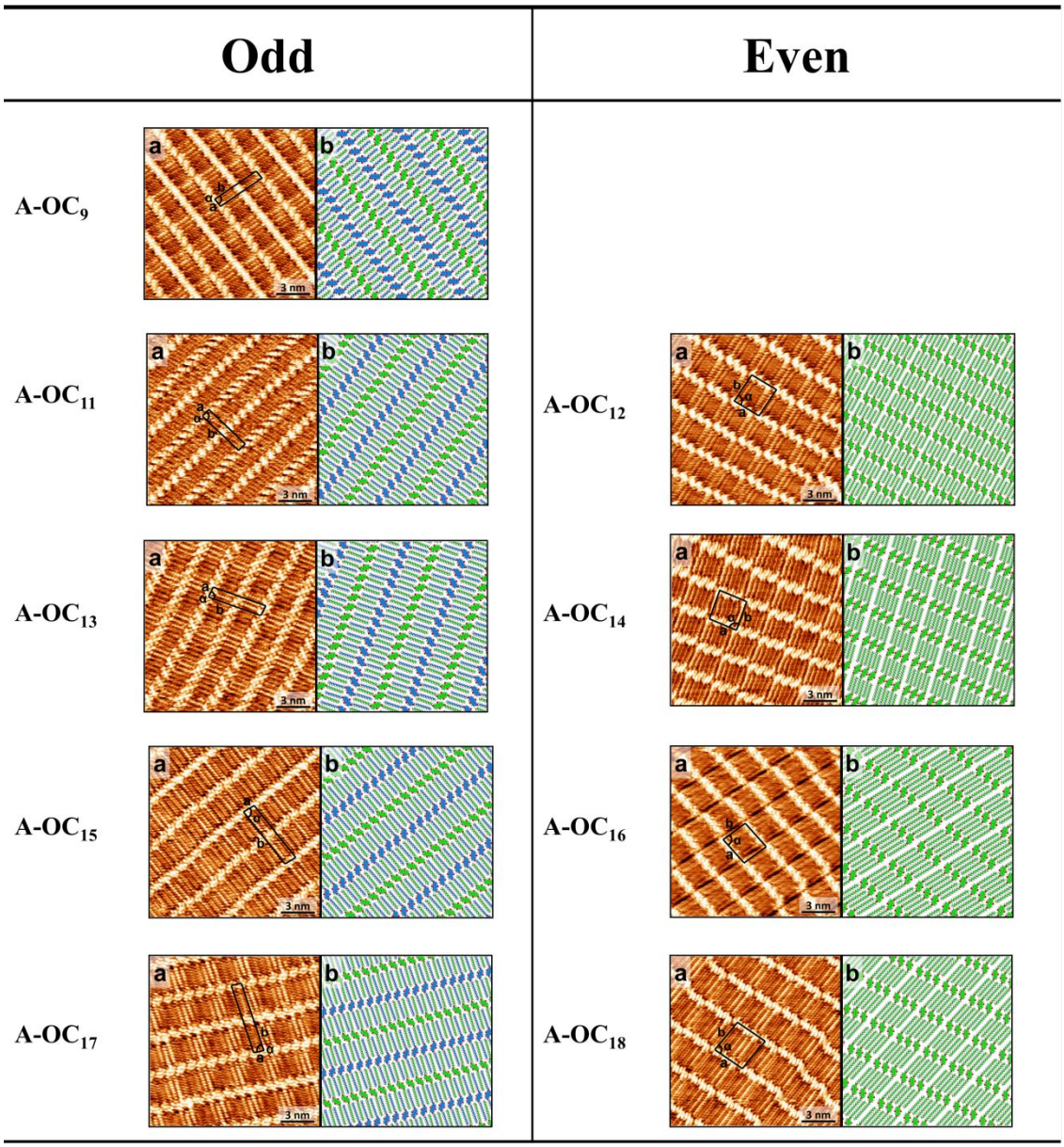


**Figure S14.** STM images and modes of the A-$OC_n$ (n = 9, 12–18) at the 1-octanoic acid/HOPG interface.