Structural Flexibility and Mobility of Coordination Polymers on Cu(111)

Waka Nakanishi,*[a],[b] † Masayuki Takeuchi,[a],[b],[c] Keisuke Sagisaka*[d] †

[a] Molecular Design and Function Group, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
E-mail: NAKANISHI.Waka@nims.go.jp
[b] Research Center for Autonomous Systems Materialogy (ASMat), Institute of Integrated Research (IIR), Institute of Science Tokyo (Science Tokyo), 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8501, Japan
[c] Department of Materials Science and Engineering, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan
[d] Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
Email: SAGISAKA.Keisuke@nims.go.jp
† These two authors contributed equally to this work.

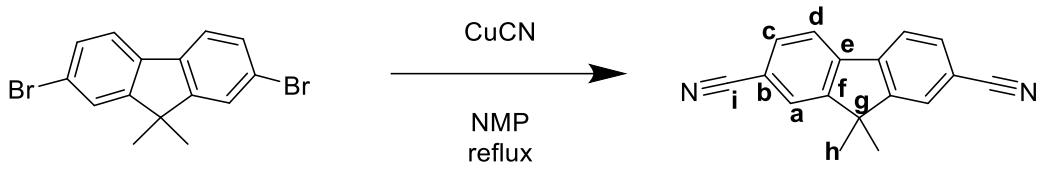
Contents

1. General and materials

Analytical thin-layer chromatography (TLC) was performed on a glass almina coated with silica gel (230-400 mesh, 0.25 mm thickness) containing a fluorescent indicator (silica gel 60F254, Merck). Automated flash purifications on regular silica gel were performed with a Biotage Isolera Prime device. Infrared (IR) spectra were recorded on Thermo Scientific Nicolet NEXUS 670 FT-IR with wavenumbers (n) in cm^{-1}. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA400 spectrometer. Mass spectra were obtained on Bruker micrOTOFII (APCI-TOF). Isotopic distribution patterns were simulated using enviPat.[1] Solvents and materials were purchased from Aldrich, Tokyo Kasei Chemical Co. and Wako Chemical Co., and were used without further purification.

2. Synthesis

Scheme S1. Synthesis of 2,7-dicyano-9,9-dimethylfluorene (DCF).



Under conditions similar to those reported,[2] to a solution of 2,7-dibromo-9,9-dimethylfluorene (1.01 g, 2.86 mmol) in NMP (10 mL), was added CuCN (1.27 g, 14.2 mmol), and the solution was refluxed under Ar atmosphere for 23 hrs. The reaction mixture was cooled to ambient temperature, was added $CHCl_3$ (100 mL), and the organic phase was washed with 10% NH_4OH (100 mL × 3). Then the organic phase was dried with brine (100 mL) and Na_2SO_4. The organic solvents were removed in vacuo, and crude product was obtained. After purification with silica-gel column chromatography (eluent: hexane/ethyl acetate), 2,7-dicyano-9,9-dimethylfluorene (DCF) was obtained as a colorless solid (0.214 g, 30.6%). FT-IR (ATR, cm^{-1}); 2925, 2850, 2359, 2047, 1715, 1591, 1506, 1459, 1362, 1238, 1156, 1078, 1018, 822, 741, 669; ^{1}H NMR (400 MHz, 25°C, $CDCl_3$) δ 1.54 (s, 6H, C^hH_3), 7.71 (dd, J = 7.6, 1.4 Hz, 2H, C^cH), 7.76 (brs, 2H, C^aH), 7.86 (d, J = 7.6 Hz, 2H, C^dH); ^{13}C NMR (100 MHz, 25°C, $CDCl_3$) δ 26.6 (C^hH_3), 47.7 (C^g), 112.2 (C^b), 119.2 (C^i), 121.8 (C^aH, C^cH or C^dH), 126.9 (C^aH, C^cH or C^dH), 131.9 (C^aH, C^cH or C^dH), 141.8 (C^e or C^f), 154.7 (C^e or C^f); HRMS (APCI-TOF) *m/z* calcd for $C_{17}H_{13}N_2$ $[M+H]^+$ 245.1079, found 245.1089.

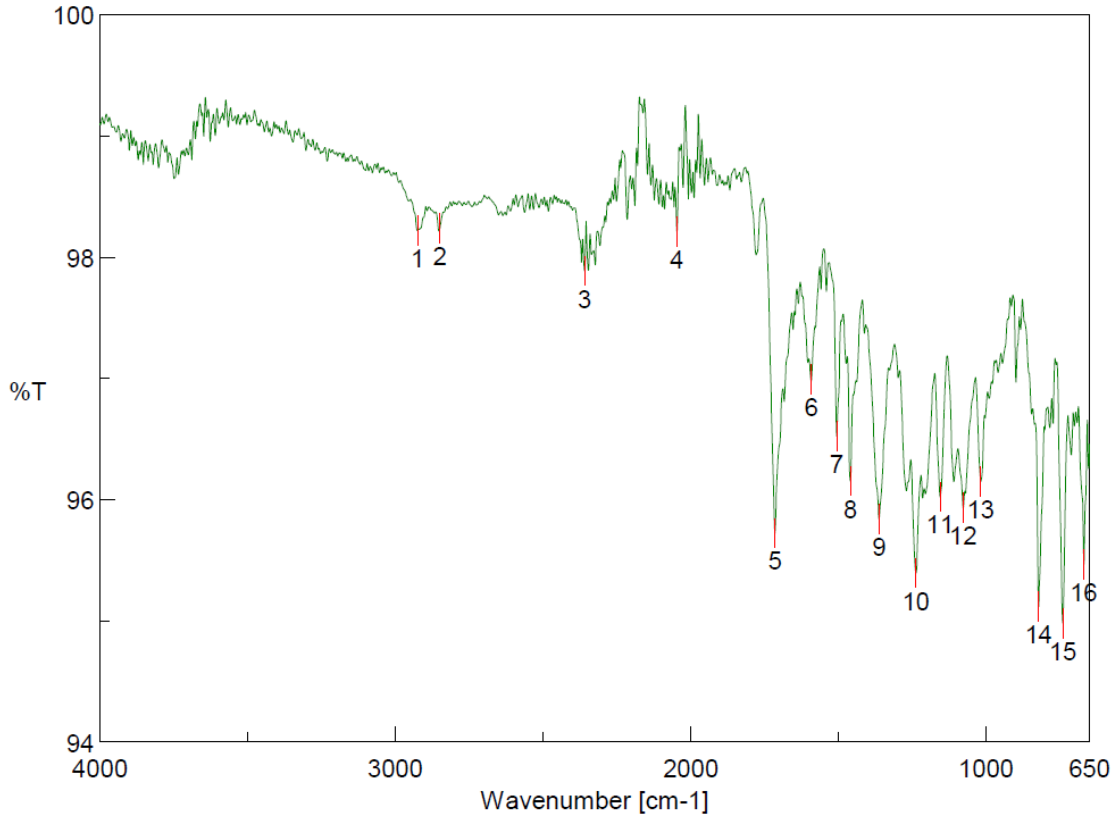


Figure S1. FT-IR of DCF.

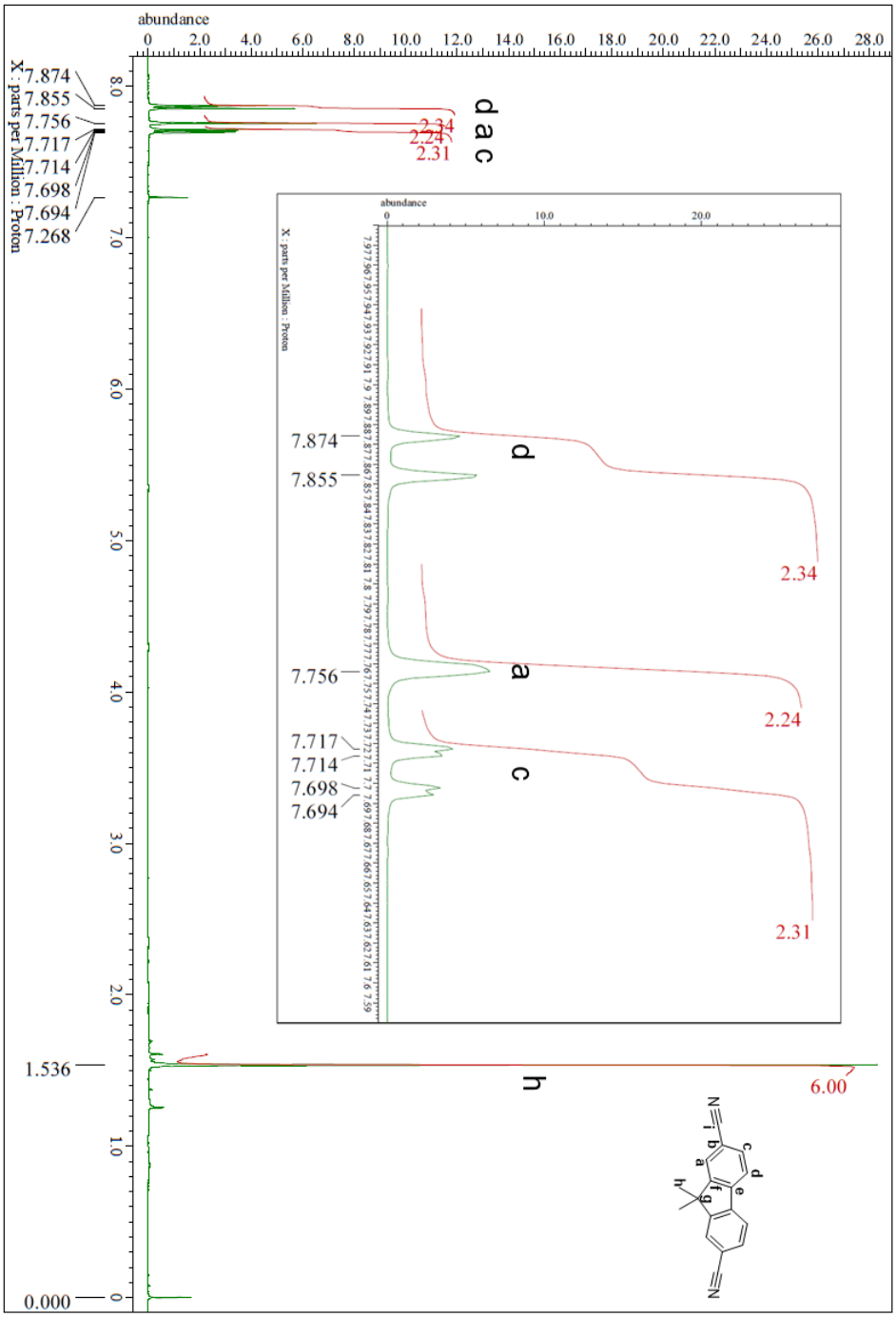


Figure S2. ^{1}H NMR of DCF in $CDCl_3$. Inset zoom of the aromatic region is also shown.

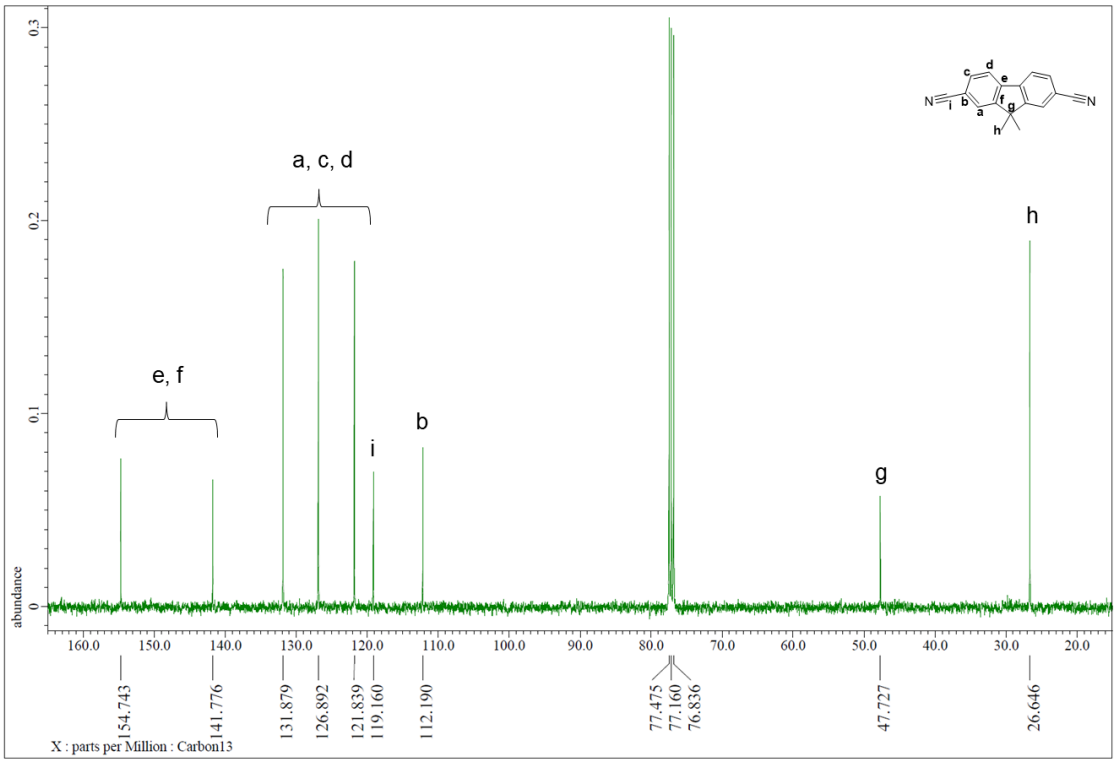


Figure S3. ^{13}C NMR of DCF in $CDCl_3$.

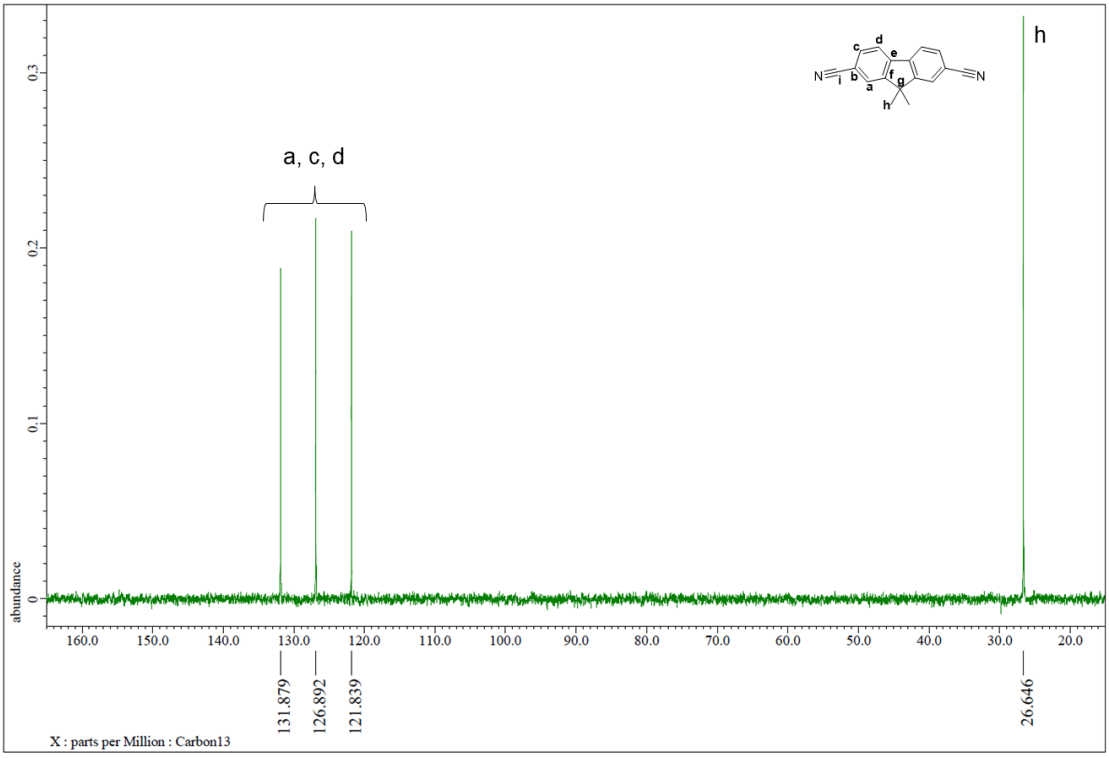


Figure S4. DEPT135 of DCF in $CDCl_3$.

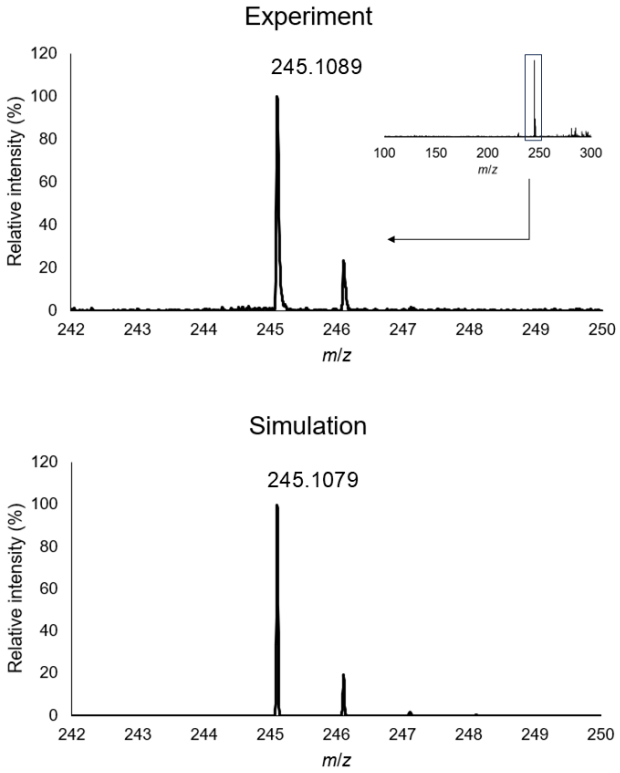


Figure S5. MS chart of DCF in the positive ion mode and its calculated isotropic distribution (calcd for $C_{17}H_{13}N_2$ $[M+H]^+$ 245.1079, found 245.1089.)

3. Theoretical calculations I: DCF-Cu complexes

Calculations in this section were performed using the Gaussian 16 program,[3] and the results were analyzed and visualized on GaussView 6.0.16. Calculations were performed at the density functional theory (DFT) level with the B3LYP functional, the gradient correction of the exchange functional by Becke[4] and the correlation functional by Lee, Yang and Parr,[5] and the 6-31G(d,p) split valence plus polarization basis set[6] was used for C, H, N, and Lanl2dz[7] ECP for Cu.

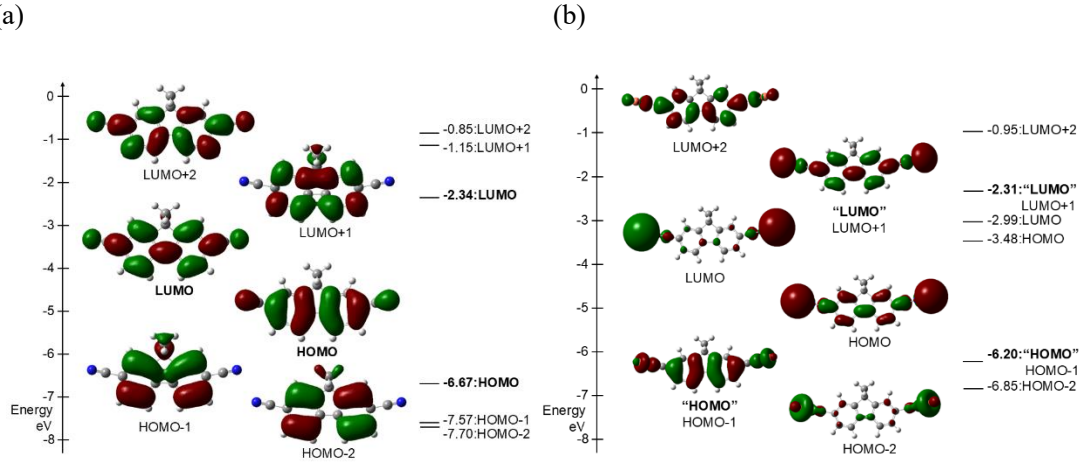


Figure S6. Frontier Kohn-Sham orbitals of (a) DCF and its Cu complex, (b) Cu-DCF-Cu.

Based on the shape and symmetry of the molecular orbitals, the orbital corresponding to the HOMO of DCF is identified as HOMO-1 in the complex, Cu-DCF-Cu, and the orbital corresponding to the LUMO of DCF is identified as LUMO+1. These orbitals are defined as "HOMO" and "LUMO," respectively. HOMO-LUMO gap for DCF is 4.33 eV, and "HOMO"-"LUMO" gap for Cu(0)-DCF-Cu(0) is 3.89 eV. Calculation conditions: (a) B3LYP//6-31G(d,p). (b) B3LYP//LanL2DZ[Cu]/6-31G(d,p)[C, H, N]. Valency of Cu is 0.

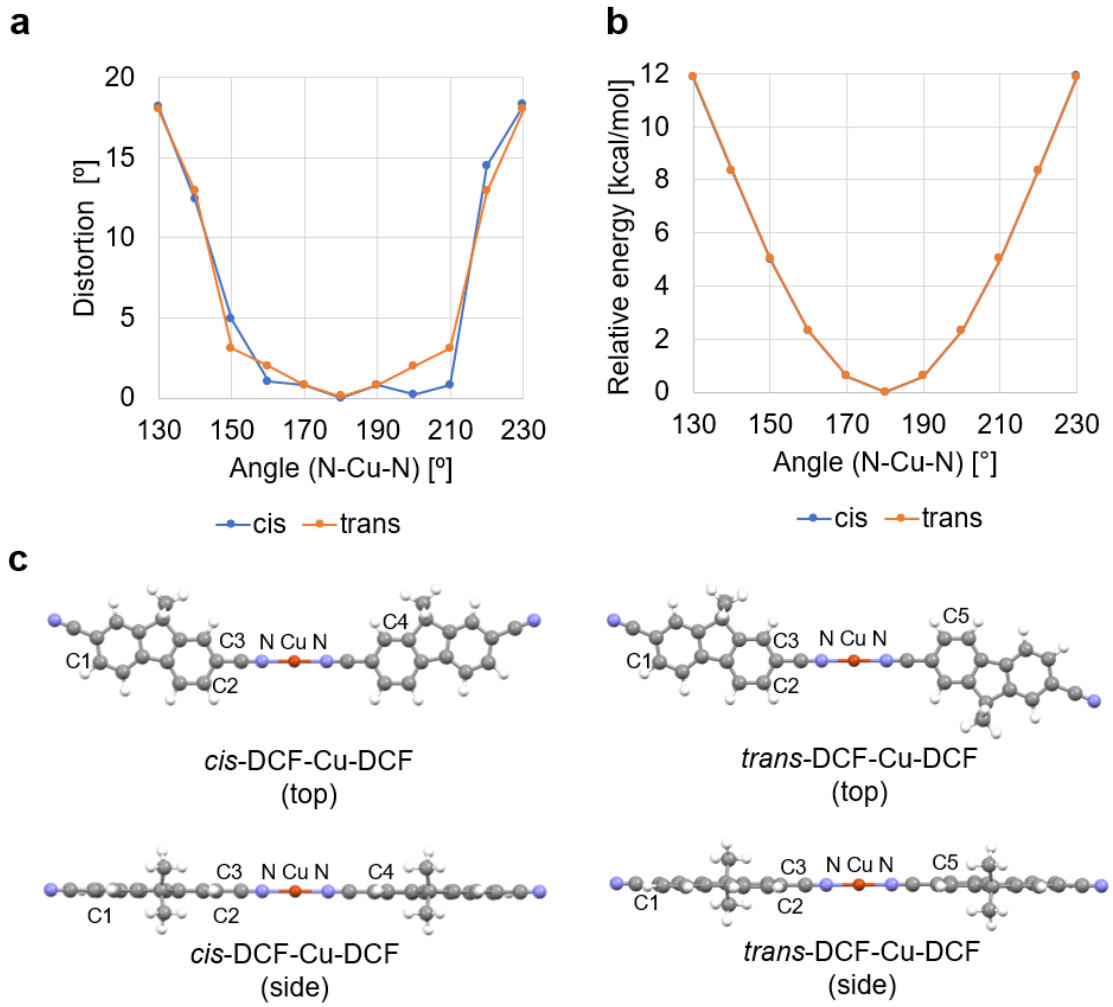


Figure S7. Planarity and relative energy of *cis*- and *trans*-DCF-Cu-DCF complexes by varying coordination angles. (a) Deviations of torsion angles (C1-C2-C4-C4 for *cis*-DCF-Cu-DCF and C1-C2-C2-C5 for *trans*-DCD-Cu-DCF) from 180° with changes in coordination angles (N-Cu-N). (b) Changes in relative energies with different coordination angles (N-Cu-N). (c) Optimized top and side views of cis- and trans-DCF-Cu-DCF complexes. Atoms used for angle adjustments or measurements are labeled. Calculation conditions: B3LYP//LanL2DZ[Cu]/6-31G(d,p)[C, H, N]. Structural and energy analysis by varying coordination angles was conducted via a relaxed potential energy surface (PES) scan method. The coordination angle was changed in steps of ±10° from the optimized structure at 180° and other parts are optimized. Valency of Cu is 0. The *cis*-DCF-Cu-DCF and *trans*-DCF-Cu-DCF complexes with 0 valency exhibit essentially the same behaviour in terms of distortion and deviation from the planar structure when the coordination angles are varied. Here the planarity of DCF-Cu-DCF is maintained when the coordination angle is between 160° and 200°. Between the coordination angle 160° and 200°, the change in relative energy is within 3 kcal/mol.

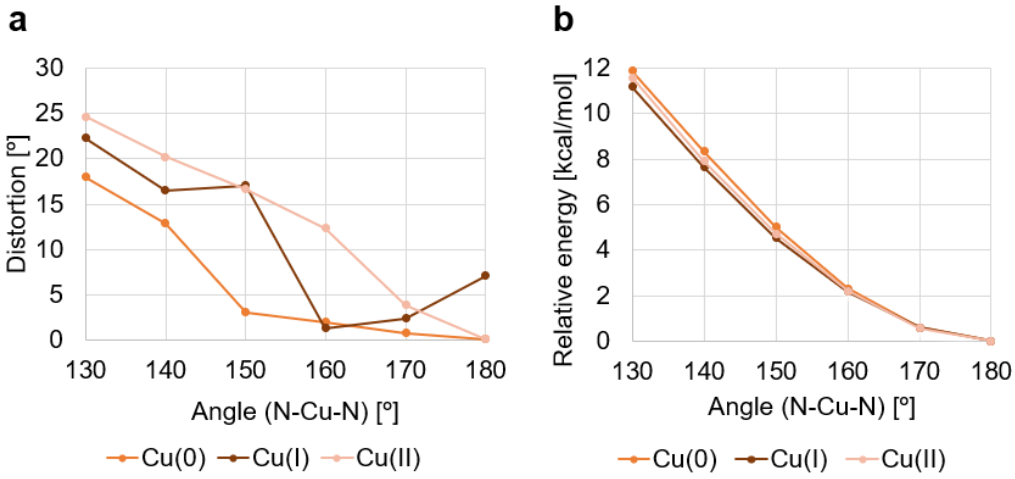


Figure S8. Comparison of planarity and relative energy of *trans*-DCF-Cu-DCF complexes with different valence (Cu = 0, +1, +2) by varying coordination angles. (a) Deviations of torsion angles (C1-C2-C2-C5) from 180° with changes in coordination angles (N-Cu-N). (b) Changes in relative energies with different coordination angles (N-Cu-N). The numbering of each atoms are indicated in Figure S7 c. Calculation conditions: B3LYP//LanL2DZ[Cu]/6-31G(d,p)[C, H, N]. Structural and energy analysis by varying coordination angles was conducted via a relaxed potential energy surface (PES) scan method. The coordination angle was changed in steps of 10° starting from the optimized structure at 180°, and the other parts are optimized. The effect of valence was compared in *trans*-DCF-Cu-DCF complexes. The planarity of *trans*-DCF-Cu-DCF complexes cannot be maintained when the valency is +1 or +2. On the other hand, the increase in the relative energies upon the diverse in the coordination angle (N-Cu-N) was essentially same among the different valence (Cu = 0, +1, +2).

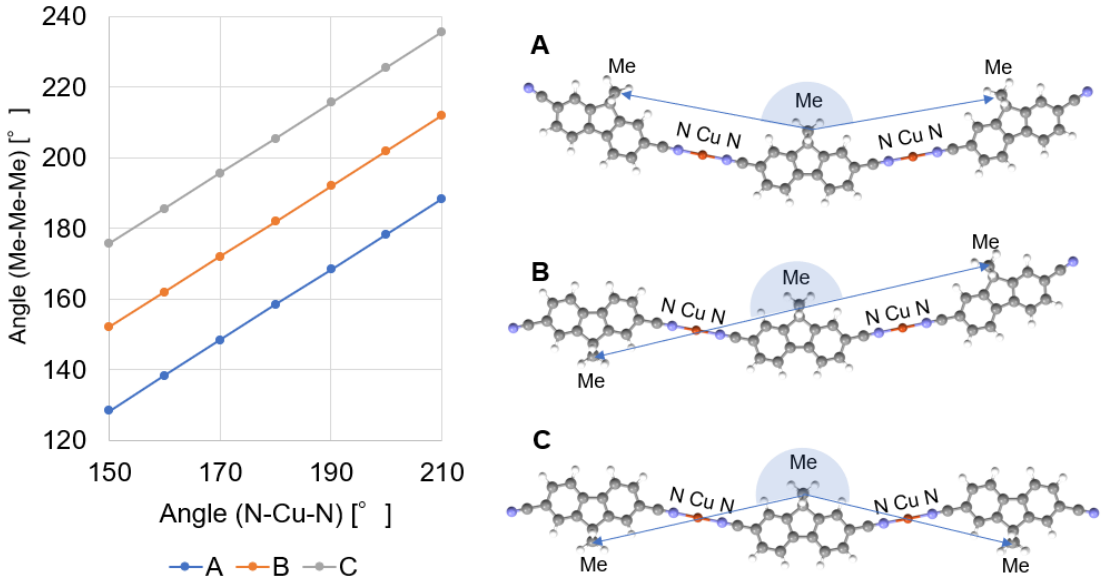


Figure S9. Angles formed by three methyl groups by varying coordination angles. The two coordination angles (N-Cu-N) are changed in ±10° increments, while other parts are frozen. Each DCF molecule has two methyl groups, one below and one above the fluorene plane, and the angles were measured using the methyl groups on the same side of the three DCF molecules.

The relative energies for molecules A, B, and C are 0.0 kcal/mol, respectively. The stabilization energies for coordination per cyano group in A, B, and C are 12.8 kcal/mol, respectively. Each value was calculated by subtracting the energy of three optimized DCF molecules and two Cu(0) atoms from the energy of A, B, and C, and then dividing the result by four, the number of cyano groups.

From the investigation of the theoretical calculation results (Figures S7, S8), the coordination angle that can be achieved while maintaining a planar structure is 180° ± 20°. Considering the relationship between the coordination angle (N-Cu-N) and the angle of the methyl groups (Me-Me-Me) (Figure S9), the possible Me-Me-Me angles are 156° ± 20° for A, 183° ± 20° for B, and 206° ± 20° for C. Therefore, the flexibility of the Me-Me-Me angle is ±20°, which matches the values observed in the STM images.

4. Theoretical calculations II: DCF-Cu complexes on Cu(111)

Bader charge analysis and projected local density of states (PDOS) calculations were performed using a slab model to investigate the DCF-Cu polymer on the Cu(111) surface. The slab model comprised two trans-configured DCF molecules coordinated with Cu adatoms on a Cu(111) surface, modeled as a four-layer slab. DFT calculations were carried out using the Vienna Ab initio Simulation Package (VASP)[8,9] with plane-wave basis sets and a cutoff energy of 500 eV. The exchange-correlation energy was treated within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.[10] Van der Waals interactions were incorporated using the DFT-D3 method.[11] The atomic structures were fully relaxed until the residual forces were less than 0.01 eV/Å, employing a 1 × 2 × 1 Monkhorst-Pack k-point mesh for Brillouin zone sampling.[12] For PDOS calculations, a denser k-point mesh of 5 × 5 × 1 was utilized.

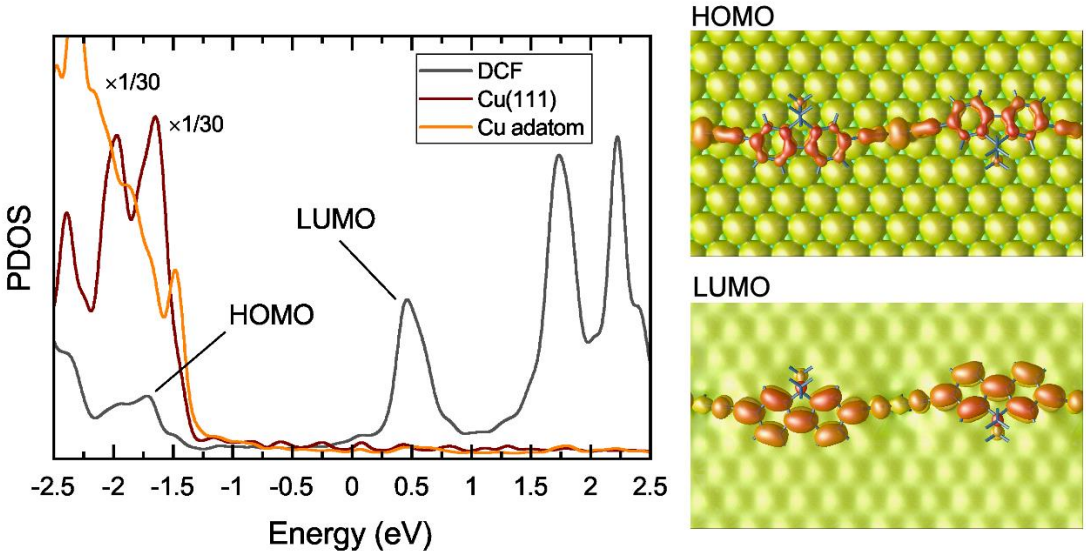


Figure S10. PDOS and charge density distributions for the HOMO and LUMO of the DCF-Cu polymer on the Cu(111) surface. Charge densities are visualized at an isosurface value of 0.05 e/Å^3, with the color scale indicating the height variation. By comparing the molecular orbitals shown in Figure S6 with the charge density distributions derived from the slab calculations, the states observed at -1.7 eV 0.5 eV were identified as the HOMO and LUMO of the DCF-Cu polymer, respectively.

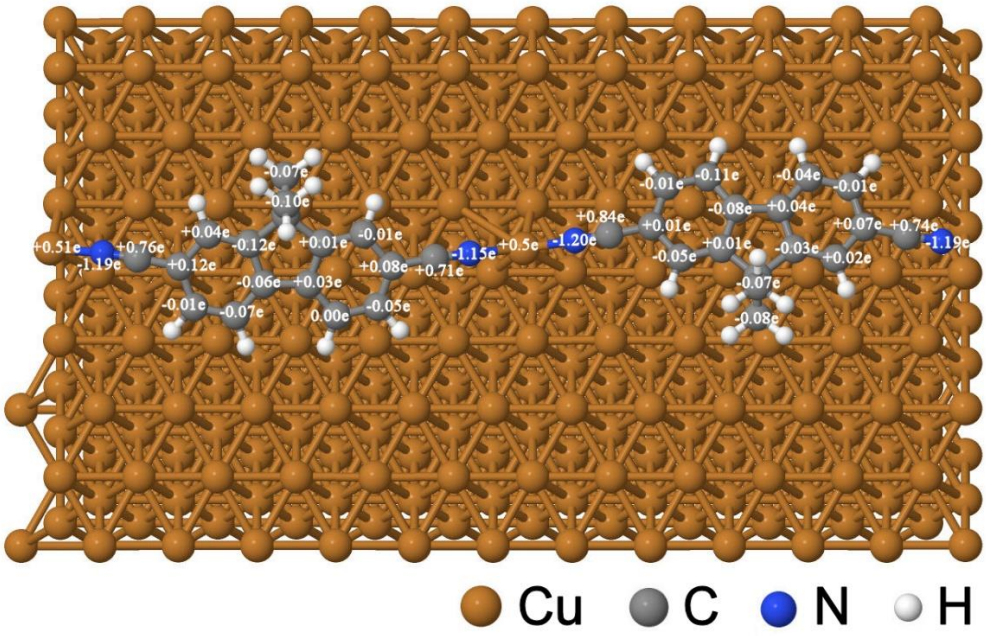


Figure S11. Bader charge analysis of the DCF-Cu polymer on the Cu(111) surface.

5. STM experiments

Experiments were conducted using an ultrahigh-vacuum, low-temperature STM system, customized based on the UNISOKU USM-1200 platform, operating at a base pressure below 1×10^{-8} Pa. STM images and spectra were acquired at 4 K with a platinum–iridium alloy tip. Differential conductance spectra were measured using a lock-in amplifier with a sample bias modulation of 10 mV at a frequency of 850 Hz. The Cu(111) substrate was prepared through repeated cycles of argon ion sputtering followed by thermal annealing. DCF molecules were deposited onto the substrate held at 7 K from a quartz crucible heated to 373 K. Subsequently, DCF-Cu polymers were synthesized by annealing the substrate at 320 K for 45 minutes.

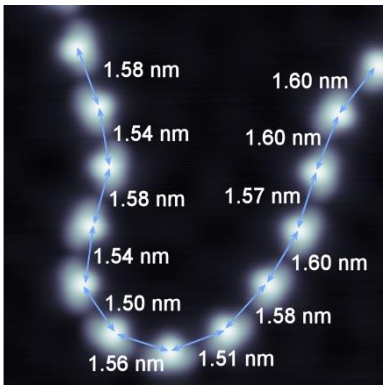


Figure S12. STM image of the DCF-Cu polymer on Cu(111) at 4K. V = 20 mV, I = 50 pA, Size: 10 nm × 10 nm. The bright spots correspond to the positions of the methyl groups, and the distances between these spots match the values obtained from DFT calculations: 1.46 nm for *cis* and 1.60 nm for *trans* configurations of two adjacent DCFs in all the trimers in Figure S9.

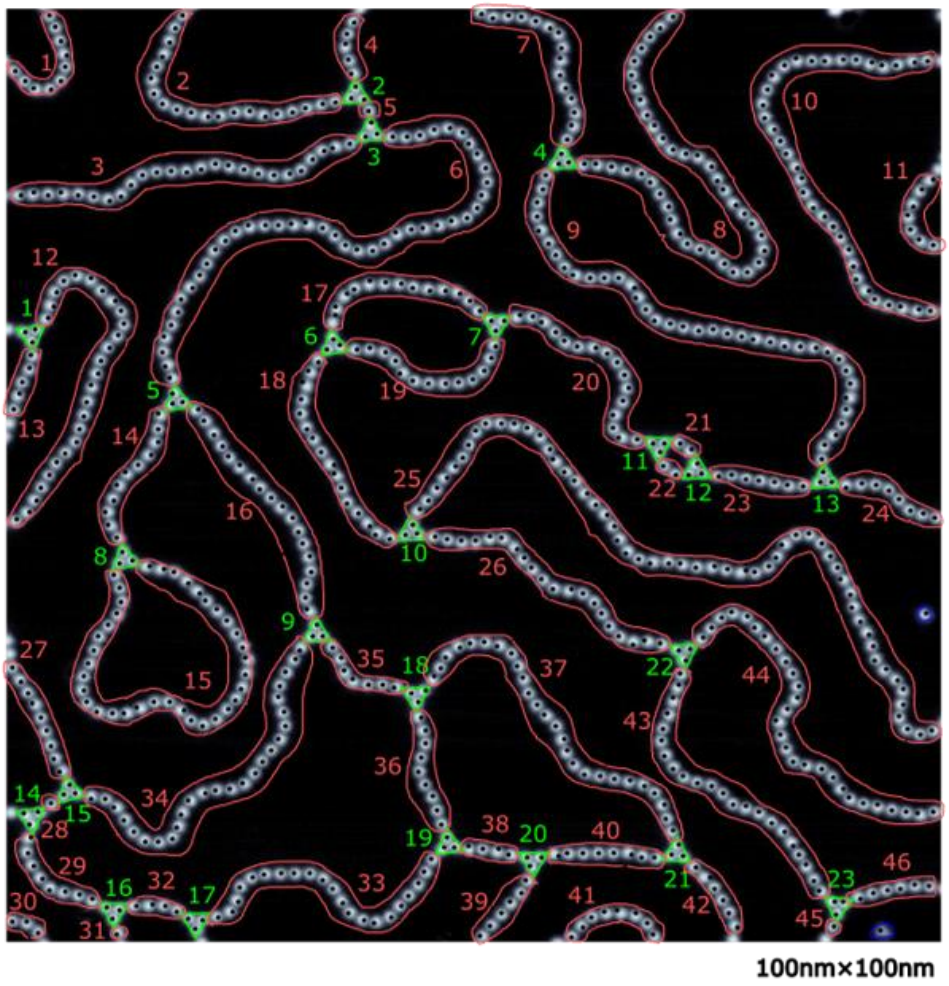


Figure S13. The composition of di-coordinated linear and tri-coordinated branched polymers was determined by identifying their respective types from three separate STM images, each recorded over a 100 nm × 100 nm aera. The results are summarized in Table S1.

Table S1 The composition of di-coordinated linear and tri-coordinated branched polymers.

	Number of di-coordinated polymer	Number of tri-coordinated polymer	Number of free-end polymer	Composition of di-coordinated polymer (%)	Composition of tri-coordinated polymer (%)
Image 1	687	69	2	90.9	9.1
Image 2	745	63	1	92.2	7.8
Image 3	612	65	0	90.4	9.6
Average				91.2	8.8
Standard deviation				0.8	0.9

Figure S14. STM image of DCF-Cu polymer on Cu(111) at 4K. Size: 100 nm x 100 nm, V = 30 mV. Each DCF ligand in the coordination polymer was sequentially numbered, and a '+' or '−' sign was assigned based on its relative orientation. Ligands with the same orientation as their neighboring ligand were assigned the same sign, while those with opposite orientations were assigned the alternate sign. When the relative orientation could not be determined, the ligand was denoted with the symbol '○'.

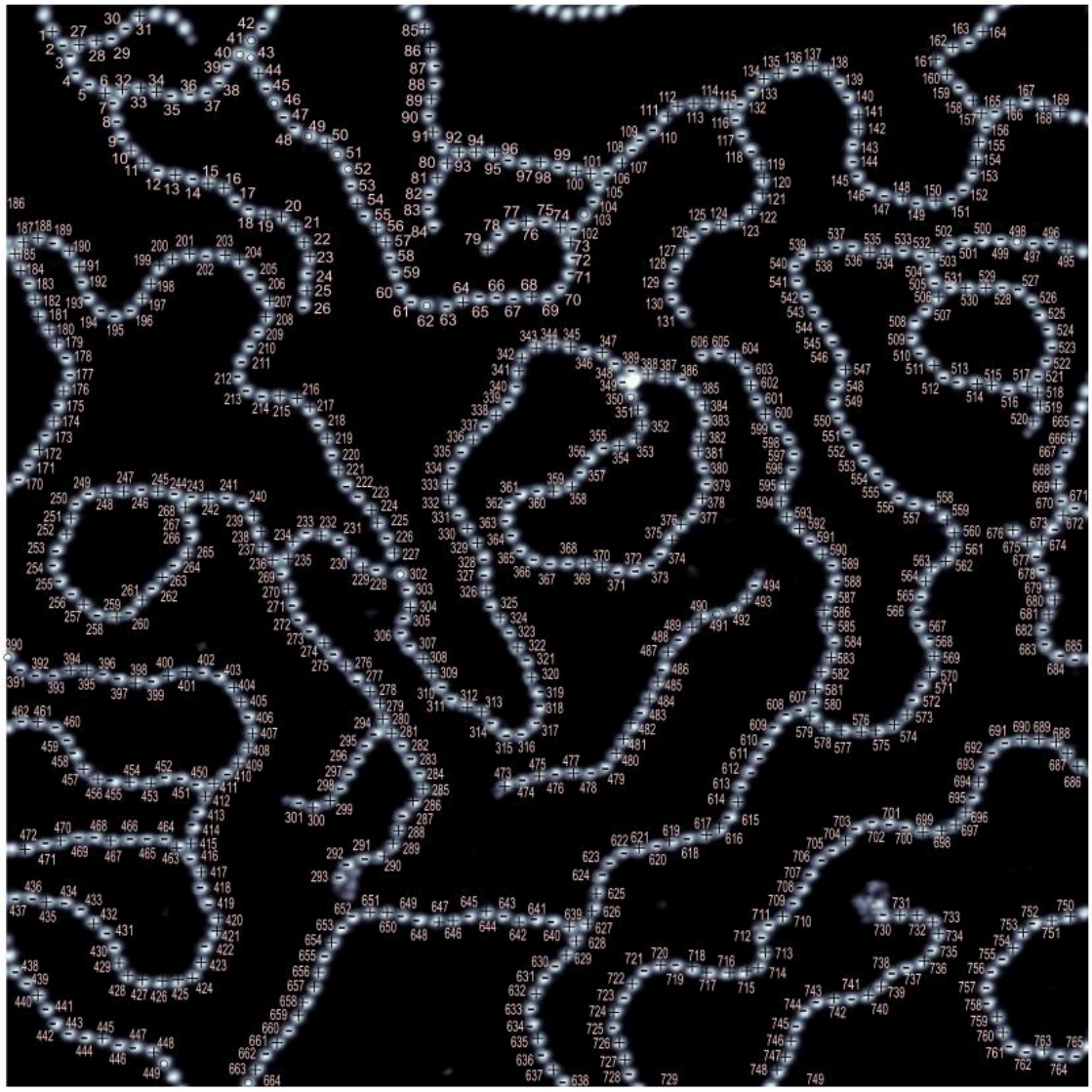


Figure S15. The STM image of DCF-Cu polymer at the same position as Figure S14, measured after leaving at 48 K for 10 minutes and then cooling to 4K. Size: 100 nm x 100 nm, V = 30 mV.

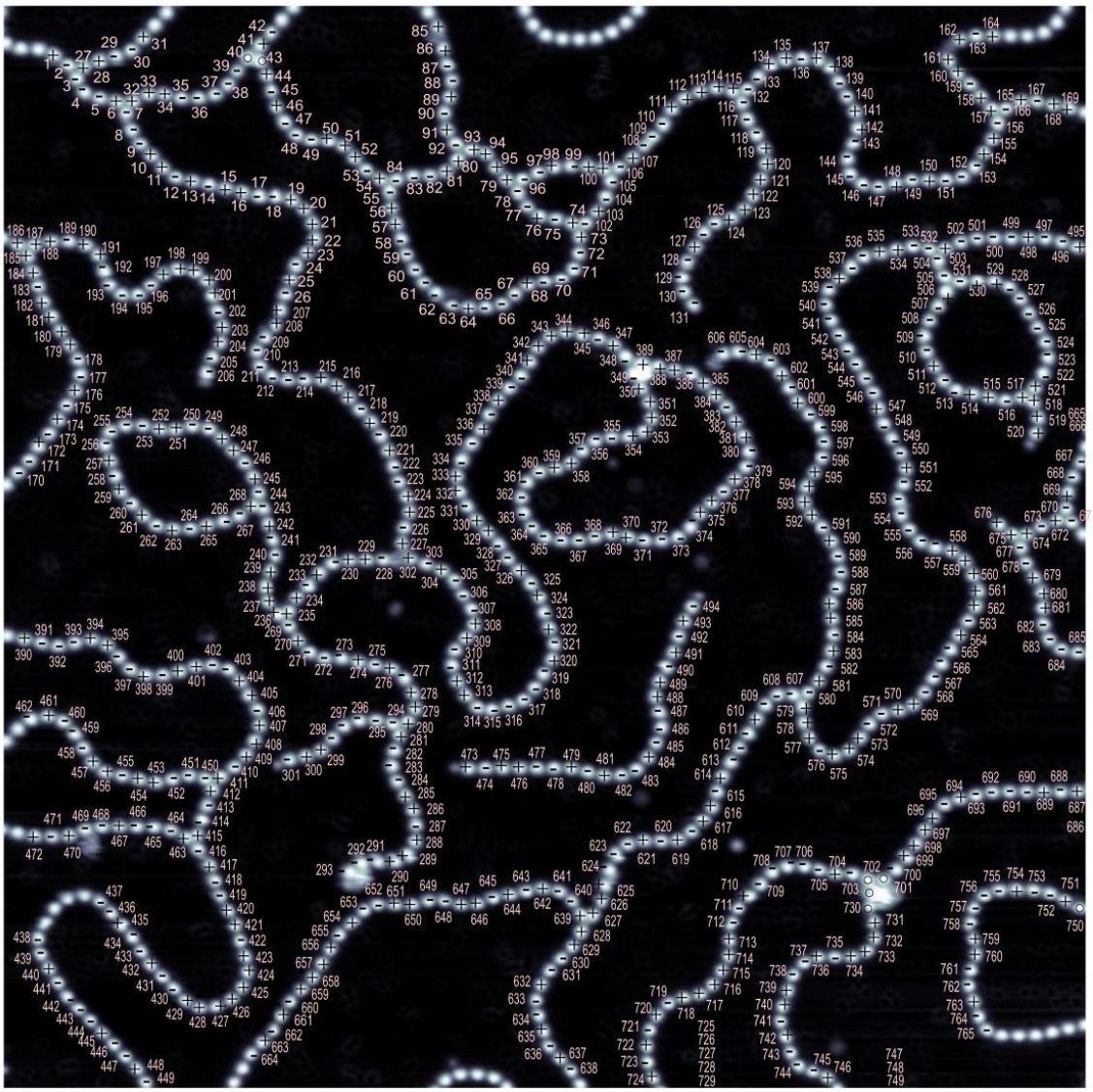


Figure S16. The STM image of DCF-Cu polymer at the same position as Figure S14, measured after leaving at 71 K for 10 minutes and then cooling to 4K. Size: 100 nm x 100 nm, V = 1 V.

Table S2. Angle distribution formed by 3-mers near the cleavage site.

Molecule[a]	Number[b]	Type[c]	Orientation[d]	Angle[e]	|Δ|[f]
	204		+		
	205	B	–	195	17.6
I	206	B	–	199	21.6
J	207	B	+	162	15.1
	208	B	+	151	25.7
	209		–		

[a] The assignment of the molecule shown in Figure 4 II.

[b] The numbering of the molecule shown in Figure S14.

[c] Type of DCF-Cu complex trimers in Figure 3c.

[d] Relative orientation assigned in Figure S14.

[e] The trimer angles.

[f] The absolute value of deviation from the average, 177^{o}.

6. Cartesian coordinates

Table S3. Cartesian coordinates of DCF.

SCF Done: E(RB3LYP) = -764.556389862 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.006687	-1.681755	-0.000131
2	6	0	3.455430	-0.347179	-0.000105
3	6	0	2.534302	0.719179	-0.000048
4	6	0	1.178283	0.433508	-0.000019
5	6	0	0.732502	-0.904752	-0.000046
6	6	0	1.644248	-1.963771	-0.000103
7	1	0	3.734770	-2.485550	-0.000176
8	1	0	2.901239	1.740638	-0.000029
9	1	0	1.304633	-2.994905	-0.000123
10	6	0	0.000000	1.406177	0.000041
11	6	0	-1.178283	0.433508	0.000044
12	6	0	-2.534302	0.719179	0.000089
13	6	0	-3.455430	-0.347179	0.000081
14	6	0	-3.006687	-1.681755	0.000029
15	6	0	-1.644248	-1.963770	-0.000016
16	6	0	-0.732502	-0.904752	-0.000008
17	1	0	-2.901239	1.740638	0.000129
18	1	0	-3.734770	-2.485550	0.000021
19	1	0	-1.304633	-2.994905	-0.000058
20	6	0	0.000034	2.292087	1.266820
21	1	0	0.884424	2.936764	1.285208
22	1	0	-0.884354	2.936765	1.285255
23	1	0	0.000058	1.684399	2.175814
24	6	0	-0.000034	2.292161	-1.266685
25	1	0	-0.884424	2.936840	-1.285036
26	1	0	0.884353	2.936842	-1.285083
27	1	0	-0.000057	1.684527	-2.175715
28	6	0	-4.861654	-0.070088	0.000132
29	6	0	4.861654	-0.070089	-0.000133

30	7	0	-6.002963	0.157088	0.000176
31	7	0	6.002962	0.157089	-0.000155

Table S4. Cartesian coordinates of *cis*-DCF-Cu-DCF.

SCF Done: E(UB3LYP) = -1725.26170443 A.U. after 7 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.126377	-2.150579	0.003641
2	6	0	-4.413734	-0.916198	-0.001968
3	6	0	-5.129256	0.319992	-0.014756
4	6	0	-6.505867	0.291906	-0.021332
5	6	0	-7.211357	-0.940666	-0.015720
6	6	0	-6.508422	-2.160492	-0.003204
7	1	0	-4.570336	-3.082309	0.013308
8	1	0	-4.578897	1.255886	-0.018852
9	1	0	-7.039855	-3.107572	0.001106
10	6	0	-7.480255	1.471165	-0.034721
11	6	0	-8.823533	0.740993	-0.035697
12	6	0	-10.096634	1.280150	-0.045527
13	6	0	-11.211023	0.410418	-0.044467
14	6	0	-11.021545	-0.987288	-0.033545
15	6	0	-9.741163	-1.526635	-0.023626
16	6	0	-8.634769	-0.662962	-0.024630
17	1	0	-10.259704	2.353546	-0.053949
18	1	0	-11.890307	-1.637230	-0.032934
19	1	0	-9.607640	-2.604287	-0.015258
20	6	0	-7.317996	2.349696	1.226179
21	1	0	-6.327147	2.815551	1.247504
22	1	0	-8.065278	3.149807	1.237570
23	1	0	-7.437521	1.757714	2.137848
24	6	0	-7.305885	2.330730	-1.307035
25	1	0	-8.052859	3.130631	-1.337514
26	1	0	-6.314777	2.796142	-1.325907

27	1	0	-7.416852	1.725172	-2.210835
28	6	0	-12.535531	0.949703	-0.054481
29	6	0	-3.014049	-0.918757	0.005267
30	7	0	-13.613027	1.392158	-0.062612
31	7	0	-1.839198	-0.918045	0.011750
32	29	0	-0.000938	-0.917395	0.021229
33	6	0	5.125031	-2.145509	0.078075
34	6	0	4.411880	-0.911857	0.045075
35	6	0	5.126855	0.324449	0.020051
36	6	0	6.503477	0.297207	0.028633
37	6	0	7.209479	-0.934644	0.061946
38	6	0	6.507075	-2.154581	0.086436
39	1	0	4.569387	-3.077334	0.096727
40	1	0	4.576089	1.259770	-0.005227
41	1	0	7.038894	-3.101113	0.111816
42	6	0	7.477393	1.476716	0.005840
43	6	0	8.820960	0.747534	0.031766
44	6	0	10.093861	1.287248	0.026946
45	6	0	11.208570	0.418375	0.054709
46	6	0	11.019627	-0.979101	0.086678
47	6	0	9.739461	-1.519010	0.091408
48	6	0	8.632757	-0.656169	0.063996
49	1	0	10.256528	2.360463	0.002455
50	1	0	11.888631	-1.628384	0.107613
51	1	0	9.606337	-2.596463	0.116197
52	6	0	7.316400	2.314145	-1.282933
53	1	0	6.325286	2.778411	-1.320593
54	1	0	8.063238	3.113939	-1.319044
55	1	0	7.437540	1.693157	-2.174880
56	6	0	7.301048	2.376763	1.249541
57	1	0	8.047466	3.177747	1.254960
58	1	0	6.309641	2.841907	1.252285
59	1	0	7.411404	1.800826	2.172569
60	6	0	12.532891	0.958175	0.050528
61	6	0	3.012183	-0.915423	0.037438
62	7	0	13.610256	1.401013	0.047078

63	7	0	1.837336	-0.915839	0.031358

Table S5. Cartesian coordinates of *trans*-DCF-Cu-DCF.

SCF Done: E(UB3LYP) = -1725.26171442 A.U. after 7 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.119650	-2.141244	-0.159870
2	6	0	-4.410245	-0.907396	-0.082783
3	6	0	-5.129007	0.324977	-0.012590
4	6	0	-6.505543	0.293792	-0.020759
5	6	0	-7.207800	-0.938258	-0.097535
6	6	0	-6.501668	-2.154306	-0.167063
7	1	0	-4.561179	-3.070067	-0.212724
8	1	0	-4.581067	1.260470	0.045839
9	1	0	-7.030616	-3.100950	-0.226030
10	6	0	-7.483059	1.468698	0.045354
11	6	0	-8.824404	0.736645	-0.004081
12	6	0	-10.098931	1.271838	0.022721
13	6	0	-11.211021	0.401023	-0.034041
14	6	0	-11.017857	-0.993771	-0.116822
15	6	0	-9.736042	-1.529134	-0.143622
16	6	0	-8.631940	-0.664381	-0.087228
17	1	0	-10.264817	2.342959	0.086166
18	1	0	-11.884895	-1.644614	-0.159412
19	1	0	-9.599684	-2.604571	-0.207505
20	6	0	-7.322322	2.261053	1.362312
21	1	0	-6.332789	2.727288	1.414284
22	1	0	-8.071844	3.056464	1.427793
23	1	0	-7.439469	1.608883	2.232262
24	6	0	-7.311997	2.412405	-1.166372
25	1	0	-8.061275	3.210382	-1.142419
26	1	0	-6.322235	2.880886	-1.154435
27	1	0	-7.421994	1.868814	-2.108856

28	6	0	-12.536964	0.936210	-0.007508
29	6	0	-3.010550	-0.906798	-0.075623
30	7	0	-13.615638	1.375326	0.014267
31	7	0	-1.835704	-0.903318	-0.069198
32	29	0	0.002559	-0.899450	-0.058173
33	6	0	5.125634	0.339343	0.044915
34	6	0	4.415360	-0.893982	-0.032563
35	6	0	5.133251	-2.126867	-0.102578
36	6	0	6.509807	-2.096686	-0.093830
37	6	0	7.212929	-0.865157	-0.016644
38	6	0	6.507657	0.351398	0.052673
39	1	0	4.567815	1.268564	0.097608
40	1	0	4.584655	-3.061954	-0.161335
41	1	0	7.037271	1.297650	0.111938
42	6	0	7.486492	-3.272298	-0.159617
43	6	0	8.828351	-2.541217	-0.109651
44	6	0	10.102501	-3.077320	-0.136042
45	6	0	11.215200	-2.207314	-0.078753
46	6	0	11.023017	-0.812396	0.004146
47	6	0	9.741581	-0.276115	0.030519
48	6	0	8.636873	-1.140064	-0.026415
49	1	0	10.267635	-4.148549	-0.199571
50	1	0	11.890511	-0.162184	0.047148
51	1	0	9.605977	0.799408	0.094500
52	6	0	7.314281	-4.215889	1.052051
53	1	0	6.324178	-4.683646	1.039749
54	1	0	8.062980	-5.014414	1.028385
55	1	0	7.424323	-3.672364	1.994569
56	6	0	7.325669	-4.064526	-1.476630
57	1	0	8.074623	-4.860495	-1.541822
58	1	0	6.335810	-4.530030	-1.528978
59	1	0	7.443634	-3.412456	-2.346547
60	6	0	12.540765	-2.743446	-0.104854
61	6	0	3.015668	-0.893519	-0.040223
62	7	0	13.619131	-3.183327	-0.126290

63	7	0	1.840822	-0.895875	-0.047074

Table S6. Cartesian coordinates of A (DCF-Cu-DCF-Cu-DCF).

SCF Done: E(RB3LYP) = -2685.98437338 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.938609	-5.475369	-3.698859
2	6	0	-1.897093	-5.057802	-4.574054
3	6	0	-2.068889	-5.153010	-5.986609
4	6	0	-3.253731	-5.653415	-6.480155
5	6	0	-4.290480	-6.069069	-5.603857
6	6	0	-4.122458	-5.975611	-4.210067
7	1	0	-2.792768	-5.396652	-2.626567
8	1	0	-1.268088	-4.831606	-6.645470
9	1	0	-4.910514	-6.291333	-3.532930
10	6	0	-3.668258	-5.850249	-7.939208
11	6	0	-5.072271	-6.430581	-7.768442
12	6	0	-5.968229	-6.819370	-8.747237
13	6	0	-7.226360	-7.335251	-8.360851
14	6	0	-7.558477	-7.449844	-6.994486
15	6	0	-6.656528	-7.058577	-6.013043
16	6	0	-5.407407	-6.546403	-6.397122
17	1	0	-5.728193	-6.737701	-9.802933
18	1	0	-8.529396	-7.848353	-6.719473
19	1	0	-6.923163	-7.151445	-4.964474
20	6	0	-3.703448	-4.505785	-8.700536
21	1	0	-2.701051	-4.068911	-8.759994
22	1	0	-4.067009	-4.651420	-9.722916
23	1	0	-4.361095	-3.787389	-8.203293
24	6	0	-2.731595	-6.845128	-8.661180
25	1	0	-3.079058	-7.029059	-9.682979
26	1	0	-1.713967	-6.444883	-8.719794
27	1	0	-2.692866	-7.803465	-8.135891

28	6	0	-8.166156	-7.742580	-9.358682
29	6	0	-0.700242	-4.552307	-4.043838
30	7	0	-8.929562	-8.073540	-10.173945
31	7	0	0.301439	-4.129697	-3.604132
32	29	0	1.875778	-3.468389	-2.915499
33	6	0	5.835823	-1.794032	0.130898
34	6	0	5.646758	-1.892448	-1.284569
35	6	0	6.700567	-1.473213	-2.166884
36	6	0	7.864641	-0.988103	-1.633033
37	6	0	8.051196	-0.890942	-0.217226
38	6	0	7.010373	-1.304758	0.653927
39	1	0	5.034181	-2.113029	0.789902
40	1	0	6.555086	-1.548590	-3.240641
41	1	0	7.133612	-1.238394	1.731080
42	6	0	9.111854	-0.487334	-2.366191
43	6	0	10.012708	-0.101538	-1.189980
44	6	0	11.279813	0.416910	-1.222396
45	6	0	11.948856	0.708927	0.015275
46	6	0	11.277796	0.452303	1.253340
47	6	0	10.004777	-0.068831	1.271554
48	6	0	9.343999	-0.357392	0.049425
49	1	0	11.790705	0.612425	-2.160769
50	1	0	11.790985	0.676075	2.183524
51	1	0	9.513317	-0.256204	2.221928
52	6	0	9.749531	-1.606147	-3.218890
53	1	0	9.068587	-1.920673	-4.017236
54	1	0	10.677300	-1.256964	-3.685035
55	1	0	9.984042	-2.481156	-2.606236
56	6	0	8.789174	0.736464	-3.251500
57	1	0	9.699514	1.127686	-3.718612
58	1	0	8.090786	0.463536	-4.050091
59	1	0	8.336487	1.538733	-2.662074
60	6	0	13.234914	1.235197	0.015371
61	6	0	4.454149	-2.389540	-1.795924
62	7	0	3.444154	-2.810760	-2.233358
63	29	0	16.021235	2.376153	0.006768

64	7	0	14.325676	1.681389	0.011703
65	6	0	18.809218	3.521107	-0.002439
66	7	0	17.724728	3.074817	0.000575
67	6	0	20.106696	4.055502	-0.009477
68	6	0	20.758131	4.348197	1.221412
69	6	0	20.770420	4.305172	-1.246815
70	6	0	22.036573	4.875989	1.227269
71	1	0	20.239995	4.152566	2.154443
72	6	0	22.043511	4.831064	-1.224205
73	1	0	20.264608	4.078241	-2.180264
74	6	0	22.690041	5.122046	0.005769
75	1	0	22.524083	5.095611	2.172425
76	6	0	22.948546	5.181492	-2.406380
77	6	0	24.007239	5.660564	-0.276391
78	6	0	24.186966	5.707463	-1.680576
79	6	0	25.026141	6.098198	0.584086
80	6	0	25.365891	6.183890	-2.223772
81	6	0	26.211539	6.577341	0.040859
82	1	0	24.898316	6.066380	1.661984
83	6	0	26.392301	6.624795	-1.357525
84	1	0	25.520833	6.226927	-3.297512
85	1	0	27.011915	6.920579	0.687932
86	6	0	23.280275	3.930819	-3.251530
87	1	0	22.374340	3.525668	-3.714484
88	1	0	23.982606	4.182678	-4.052761
89	1	0	23.730635	3.146645	-2.636631
90	6	0	22.312737	6.271788	-3.298241
91	1	0	21.391450	5.903364	-3.761570
92	1	0	22.069912	7.165618	-2.716953
93	1	0	22.998957	6.561650	-4.100554
94	6	0	27.618616	7.120833	-1.900570
95	7	0	28.616474	7.524388	-2.345989

Table S7. Cartesian coordinates of B (DCF-Cu-DCF-Cu-DCF).

SCF Done: E(RB3LYP) = -2685.98435227 A.U. after 9 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.388221	-1.903065	0.061097
2	6	0	-3.686843	-0.665693	0.014736
3	6	0	-4.407991	0.564339	-0.014614
4	6	0	-5.785047	0.528367	0.002909
5	6	0	-6.481241	-0.708030	0.049301
6	6	0	-5.771112	-1.922327	0.078167
7	1	0	-3.825335	-2.830407	0.082951
8	1	0	-3.863281	1.502836	-0.049919
9	1	0	-6.295959	-2.872331	0.113649
10	6	0	-6.767080	1.700746	-0.021557
11	6	0	-8.105056	0.962170	0.017546
12	6	0	-9.381894	1.492839	0.016815
13	6	0	-10.490038	0.616078	0.057449
14	6	0	-10.290797	-0.780005	0.098056
15	6	0	-9.006950	-1.310650	0.098674
16	6	0	-7.906924	-0.439750	0.058314
17	1	0	-9.552428	2.564639	-0.014118
18	1	0	-11.154968	-1.435284	0.128905
19	1	0	-8.865858	-2.386906	0.130189
20	6	0	-6.589247	2.609841	1.215504
21	1	0	-5.601484	3.082578	1.208842
22	1	0	-7.341730	3.405071	1.220535
23	1	0	-6.689396	2.039030	2.142866
24	6	0	-6.619750	2.531110	-1.316603
25	1	0	-7.372825	3.324960	-1.352998
26	1	0	-5.632519	3.002728	-1.363024
27	1	0	-6.741594	1.903789	-2.204004
28	6	0	-11.818119	1.146171	0.057506
29	6	0	-2.283699	-0.659096	-0.001456
30	7	0	-12.898747	1.581169	0.057486
31	7	0	-1.111064	-0.650632	-0.014676
32	29	0	0.730120	-0.639078	-0.027059

33	6	0	5.860187	-1.836693	0.009215
34	6	0	5.130463	-0.605915	-0.032099
35	6	0	5.848776	0.638043	-0.068739
36	6	0	7.218089	0.618500	-0.062404
37	6	0	7.945327	-0.613591	-0.020115
38	6	0	7.235850	-1.841960	0.015072
39	1	0	5.309139	-2.771727	0.036365
40	1	0	5.293190	1.570864	-0.100340
41	1	0	7.770436	-2.786974	0.046991
42	6	0	8.186988	1.803428	-0.095589
43	6	0	9.537686	1.083333	-0.064167
44	6	0	10.793768	1.628884	-0.072418
45	6	0	11.935937	0.757714	-0.036802
46	6	0	11.736778	-0.659164	0.005423
47	6	0	10.469349	-1.194022	0.013047
48	6	0	9.341344	-0.333845	-0.021088
49	1	0	10.947121	2.703711	-0.104614
50	1	0	12.605553	-1.309713	0.031846
51	1	0	10.340141	-2.272028	0.045631
52	6	0	8.020402	2.628357	-1.390670
53	1	0	7.025282	3.084214	-1.434249
54	1	0	8.762384	3.432961	-1.435776
55	1	0	8.146034	1.998582	-2.275874
56	6	0	8.005744	2.712178	1.139978
57	1	0	8.747247	3.518487	1.140151
58	1	0	7.010307	3.169418	1.141905
59	1	0	8.121141	2.142575	2.066379
60	6	0	13.223220	1.280978	-0.041158
61	6	0	3.740949	-0.619055	-0.034842
62	7	0	2.562470	-0.626522	-0.036605
63	29	0	16.008853	2.423669	-0.036472
64	7	0	14.313572	1.728188	-0.044246
65	6	0	18.797163	3.567755	-0.014051
66	7	0	17.712287	3.122544	-0.026029
67	6	0	20.096523	4.097455	0.000809
68	6	0	20.286541	5.507147	-0.041124

69	6	0	21.223519	3.225407	0.058434
70	6	0	21.562361	6.041110	-0.026245
71	1	0	19.419060	6.157420	-0.084843
72	6	0	22.487719	3.772672	0.072682
73	1	0	21.067468	2.151465	0.090143
74	6	0	22.673259	5.179589	0.030847
75	1	0	21.695622	7.118340	-0.058595
76	6	0	23.835352	3.051596	0.131389
77	6	0	24.095810	5.462861	0.058202
78	6	0	24.801595	4.236240	0.117112
79	6	0	24.792048	6.681422	0.035929
80	6	0	26.183761	4.220498	0.153586
81	6	0	26.180700	6.668344	0.072455
82	1	0	24.260413	7.627233	-0.009151
83	6	0	26.885354	5.447520	0.131209
84	1	0	26.741004	3.289785	0.198909
85	1	0	26.738441	7.598820	0.056163
86	6	0	23.976023	2.226108	1.430279
87	1	0	23.235785	1.419591	1.457805
88	1	0	24.970040	1.771357	1.491818
89	1	0	23.832078	2.853348	2.314419
90	6	0	24.041368	2.142119	-1.101009
91	1	0	23.302259	1.334184	-1.113098
92	1	0	23.944105	2.709077	-2.031035
93	1	0	25.036515	1.686120	-1.081043
94	6	0	28.314842	5.451520	0.168313
95	7	0	29.479342	5.451438	0.198663

Table S8. Cartesian coordinates of C (DCF-Cu-DCF-Cu-DCF).

SCF Done: E(RB3LYP) = -2685.98434910 A.U. after 3 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.401231	-0.628172	1.247968

2	6	0	-3.685945	-0.661848	0.018175
3	6	0	-4.392892	-0.728967	-1.218581
4	6	0	-5.770012	-0.760641	-1.196413
5	6	0	-6.480076	-0.727068	0.032489
6	6	0	-5.783976	-0.660436	1.253368
7	1	0	-3.849023	-0.577054	2.180553
8	1	0	-3.837643	-0.754320	-2.151199
9	1	0	-6.319509	-0.634358	2.197690
10	6	0	-6.738500	-0.832940	-2.378058
11	6	0	-8.084482	-0.835667	-1.653112
12	6	0	-9.354961	-0.889253	-2.196233
13	6	0	-10.472733	-0.880779	-1.330870
14	6	0	-10.289394	-0.818402	0.066567
15	6	0	-9.011913	-0.764648	0.609720
16	6	0	-7.902331	-0.773107	-0.249868
17	1	0	-9.513280	-0.937542	-3.269246
18	1	0	-11.160762	-0.812970	0.712959
19	1	0	-8.883051	-0.716930	1.686897
20	6	0	-6.597025	0.400540	-3.298316
21	1	0	-5.604990	0.425411	-3.761406
22	1	0	-7.341190	0.369699	-4.100751
23	1	0	-6.736893	1.329355	-2.738332
24	6	0	-6.535331	-2.129971	-3.193398
25	1	0	-7.278578	-2.202078	-3.994033
26	1	0	-5.542399	-2.144679	-3.654993
27	1	0	-6.630722	-3.014927	-2.558116
28	6	0	-11.794466	-0.935617	-1.873869
29	6	0	-2.283052	-0.630140	0.026175
30	7	0	-12.869915	-0.980400	-2.319280
31	7	0	-1.110590	-0.604684	0.030703
32	29	0	0.730462	-0.576541	0.041756
33	6	0	5.862449	-0.567074	-1.150960
34	6	0	5.130660	-0.541807	0.079022
35	6	0	5.846909	-0.513021	1.324379
36	6	0	7.216267	-0.511431	1.306887
37	6	0	7.945578	-0.537521	0.075568

38	6	0	7.238133	-0.564852	-1.154168
39	1	0	5.312966	-0.588380	-2.087063
40	1	0	5.289764	-0.493748	2.256606
41	1	0	7.774299	-0.584495	-2.098620
42	6	0	8.183199	-0.484780	2.493589
43	6	0	9.535133	-0.501508	1.775305
44	6	0	10.790339	-0.492072	2.322854
45	6	0	11.934016	-0.512708	1.453146
46	6	0	11.737210	-0.541420	0.035621
47	6	0	10.470631	-0.550520	-0.501248
48	6	0	9.341156	-0.531424	0.357468
49	1	0	10.941910	-0.470025	3.398189
50	1	0	12.607080	-0.556423	-0.613822
51	1	0	10.343221	-0.572778	-1.579726
52	6	0	8.008210	0.800999	3.331226
53	1	0	7.012151	0.834522	3.785882
54	1	0	8.748682	0.842081	4.137436
55	1	0	8.129949	1.693170	2.710595
56	6	0	8.007394	-1.730402	3.389563
57	1	0	8.747692	-1.734651	4.196971
58	1	0	7.011305	-1.742397	3.845229
59	1	0	8.128717	-2.650362	2.810827
60	6	0	13.220344	-0.507394	1.978772
61	6	0	3.741167	-0.547207	0.063807
62	7	0	2.562707	-0.552580	0.054580
63	29	0	16.000856	-0.517135	3.133868
64	7	0	14.309717	-0.503799	2.428365
65	6	0	18.776419	-0.555891	4.308171
66	7	0	17.698095	-0.535159	3.847604
67	6	0	20.067377	-0.581828	4.857655
68	6	0	20.234442	-0.568227	6.270844
69	6	0	21.208374	-0.622989	4.003092
70	6	0	21.501343	-0.595194	6.825135
71	1	0	19.356484	-0.536735	6.907607
72	6	0	22.463497	-0.649552	4.570526
73	1	0	21.069845	-0.632979	2.926326

74	6	0	22.626062	-0.636276	5.980848
75	1	0	21.617065	-0.584682	7.904826
76	6	0	23.822750	-0.695209	3.870585
77	6	0	24.043722	-0.671435	6.286783
78	6	0	24.769471	-0.706663	5.070973
79	6	0	24.719835	-0.675081	7.516833
80	6	0	26.151664	-0.745126	5.077208
81	6	0	26.108457	-0.713686	7.525835
82	1	0	24.172755	-0.648386	8.454492
83	6	0	26.833008	-0.748855	6.315807
84	1	0	26.724090	-0.772522	4.155054
85	1	0	26.650847	-0.717288	8.465488
86	6	0	23.975711	-1.976830	3.020723
87	1	0	23.248871	-1.986638	2.201748
88	1	0	24.977035	-2.030290	2.581254
89	1	0	23.820584	-2.873607	3.627004
90	6	0	24.044998	0.555577	2.990469
91	1	0	23.319349	0.585467	2.170835
92	1	0	23.939352	1.473731	3.574962
93	1	0	25.047498	0.543714	2.550631
94	6	0	28.262179	-0.788489	6.342594
95	7	0	29.426476	-0.820818	6.361225

---

7. References

1 M. Loos, C. Gerber, F. Corona, J. Hollender, H. Singer, *Anal. Chem.*, 2015, **87**, 5738–5744.
2. A. Jocic, D. Galindo, A. Weidlich, J. Zerhoch, F. Rominger, T. Buckup, F. Deschler, A. Dreuw and M. Kivala, *Adv. Opt. Mater.*, 2024, DOI: 10.1002/adom.202401656.
3. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
4. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100; A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648–5652; A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.
5. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* 1988, **37**, 785–789.
6. R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.,* 1971, **54**, 724–728; W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.,* 1972, **56**, 2257–2261; P. C. Hariharan and J. A. Pople, *Mol. Phys.,* 1974, **27**, 209–214.; P. C. Hariharan and J. A. Pople, *Theor. Chem. Acc.,* 1973, **28**, 213–222.
7. P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270–283.
8. G. Kresse and J. Hafner, *Phys. Rev. B,* 1993, **47**, 558–561.
9. G. Kresse and J. Furthmüller, *Phys. Rev. B,* 1996, **54**, 11169–11186.
10. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.,* 1996, **77**, 3865–3868.
11. S. Grimme, J. Antony, S. Ehrlich and S. Krieg, *J. Chem. Phys.,* 2010, **132**, 154104.
12. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B,* 1976, **13**, 5188–5192.