

Supporting Information

Effects of the position and number of bromine substituent on concentration-mediated 2D self-assembly of phenanthrene derivatives

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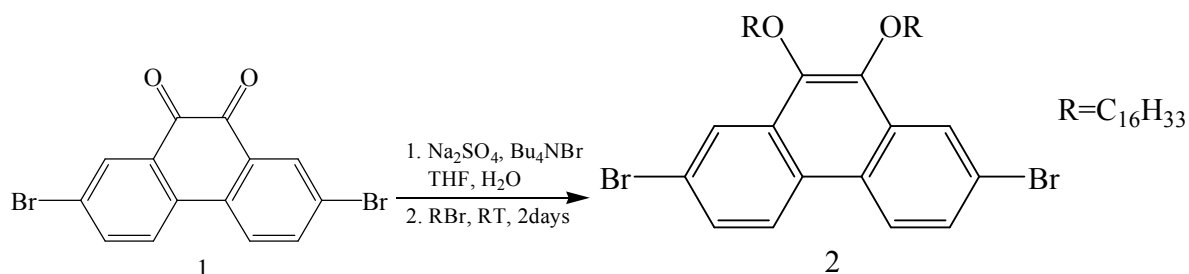
Experimental Section

1. General Information

^1H and ^{13}C NMR spectra were recorded out on a Bruker AV-400 MHz/Avance II 600 MHz NMR spectrometer. Mass spectra were determined using a Esquire HCT PLUS instrument. Infrared spectra were obtained with a LabRAM Aramis spectrometer.

2. Synthesis and Characterization of (2) 2,7-DBHP, (4) 3,6-DBHP and (6) 3-BBHP (8) BHP.

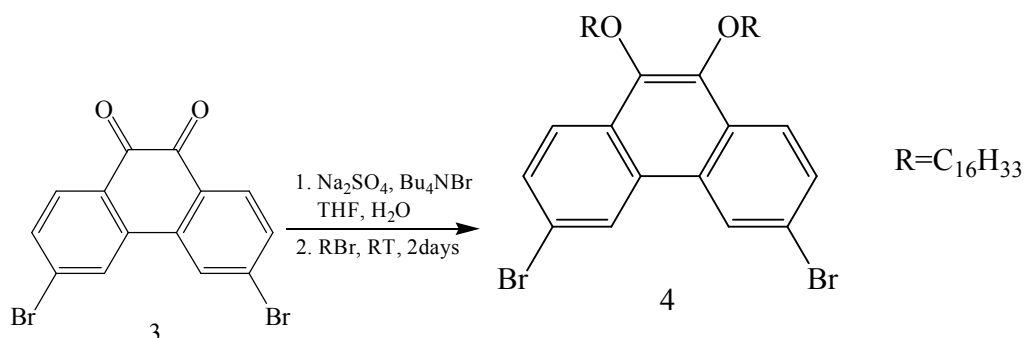
2.2. Scheme S1. Synthesis of Compound 2



Compound 2 A mixture of 2,7-dibromo-9,10-phenanthrenequinone (3.66 g, 10 mmol), Bu_4NBr (3.66 g, 11.34 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (17.60 g, 101.0 mmol) in H_2O (73 mL) and THF (73 mL) was stirred at room temperature for 5 min. Then, 1-bromohexadecane (79.70 g, 261.0 mmol) was added followed by sodium hydroxide (10.44 g, 261.0 mmol) in H_2O (73 mL). After stirring for 2 days, the reaction mixture was diluted with H_2O (200 mL) before the white suspension was filtered through a sintered funnel. The white residue was washed with H_2O (1×200 mL), dried over MgSO_4 , and evaporated to dryness. The product was recrystallized from hot n-hexane. Further purification was achieved in two successive columns (SiO_2 , CHCl_3) to give a fluffy white product.

Data for 2. ^1H NMR (600 MHz, CDCl_3 , ppm): δ 8.42 (2H, m), 8.38 (2H, m), 7.68 (2H, m), 4.18 (4H, m), 1.89 (4H, m), 1.36 (4H, m), 1.26 (48H, m), 0.88 (6H, m).

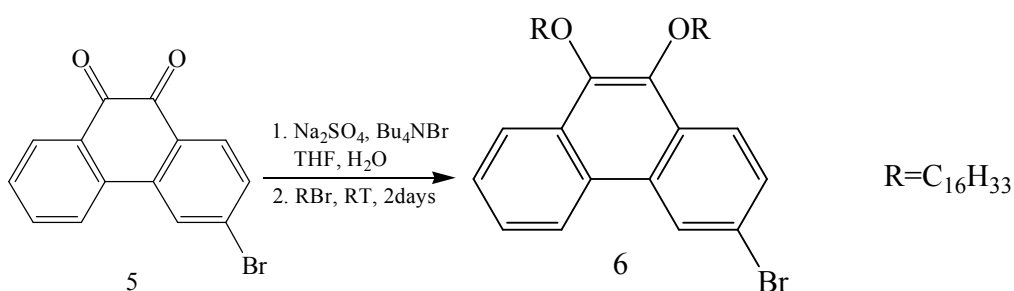
2.3. Scheme S2. Synthesis of Compound 4



Compound 4 A mixture of 3,6-dibromo-9,10-phenanthrenequinone (3.66 g, 10 mmol), Bu_4NBr (3.66 g, 11.34 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (17.60 g, 101.0 mmol) in H_2O (73 mL) and THF (73 mL) was stirred at room temperature for 5 min. Then, 1-bromohexadecane (79.70 g, 261.0 mmol) was added followed by sodium hydroxide (10.44 g, 261.0 mmol) in H_2O (73 mL). After stirring for 2 days, the reaction mixture was diluted with H_2O (200 mL) before the white suspension was filtered through a sintered funnel. The white residue was washed with H_2O (1×200 mL), dried over MgSO_4 , and evaporated to dryness. The product was recrystallized from hot n-hexane. Further purification was achieved in two successive columns (SiO_2 , CHCl_3) to give a fluffy yellowish product.

Data for 4. ^1H NMR (600 MHz, CDCl_3 , ppm): δ 8.68 (2H, m), 8.09 (2H, m), 7.71 (2H, m), 4.18 (4H, m), 1.88 (4H, m), 1.37 (4H, m), 1.26 (48H, m), 0.88 (6H, m).

2.4. Scheme S3. Synthesis of Compound 6

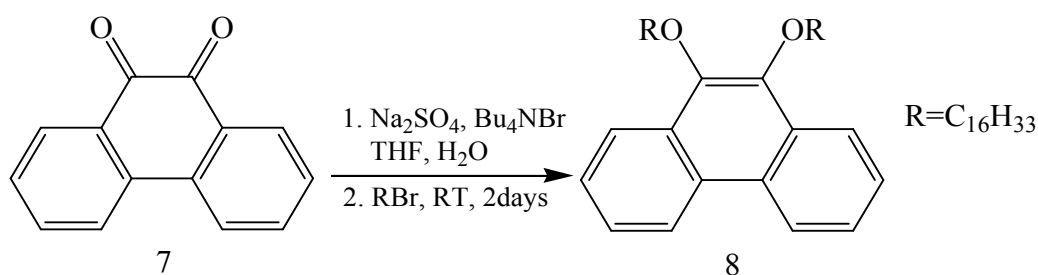


Compound 6 A mixture of 3-bromo-9,10-phenanthrenequinone (2.87 g, 10 mmol), Bu_4NBr (3.66 g, 11.34 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (17.60 g, 101.0 mmol) in H_2O (73 mL) and THF (73 mL) was stirred at room temperature for 5 min. Then, 1-bromohexadecane (79.70 g, 261.0 mmol) was added followed by sodium hydroxide (10.44 g, 261.0 mmol) in H_2O (73 mL). After stirring for 2 days, the reaction mixture was diluted with H_2O (200 mL) before the white suspension was filtered through a sintered funnel. The white residue was washed with H_2O (1×200 mL), dried over MgSO_4 , and evaporated

to dryness. The product was recrystallized from hot n-hexane. Further purification was achieved in two successive columns (SiO_2 , CHCl_3) to give a fluffy white product.

Data for 6. ^1H NMR (600 MHz, CDCl_3 , ppm): δ 8.68 (2H, m), 8.09 (2H, m), 7.71 (2H, m), 4.18 (4H, m), 1.88 (4H, m), 1.37 (4H, m), 1.26 (48H, m), 0.88 (6H, m).

2.4. Scheme S4. Compound 8



Compound 8 A mixture of 9,10-phenanthrenequinone (2.08 g, 10 mmol), Bu_4NBr (3.66 g, 11.34 mmol), $\text{Na}_2\text{S}_2\text{O}_4$ (17.60 g, 101.00 mmol) in H_2O (73 mL) and THF (73 mL) was stirred at room temperature for 5 min. Then, 1-bromohexadecane (79.70 g, 261.0 mmol) was added followed by sodium hydroxide (10.44 g, 261.0 mmol) in H_2O (73 mL). After stirring for 2 days, the reaction mixture was diluted with H_2O (200 mL) before the white suspension was filtered through a sintered funnel. The white residue was washed with H_2O (1×200 mL), dried over MgSO_4 , and evaporated to dryness. The product was recrystallized from hot n-hexane. Further purification was achieved in two successive columns (SiO_2 , CHCl_3) to give a fluffy white product.

Data for 8. ^1H NMR (600 MHz, CDCl_3 , ppm): δ 8.63 (2H, m), 8.26 (2H, m), 7.61 (2H, m), 7.59 (2H, m), 4.22 (4H, m), 1.91 (4H, m), 1.31 (4H, m), 1.27 (40H, m), 0.89 (6H, m).

3. Computational simulation

Molecular models of the assembled structures were built by Materials Studio 4.4. The model of monolayer was constructed by placing the molecules according to the intermolecular distances and angles that were obtained from the analysis of STM images. Semiempirically calculated spatial distribution of the HOMO for BHP, 2,7-DBHP, 3,6-DBHP and 3-BBHP is performed by Gaussian 03W.

DFT calculations were performed with Gaussian 03 software package. All the geometry full-optimization of those structures were done through the hybrid B3LYP method together with the

split-valence polarized 6-31G(d) basis set. The B3LYP functional has been found to provide good agreement with experimental results for the adsorption of organic molecules on different surface.^{3,4} The 6-31G(d) basis set was found to provide the lowest total energy and to be more suitable for modeling hydrogen bonded (ad) species.⁵ Halogen bond is similar to hydrogen bond known as a kind of non-covalent intermolecular interaction.

References:

- [1] Bhatt, M. V. Tetrahedron 1964, 20, 803.
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- [3] Tao, F.; Qiao, M.; Li, Z.; Yang, L.; Dai, Y.; Huang, H.; Xu, G. Phys. Rev. B. 2003, 67,1–7.
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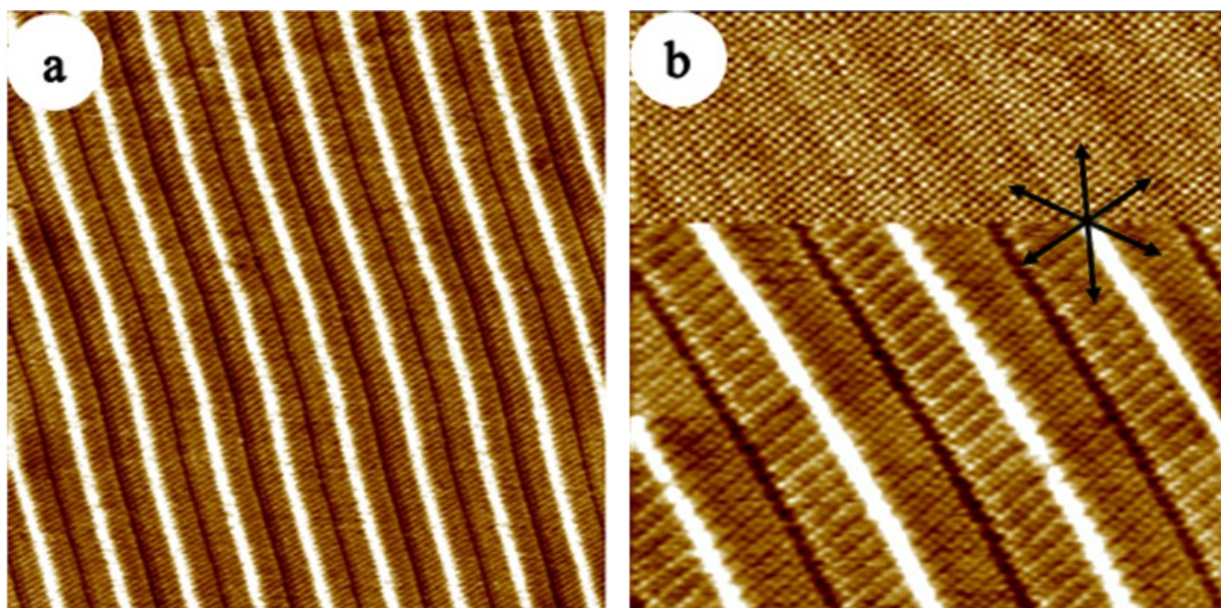


Figure S1. (a) Large-scale STM image of **2,7-DBHP** showing the linear arrangement formed at 1-octanoic acid/HOPG interface with high concentrations ($1.84 \times 10^{-3} \text{ mol L}^{-1}$): scan area $45 \times 45 \text{ nm}^2$; $V_{\text{bias}} = 520 \text{ mV}$; $I_{\text{t}} = 450 \text{ pA}$. (b) Corresponding high-resolution STM image showing the molecules are tightly packed forming parallel rows: scan area $15 \times 15 \text{ nm}^2$; $V_{\text{bias}} = 100 \text{ mV}$; $I_{\text{t}} = 400 \text{ pA}$. The image was obtained by switching the bias during the STM scan from the bottom to the upper frame.

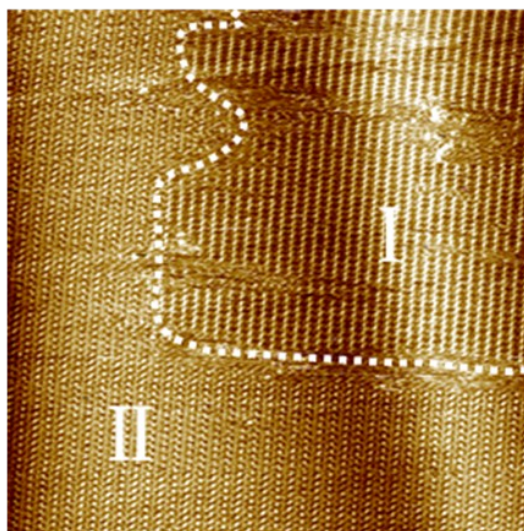


Figure S2. Alternate pattern was observed which coexists with the linear structure. Scan area: $200 \times 200 \text{ nm}^2$.

Table S1. Summary of Structural Parameters of the 2D Nanopatterns Assembled by 2,7-DBHP , 3,6-DBHP,

3-BBHP, BHP.

Molecule	Structure	a (nm) ^A	b (nm) ^B	γ (°) ^C	Molecular density(nm ² /molecule)
2,7-DBHP	Linear pattern	0.46 ± 0.02	4.19 ± 0.05	89 ± 1	1.93
	Alternate pattern	2.73 ± 0.02	10.10 ± 0.03	87 ± 1	2.29
	Linear dimer pattern	1.81 ± 0.03	7.36 ± 0.03	76 ± 1	3.22
3,6-DBHP	Linear pattern	0.44 ± 0.02	4.20 ± 0.02	89 ± 1	1.85
	Zigzag pattern	1.09 ± 0.02	2.46 ± 0.02	84 ± 1	1.33
3-BBHP	Linear pattern	1.43 ± 0.04	2.53 ± 0.03	73 ± 1	2.31
BHP	Linear pattern	0.45 ± 0.02	4.21 ± 0.04	89 ± 1	1.94

^A Distance between two molecular aggregations (see figures). ^B Period of the pattern (see figures). ^C Angel between side chain axis and the packing orientation.

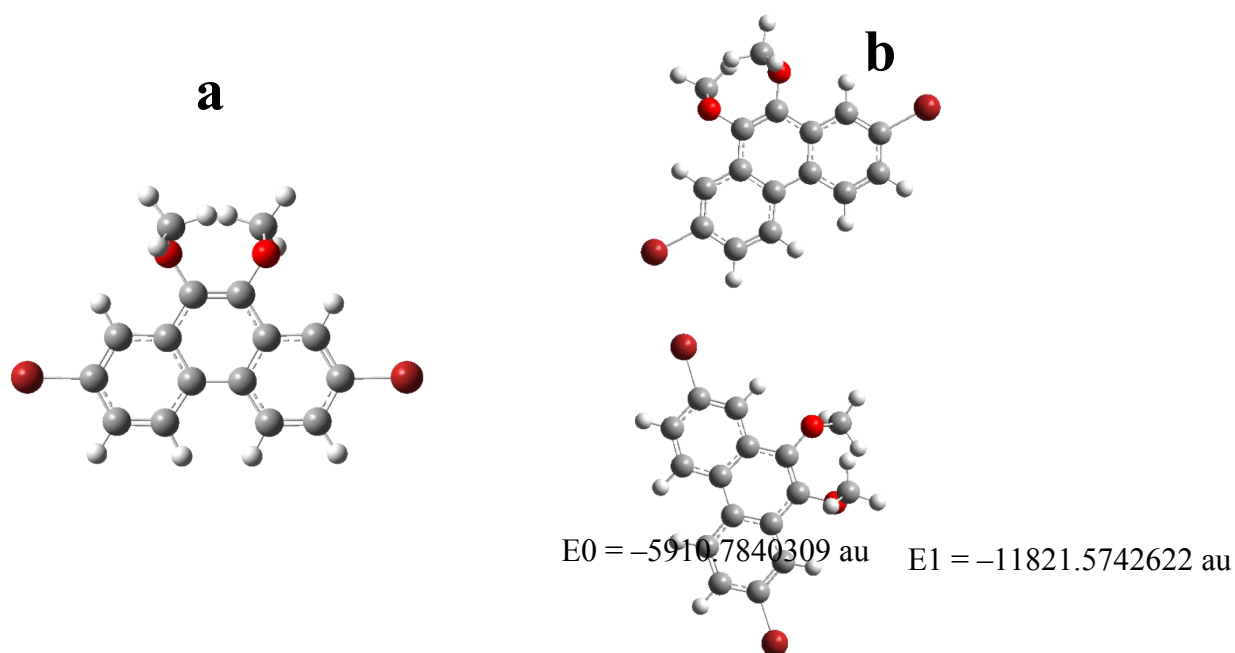


Figure S3. DFT optimized atomic structure of 2,7-DBHP. (a) single molecule, (b) dimer structure. The calculated energy was indicated in each figure.

The binding energy was calculated as below.

$$\Delta E_1 = E_1 - 2E_0 = -0.0075553 \text{ a.u} = -4.74 \text{ kcal/mol}$$

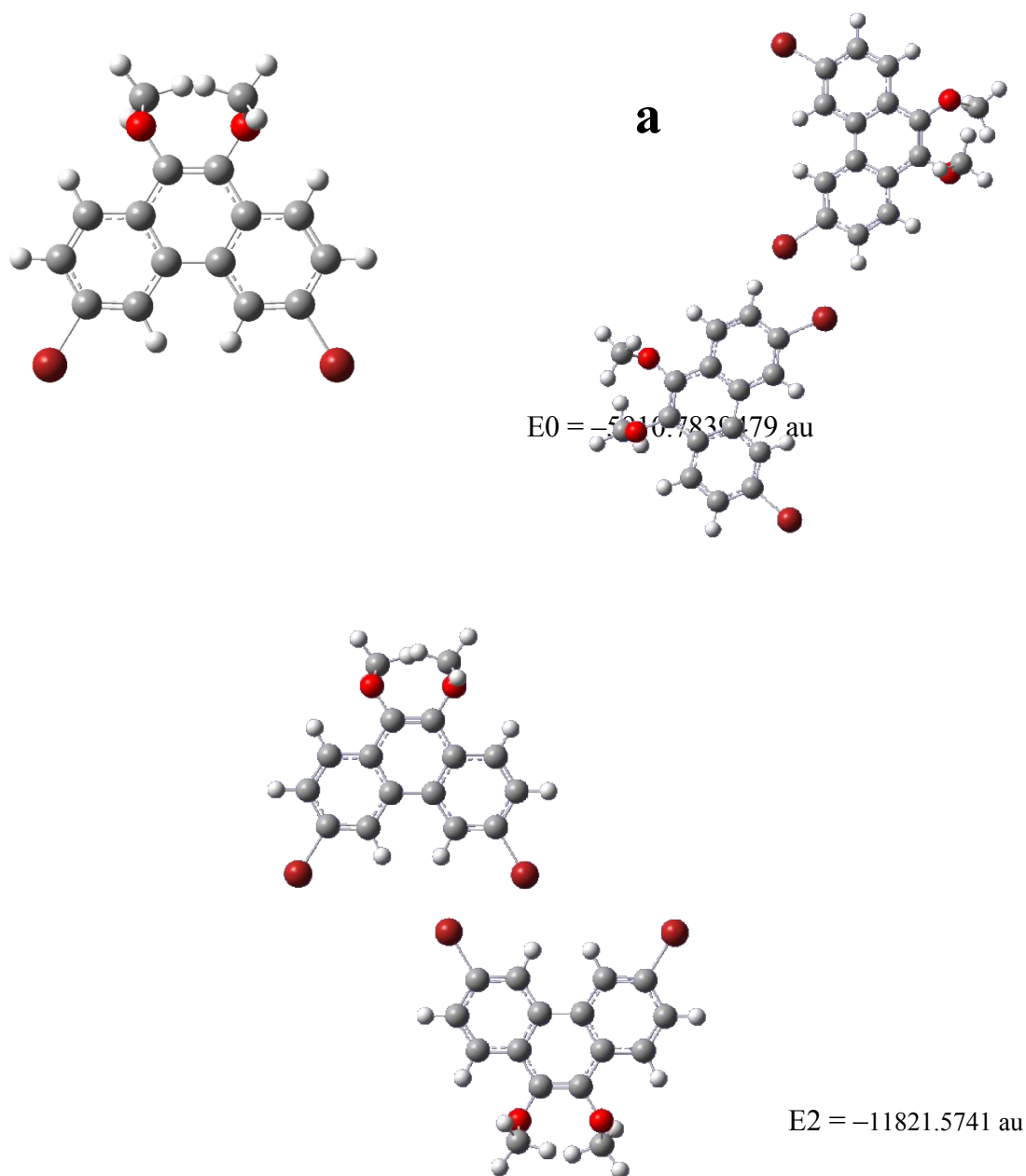


Figure S4. DFT optimized atomic structure of 3,6-DBHP. (a) single molecule, (b) dimer I structure and dimer II. The calculated energy was indicated in each figure.

The binding energy was calculated as below.

$$\Delta E_1 = E_1 - 2E_0 = -0.0074204 \text{ a.u} = -4.6563 \text{ kcal/mol}$$

$$\Delta E_2 = E_2 - 2E_0 = -0.006223 \text{ a.u} = -3.904 \text{ kcal/mol}$$

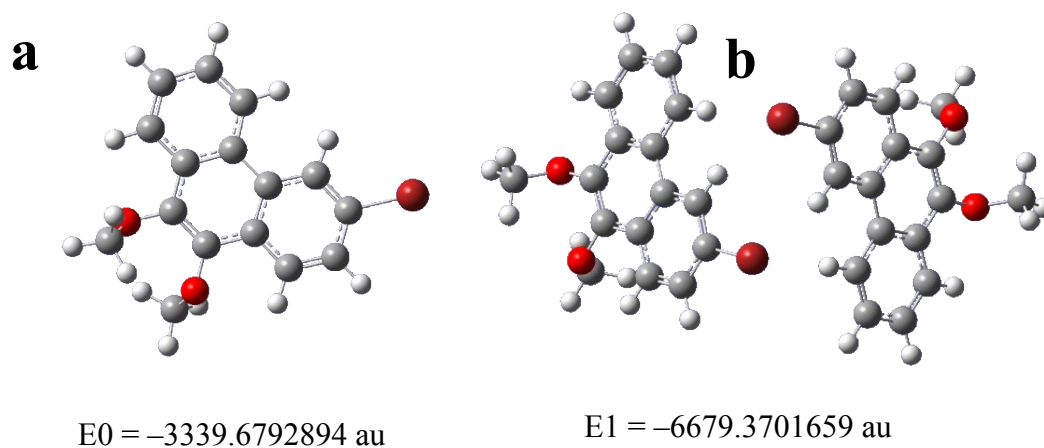


Figure S5. DFT optimized atomic structure of 3-BBHP (a) single molecule, (b) dimer structure. The calculated energy was indicated in each figure.

The binding energy was calculated as below.

$$\Delta E_1 = E_1 - 2E_0 = -0.0115859 \text{ a.u} = -7.27 \text{ kcal/mol}$$