Supporting Information

Diverse supramolecular structures self-assembled by a simple aryl chloride on Ag(111) and Cu(111)

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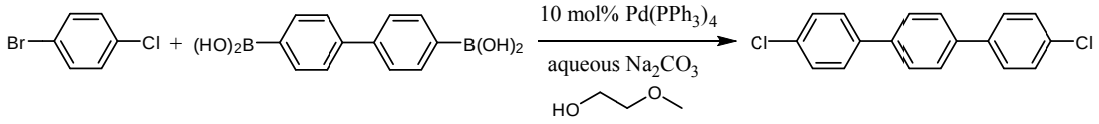
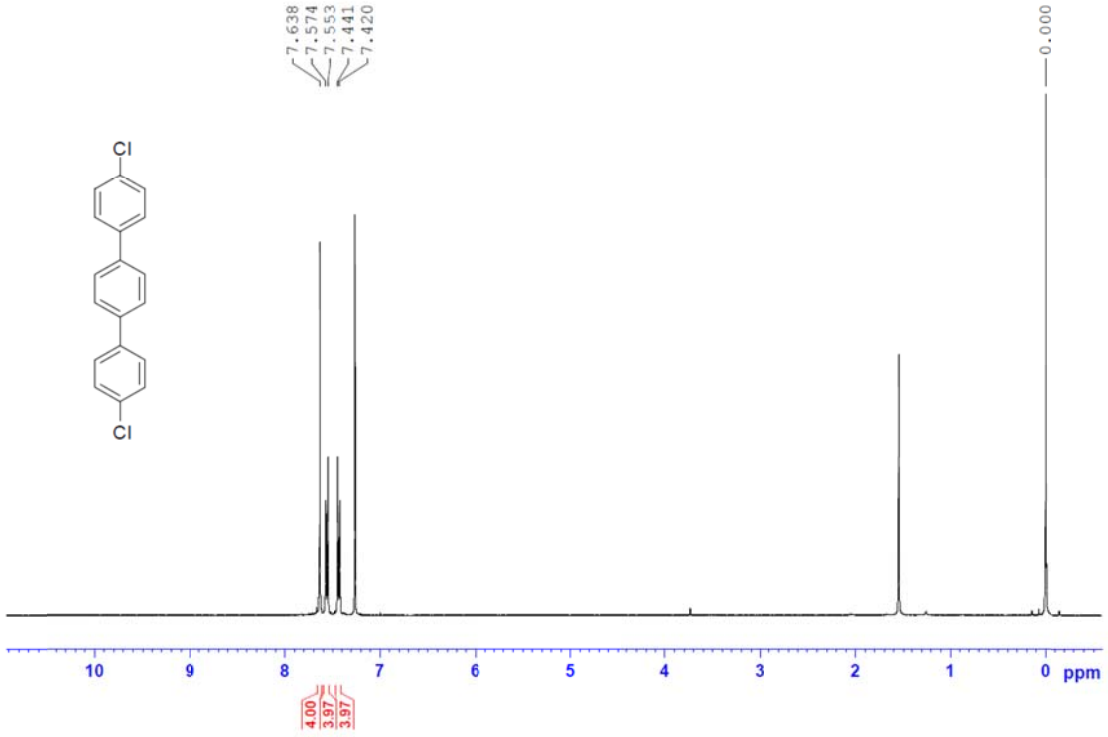
Content

1. Synthesis of the organic molecule



4, 4''-Dichloro-*p*-terphenyl (DCTP). To a solution of 1-bromo-4-chlorobenzene (7.2 mmol), [1,1'-biphenyl]-4,4'-diyldiboronic acid (3.0 mmol) and $Pd(PPh_3)_4$ (0.3 mmol, 10 mol%) in 2-methoxyethanol (30 mL) was added 2 M degassed aqueous Na_2CO_3 solution (6 mL) under N_2 atmosphere. The resulting mixture was stirred at reflux for 24 h. After cooling to room temperature, the mixture was filtered and the solid residue was washed with ethyl acetate (5 * 30 mL) and petroleum ether (3 * 30 mL). The solid residue was then purified by sublimation twice in *vaccum* to give the product as white solid in 12% yield (107 mg). Mp: 285-288 ^oC; ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC) δ 7.43 (d, J = 8.6 Hz, 4H); 7.56 (d, J = 8.6 Hz, 4H), 7.64 (s, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 ^oC) δ 127.6, 128.4, 129.2, 133.7, 139.1, 139.4; HRMS (EI, TOF) calcd for $C_{18}H_{12}Cl_2^+$ $[M]^+$: 298.0316, found: 298.0319 .

^{1}H NMR of 4,4''-dichloro-1,1':4',1''-terphenyl (DCTP)



1,1':4',1''-terphenyl is the commercially available compound.

2. General procedure for STM experiments

STM imaging was performed using a commercial ultrahigh vacuum system (base pressure, 2 * 10^{-10} mbar) equipped with a variable temperature scanning tunneling microscope (SPECS, Aarhus 150), a molecular evaporator, and standard facilities for sample preparation. Single-crystalline Cu(111) and Ag(111) surfaces were cleaned through cycles of argon ion sputtering and annealing. After thorough degassing, DCTP (or TP) were deposited onto the substrate held at 293 K by thermal sublimation (DCTP: 400 K, 2 min; TP: 293 K, 0.5 min) and annealed to the indicated temperature and maintained for 20 min. STM measurements were taken at ~120 K.

3. General procedure for the calculations

All periodic calculations were carried out by using of the Vienna Ab initio Simulation Package (VASP, version 5.3.5)[1-4] based on the plane-wave density functional theory (PW-DFT) within the projector augmented wave (PAW) potential method.[5] The exchange-correlation interaction is described by generalized gradient approximation (GGA) with the parametrization of Perdew-Burke-Ernzerhof (PBE).[6] The DFT-D3 method,[7] developed by the group of Grimme, was applied to correct the dispersion calculations, and the Becke-Johnson damping[8] with the most recent damping function[9] was employed to avoid the vanishing forces at short distances. The plane-wave cutoff energy is set as 400 eV. The optimization was performed by means of the conjugate gradient algorithm and 2 * 2 * 1 Monkhorst-Pack k-point grid, [10] with the convergence criteria set such the difference in total energy is within 1 * 10^{-5} eV and the force is less than 0.05 eV/Å for each ion.

4. Supplementary Table

Table S1. Geometric, Topological and Energetic Data for All the Self-assembling Models under Study[a]

			Interaction	d	$10^2\rho$	10^2V	E_B
Cu(111)-RT-1							
A	B	CP1	C-H···Cl	3.029	0.378	-0.151	-20.5
		CP2	C-Cl···Cl	4.061	0.291	-0.112	-15.2
		CP3	C-H···Cl	2.894	0.553	-0.254	-34.5
Cu(111)-RT-2							
A	B	CP1	C-H···Cl	2.936	0.519	-0.229	-31.2
		CP2	C-Cl···Cl	4.105	0.269	-0.104	-14.1
		CP3	C-H···Cl	2.931	0.520	-0.232	-31.5
B	C	CP4	C-H···Cl	3.389	0.195	-0.076	-10.3
		CP5	C-H···Cl	3.475	0.157	-0.063	-8.5
A	C	CP6	C-Cl···Cl	3.546	0.588	-0.279	-38.0
		CP7	C-H···Cl	2.998	0.531	-0.225	-30.6
Ag(111)-RT							
A	B	CP1	C-H···Cl	3.019	0.451	-0.186	-25.3
		CP2	C-H···Cl	3.068	0.414	-0.165	-22.5
B	C	CP3	C-H···Cl	4.358	0.030	-0.012	-1.6
C	D	CP4	C-H···Cl	2.993	0.446	-0.191	-26.0
		CP5	C-H···Cl	3.037	0.411	-0.171	-23.3
C	E	CP6	C-H···Cl	4.194	0.042	-0.015	-2.1
E	F	CP7	C-H···Cl	2.989	0.485	-0.204	-27.8
		CP8	C-H···Cl	3.024	0.452	-0.185	-25.2
C	F	CP9	C-H···Cl	5.257	0.004	-0.001	-0.2
Ag(111)-373K							
A_1	A_2	CP1	C-H···Cl	2.893	0.762	-0.386	-52.6
		CP2	C-H···Cl	3.020	0.429	-0.207	-28.1
A_2	A_3	CP3	C-H···Cl	2.855	0.636	-0.299	-40.7
		CP4	C-H···Cl	2.971	0.404	-0.189	-25.8
A_3	A_1	CP5	C-H···Cl	2.797	0.678	-0.328	-44.6
		CP6	C-H···Cl	2.986	0.447	-0.214	-29.1
A_1	B_1	CP7	C-H···Cl	3.413	0.217	-0.083	-11.3
B_1	A_2	CP8	C-Cl···Cl	3.770	0.373	-0.149	-20.3
A_2	B_2	CP9	C-H···Cl	3.241	0.171	-0.064	-8.7

B_2	A_3	CP10	C-Cl···Cl	3.671	0.427	-0.176	-23.9
A_3	B_3	CP11	C-H···Cl	3.307	0.246	-0.096	-13.1
B_3	A_1	CP12	C-Cl···Cl	3.848	0.514	-0.223	-30.3
B_1	C_1	CP13	C-H···Cl	3.223	0.373	-0.168	-22.9
		CP14	C-H···Cl	2.963	0.750	-0.364	-49.5
C_1	A_2	CP15	C-H···Cl	3.197	0.443	-0.204	-27.7
		CP16	C-H···Cl	2.766	0.816	-0.412	-56.0
B_2	C_2	CP17	C-H···Cl	2.981	0.298	-0.131	-17.8
		CP18	C-H···Cl	3.032	0.589	-0.260	-35.4
C_2	A_3	CP19	C-H···Cl	2.829	0.873	-0.453	-61.7
B_3	C_3	CP20	C-H···Cl	2.848	0.531	-0.229	-31.2
		CP21	C-H···Cl	3.151	0.481	-0.218	-29.6
C_3	A_1	CP22	C-H···Cl	2.808	0.772	-0.380	-51.8
A_1	D_1	CP23	C-H···Cl	2.924	0.821	-0.416	-56.6
		CP24	C-H···Cl	2.991	0.390	-0.147	-20.0
D_2	A_1	CP25	C-H···Cl	3.098	0.671	-0.312	-42.4
		CP26	C-H···Cl	3.043	0.515	-0.215	-29.2
D_2	B_1	CP27	C-H···Cl	2.812	0.182	-0.066	-8.9
A_2	D_3	CP28	C-H···Cl	2.922	0.614	-0.273	-37.1
		CP29	C-H···Cl	3.110	0.535	-0.224	-30.5
A_2	D_4	CP30	C-H···Cl	2.971	0.477	-0.193	-26.3
		CP31	C-H···Cl	2.881	0.426	-0.165	-22.4
D_4	B_2	CP32	C-H···Cl	3.149	0.640	-0.317	-43.2
A_3	D_5	CP33	C-H···Cl	2.773	0.613	-0.272	-37.0
		CP34	C-H···Cl	3.144	0.420	-0.161	-22.0
A_3	D_6	CP35	C-H···Cl	2.860	0.655	-0.299	-40.7
		CP36	C-H···Cl	2.997	0.551	-0.234	-31.8
D_6	B_3	CP37	C-H···Cl	4.025	0.221	-0.087	-11.8
		CP38	C-H···Cl	3.393	0.296	-0.117	-15.9

[a]The bond length are given in angstrom, topological parameters in a.u., and bond energies in meV.

5. Supplementary Figures

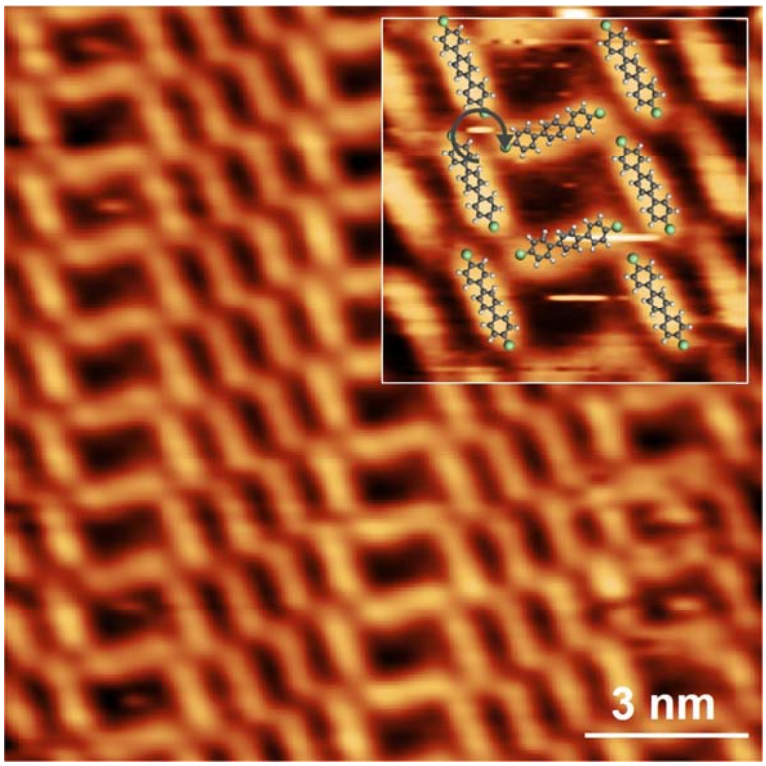


Figure S1. Self-assembled phase **II** on Cu(111) with clockwise nodes in the ladder-like structure. Scanning parameters: I = 0.07 nA, U = -1.68 V.

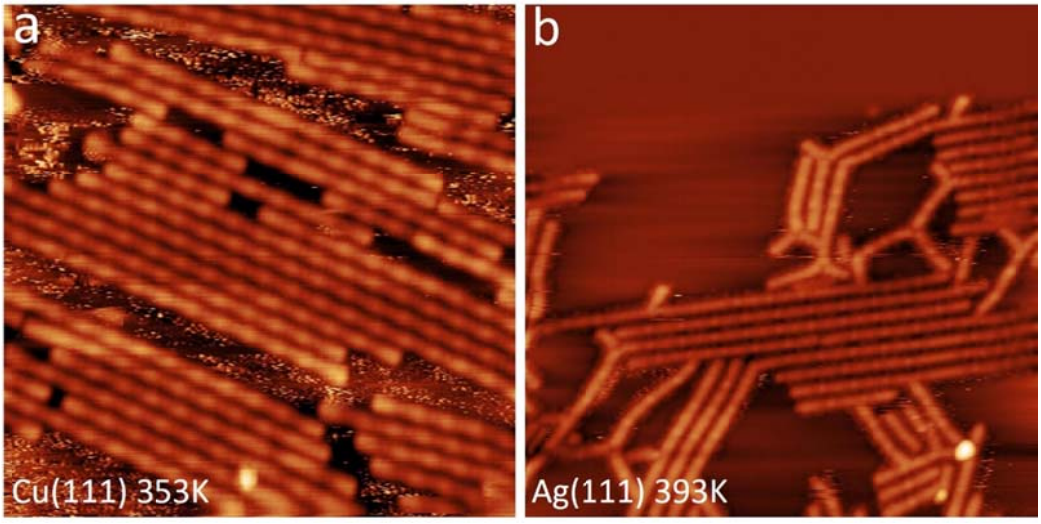


Figure S2. (a) the organomtallic chain of DCTP on Cu(111), annealed at 353K. (b) the organomtallic chain of DCTP on Ag(111), annealed at 393 K. scanning condition: (a) I = 0.08 nA, U = -1.0 V; (b) I = 0.08 nA, U = -2.0 V.

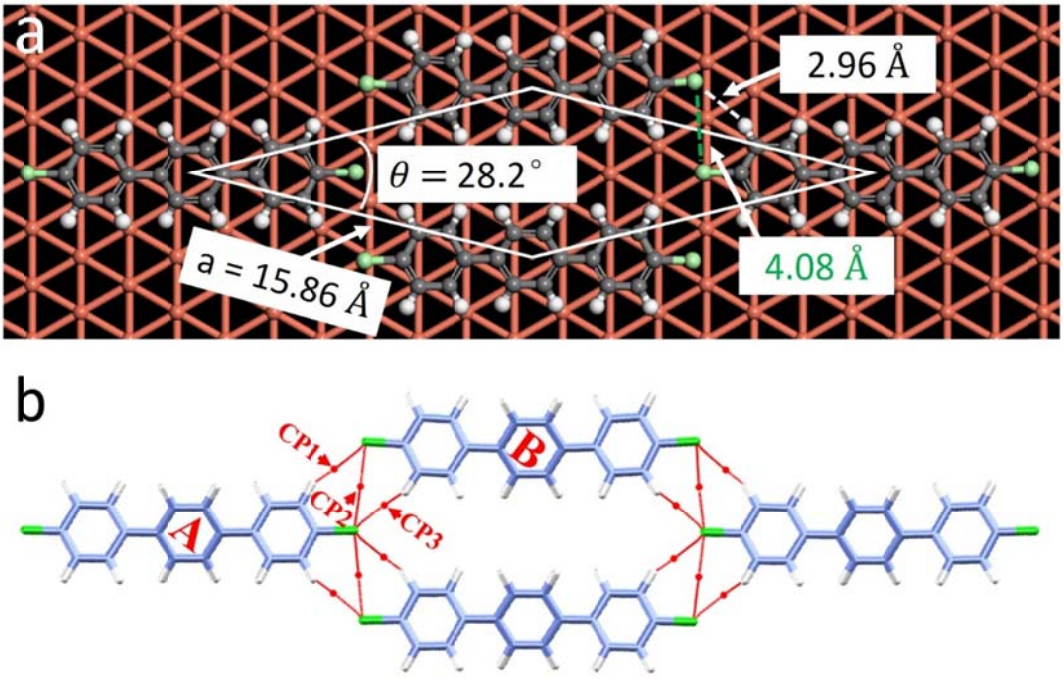


Figure S3. (a) The optimized structure of the self-assembled phase **I** on Cu(111) calculated by DFT. (b) Corresponding critical points (CPs) of the self-assembled phase **I**.

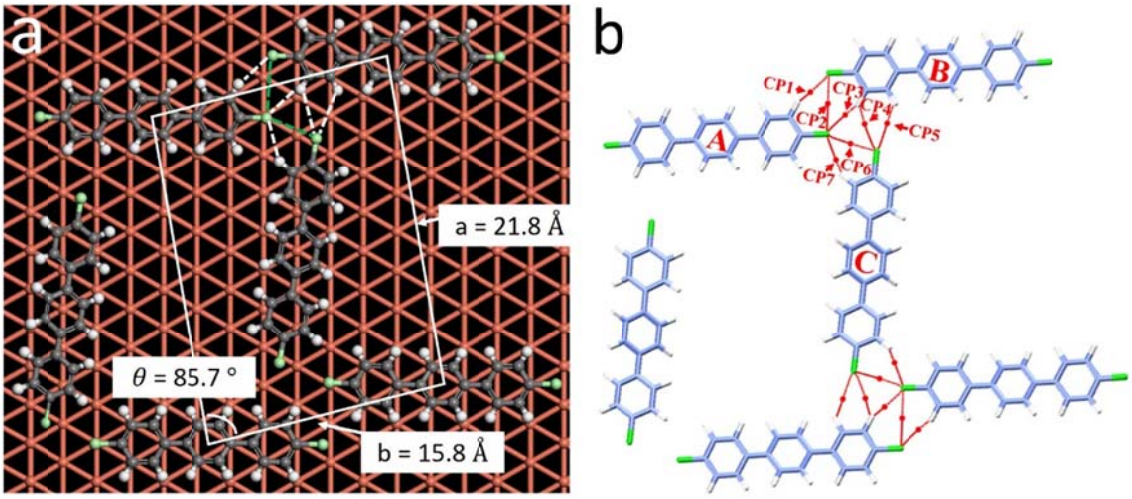


Figure S4. (a) The optimized structure of the self-assembled phase **II** on Cu(111) calculated by DFT. (b) Corresponding critical points (CPs) of the self-assembled phase **II**.

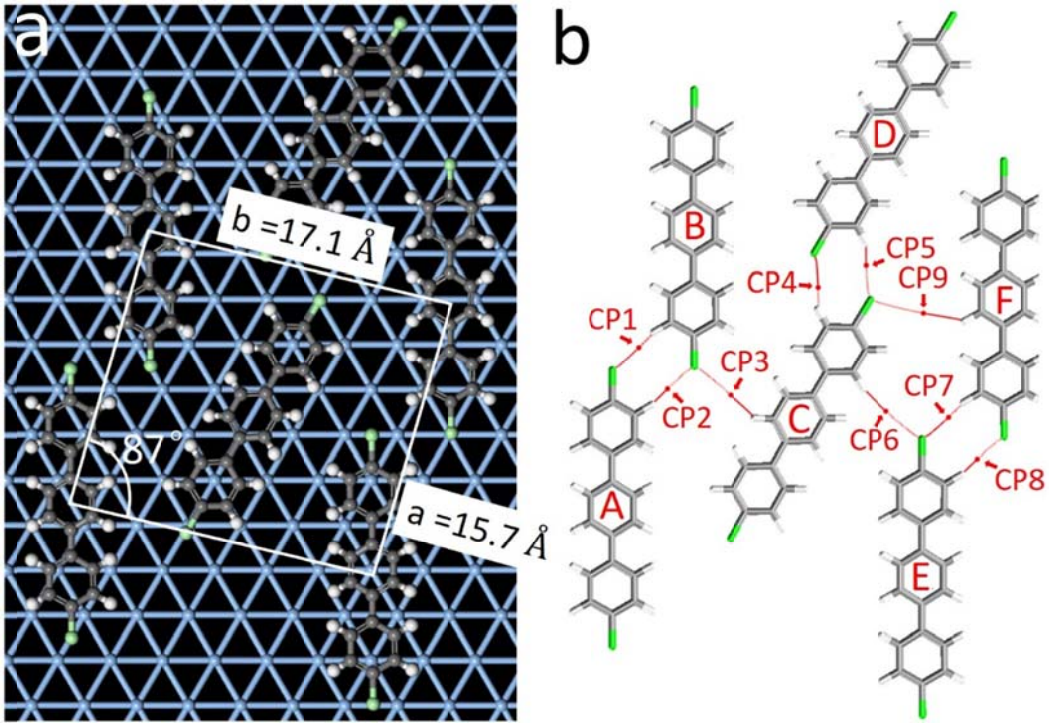


Figure S5. (a) The optimized structure of herringbone-like structure on Ag(111) calculated by DFT. (b) Corresponding critical points (CPs) of herringbone-like structure.

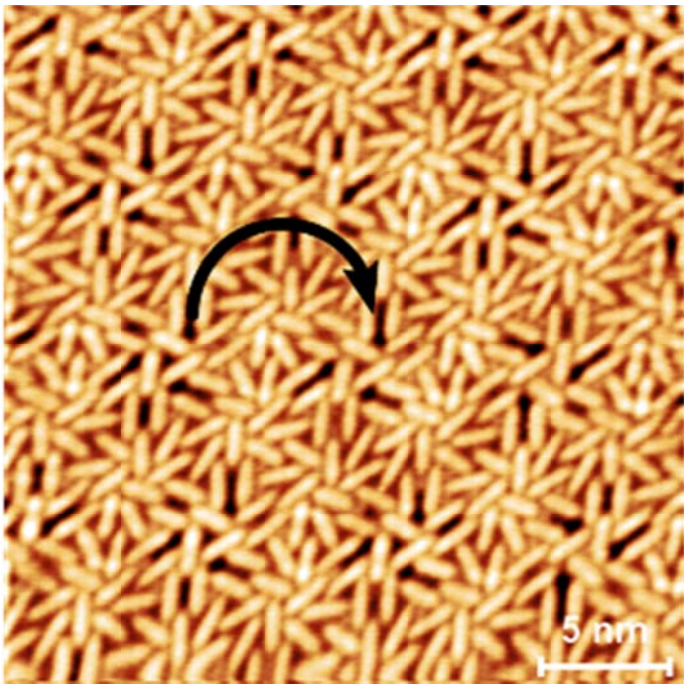


Figure S6. The clockwise vortex structure after 373 K annealing.

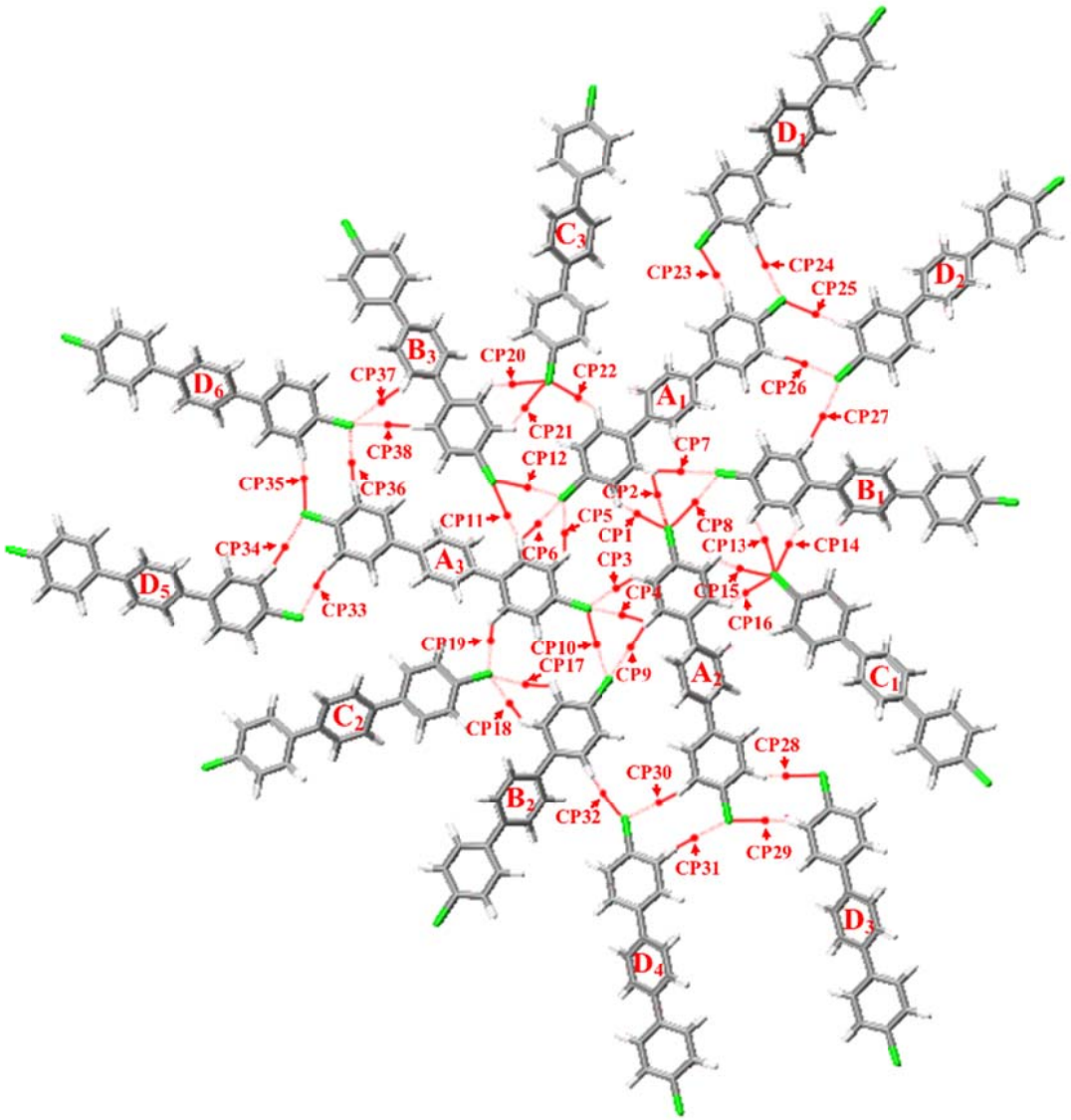


Figure S7. Corresponding CPs of vortex structure calculated in vacuum.

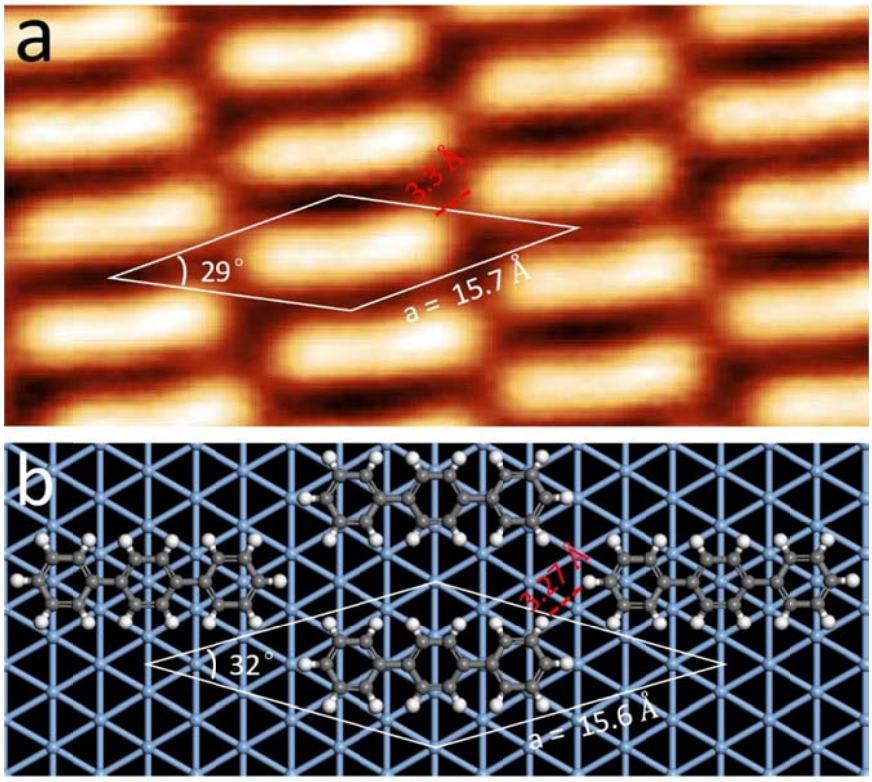


Figure S8. (a) STM image of 1,1':4',1"-terphenyl on Ag(111) at 373 K. (b)The optimized self-assembly structure of 1,1':4',1"-terphenyl on Ag(111) calculated by DFT.

6. References

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