Facet-Selective Dissociation and Radical-Mediated Reaction of

Dibenzotetrathiafulvalene Molecules on Low-Index Copper Surfaces

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Figure S1: Chemical structure of the DBTTF molecule, in which the four specific chemical bonds are highlighted: C_{Et} – C_{Et} (Bond 1), C_{Et} –S (Bond 2), C_{Ph} –S (Bond 3) and C_{Ph} – C_{Ph} (Bond 4) bonds. Et is the abbreviation of ethylene. Ph is the abbreviation of phenyl. After adsorption on the substrates, the C_{Et} –S and C_{Ph} –S bonds are weakened and elongated due to the chemical interactions between the S atoms and substrate copper atoms and could be further broken due to thermal activation at different substrate temperatures.



Figure S2: Summary of the synthesized chemical species for DBTTF molecules on Cu(110) and Cu(100). Their names used in this paper are also supplied for clarity.



Length	Single species	Back-to-back	Two molecules with	Two molecules with
(nm)		molecules	one bright spot	three bright spots
Count 1	0.74 (Line 1)	1.94 (Line 9)	2.45 (Line 6)	3.47 (Line 5)
Count 2	0.74 (Line 2)	1.95 (Line 10)	2.46 (Line 7)	
Count 3	0.75 (Line 3)	1.93 (Line 11)	2.43 (Line 8)	
Count 4	0.73 (Line 4)			
Average	0.74	1.94	2.45	3.47

Figure S3: Supplementary size information for the 1,2-BDT-Cu complexes in Fig. 1b.



Figure S4: Four ab initio atomic structures among all 16 considered candidates for adsorbed 1,2-BDT molecules on Cu(110). In panels (a) and (b), 1,2-BDT complex adsorb on the surface directly with formation energies (FEs) of -2.51 and -4.21 eV, respectively. In panels (c) and (d), 1,2-BDT with a Cu adatom complex adsorb on Cu(110) with FEs of -3.10 and -3.34 eV, respectively. The configuration with one 1,2-BDT molecule coordinated with a Cu adatom is energetically more stable than that of barely adsorbed 1,2-BDT. Furthermore, the configuration with the complex oriented along the $[1\overline{10}]$ direction has the lowest FE of -3.34 eV, indicating that it is the most stable configuration. The corresponding STM simulation of (d) is also consistent with the STM images. The filled green, white, yellow, magenta, and light gray balls represent C, H, S, Cu adatoms, and Cu surface, respectively. In (a), the Cu atom bonding with the two S atoms is not the surface adatom (different from (c) and (d)) but the shifted substrate atom (from the row to the trough), which is clearly displayed in (e) and (f).



Quantity of	1,2-BDT-Cu	C2 species in Cu-C2-Cu	C2 between two 1,2-BDT-
	complexes	chain	Cu complexes
Image 1	256	54	65
Image 2	215	51	53
Image 3	310	89	55
Sum	781	367 (C2 in total)	
Ratio	1.00	0.47	

Figure S5: Statistical analysis of the ratio between 1,2-BDT-Cu complexes and C₂ fragments. Three images are used in the analysis. Image 1 (-1.0 V, 100 pA, 21.9 nm \times 25.5 nm); Image 2 (-0.1 V, 100 pA, 21.9 nm \times 25.5 nm); Image 3 (-0.1 V, 100 pA, 27.4 nm \times 31.9 nm).



Quantity of	Two lobed species	Cu-C2-Cu chain	Sulfur atoms
Image 1	189	71	399
Image 2	1.00	0.38	2.11

Figure S6: Statistical analysis of the chemicals species on Cu(100) after deposition of DBTTF molecules (-1.0 V, 20 pA, 27.1 nm \times 31.6 nm).



Length (nm)	Two lobes	Two adjacent molecules	Two equivalent molecules
Count 1	0.35 (Line 1)	0.65 (Line 5)	1.06*2 (Line 9)
Count 2	0.36 (Line 2)	0.65 (Line 6)	1.07*2 (Line 10)
Count 3	0.37 (Line 3)	0.63 (Line 7)	
Count 4	0.35 (Line 4)	0.65 (Line 8)	
Average	0.36	0.65	1.07

Figure S7: Supplementary size information for the 1,2-phenyl diradical on Cu(100) in Fig. 3.



Figure S8: Top view (left) and side view (right) of the atomic structure of 1,2-phenyl diradicals on a Cu(100) substrate. Phenyl diradicals "stand up" via the two carbon radicals bonding to copper atoms at the bridge sites.



Figure S9: Atomic structure of absorbed 1,2-BDT on Cu(100) surface. Each column represents a possible configuration. The first two rows represent the structure before and after relaxation, and the third row shows the side view. 1,2-BDT tends to ``lie down'' on the surface thus it's unlikely that it would show the two-lobed feature as observed.



Figure S10: DCD image of the assembly structure shown in Fig. 3b-e. Intermolecular parts explicitly indicate an appreciable pi-pi stacking interaction of weak Lewis acid Ph-H+ and electronrich phenyl rings, lowering the total energy by 0.24 eV per molecule according to our DFT calculation. This interaction primarily occurs in the middle region of the vertically adsorbed radical, which may lower the tunneling barrier width at certain positions but cannot significantly affect the charge distribution around the two topmost H atoms. Therefore, such intermolecular interactions cannot be clearly reflected in an STM simulation based on the Tersoff-Hamann approximation. In addition, as the tip passes through a molecule during scanning, the molecule may tilt toward the tip due to attractive interactions between them, which may result in apparent intermolecular features.



Figure S11: Molecular species on Cu(100) after annealing at HT. STM image of chemical products on Cu(100) under different sample voltages (30 pA, 13 nm \times 13 nm). The two triphenylene molecules are highlighted by green ellipses.



Figure S12: Schematics of the supposed facet-dependent synthesis pathways on Cu(110) and Cu(100) surfaces: (a) The phenyl diradicals can only diffuse within the troughs (shown by the arrow) on the anisotropic Cu(110) surface due to their preferred adsorption sites. The reaction sites of the biphenyl diradicals (from the biphenyl-Cu complex) are on the top atom row, so the phenyl diradicals almost cannot react with the biphenyl diradicals to form triphenylene. The biphenyl diradicals (from the biphenyl-Cu complex) have a few possibilities to form biphenylene by closing the four-membered ring (even though it is not very stable). (b) The phenyl diradicals can diffuse along the <110> direction (shown by the arrow) on the flat Cu(100) surface. The reaction sites of the biphenyl diradicals (from the biphenyl-Cu complex) are only along the diffusion path of the phenyl diradicals, so they can react with each other to form triphenylene.