Electronic Supplementary Information

Single Crystal Structure of Copper Hexadecafluorophthalocyanine (F_{16}CuPc) Ribbon

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Experimental methods

Synthesis of F_{16}CuPc ribbons: F_{16}CuPc powder was purchased from Aldrich (80 %), and purified by sublimating in vacuum before use. 0.04g of purified F_{16}CuPc powder was loaded in a ceramic boat, which was then located at the center of a quartz tube having one-inch diameter. The quartz tube was then placed in a single-zone tube-type heating furnace as the boat containing precursors in the quartz tube to be centered in the furnace. A pre-cleaned Si(100) substrate was placed at the end of the inside quartz tube (i.e. at the end of heating furnace) to collect F_{16}CuPc ribbons. The quartz tube was thoroughly flushed with Ar gas before the temperature increase to remove ambient gases. The growth of F_{16}CuPc ribbons were then performed at designated substrate temperatures (increase rate = 1.05 ^{o}C/sec) for 40 min under the Ar environment (100 standard cubic centimeters per minute~~s~~ (sccm)). Note that the substrate temperature applied for the synthesis of large F_{16}CuPc ribbons becomes 360 ^{o}C when the precursor temperature was set at 500 ^{o}C.

Crystal structure analysis: A crystal of F_{16}CuPc ribbon was measured on ADSC Quantum 210 CCD diffractometer with synchrotron radiation (λ = 0.80000 Å) at Macromolecular Crystallography Wiggler Beamline 6B, Pohang Accelerator Laboratory (PAL). The diffraction data from a single crystal F_{16}CuPc ribbon was collected at 173 K. The raw data was processed and scaled using the program HKL2000. The structure was solved by direct methods, and the refinements were carried out with full-matrix least-squares on F^2 using the Bruker SHELXTL program package.[1] All the atoms were refined anisotropically. X-ray diffraction pattern of F_{16}CuPc ribbon was obtained from 5C2 XRS beam line at PAL. Simulated XRD pattern of F_{16}CuPc ribbon was extracted using a Mercury 1.4.2. software (The Cambridge Crystallographic Data Centre)

Fabrication of F_{16}CuPc ribbon FET device: F_{16}CuPc ribbons dispersed in ethanol were drop-casted on a Si/SiO_2 (100nm) substrate, on which Au (200 nm)/Cr (20 nm) metal electrodes were addressed by E-beam lithography using poly methyl methacrylate (PMMA, Microchem^{TM}) as an E-beam resist. The electrical transport properties were measured using a semiconductor analyzer (SCS 4200, Keithley) at room temperature in air. A solar simulator (No. 69920 New Port) was used for the photo-switching properties

Table S1. Crystal data and structure refinement for F_{16}CuPc. CCDC- 698474 contains supplementary crystallographic data of a F_{16}CuPc. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk./data_request/cif.

Identification code	F_{16}CuPc	
Empirical formula	C32 Cu F16 N8	
Formula weight	863.94	
Temperature	173(2) K	
Wavelength	0.8000 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 4.796(1) Å	α= 86.41(3)°
	b = 10.228(2) Å	β= 87.89(3)°
	c = 28.002(6) Å	γ= 81.39(3)°
Z, Volume	2, 1354.9(5) $Å^3$	
Density (calculated)	2.118 Mg/m^3	
Absorption coefficient	0.964 mm^{-1}	
F(000)	842	
Crystal size	0.120 x 0.05 x 0.010 mm^3	
Theta range for data collection	2.02 to 29.36°	
Index ranges	$-5 \leq h \leq 5$, $-12 \leq k \leq 12$, $-34 \leq l \leq 34$	
Reflections collected	5204	
Independent reflections	5204 [R(int) = 0.0142]	
Completeness to theta = 29.36°	99.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.995 and 0.891	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5204 / 0 / 517	
Goodness-of-fit on F^2	1.123	
Final R indices [I>2sigma(I)]	R1 = 0.0981, wR2 = 0.2041	
R indices (all data)	R1 = 0.0992, wR2 = 0.2101	
Largest diff. peak and hole	1.345 and -0.697 e. $Å^{-3}$	

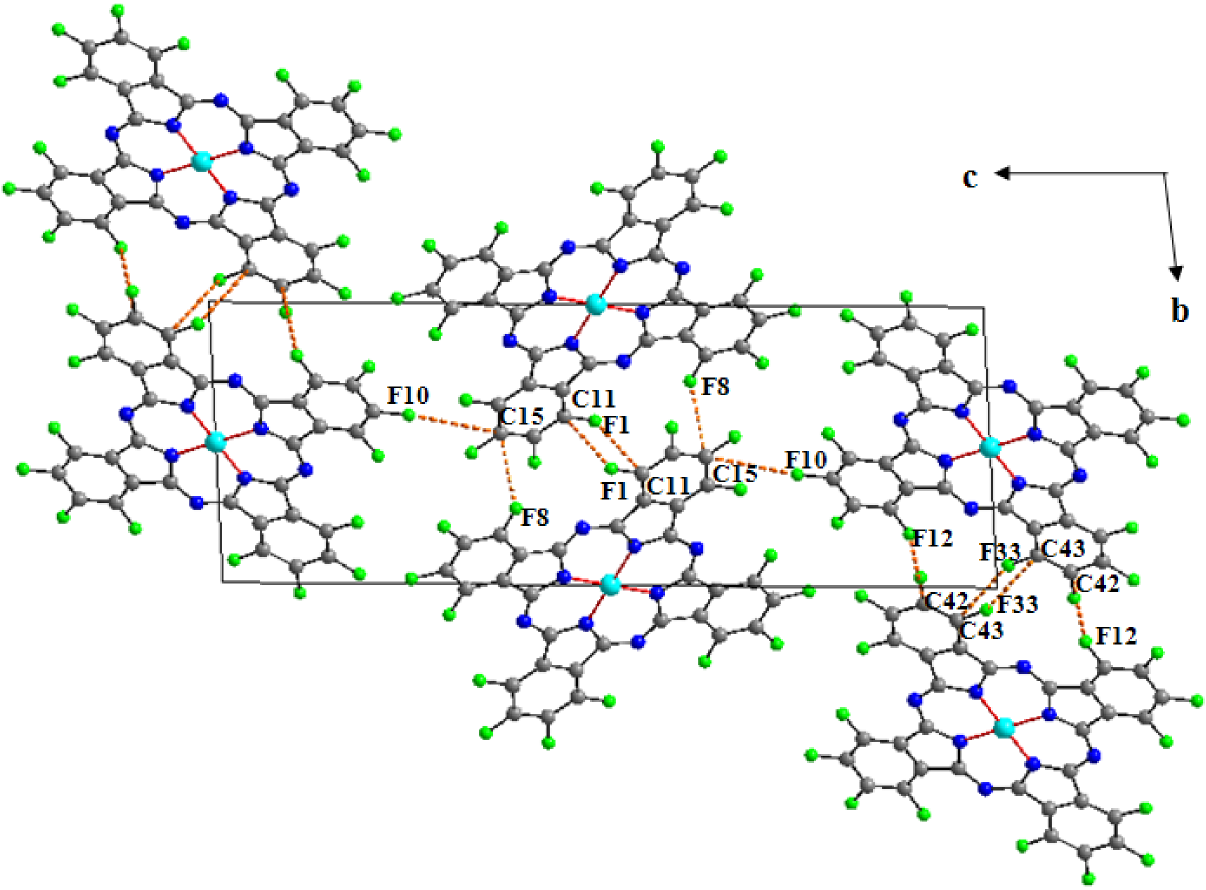

Fig. S1 Unit cell of a $F_{16}CuPc$ ribbon. The orange dashed lines indicate F···π interactions.

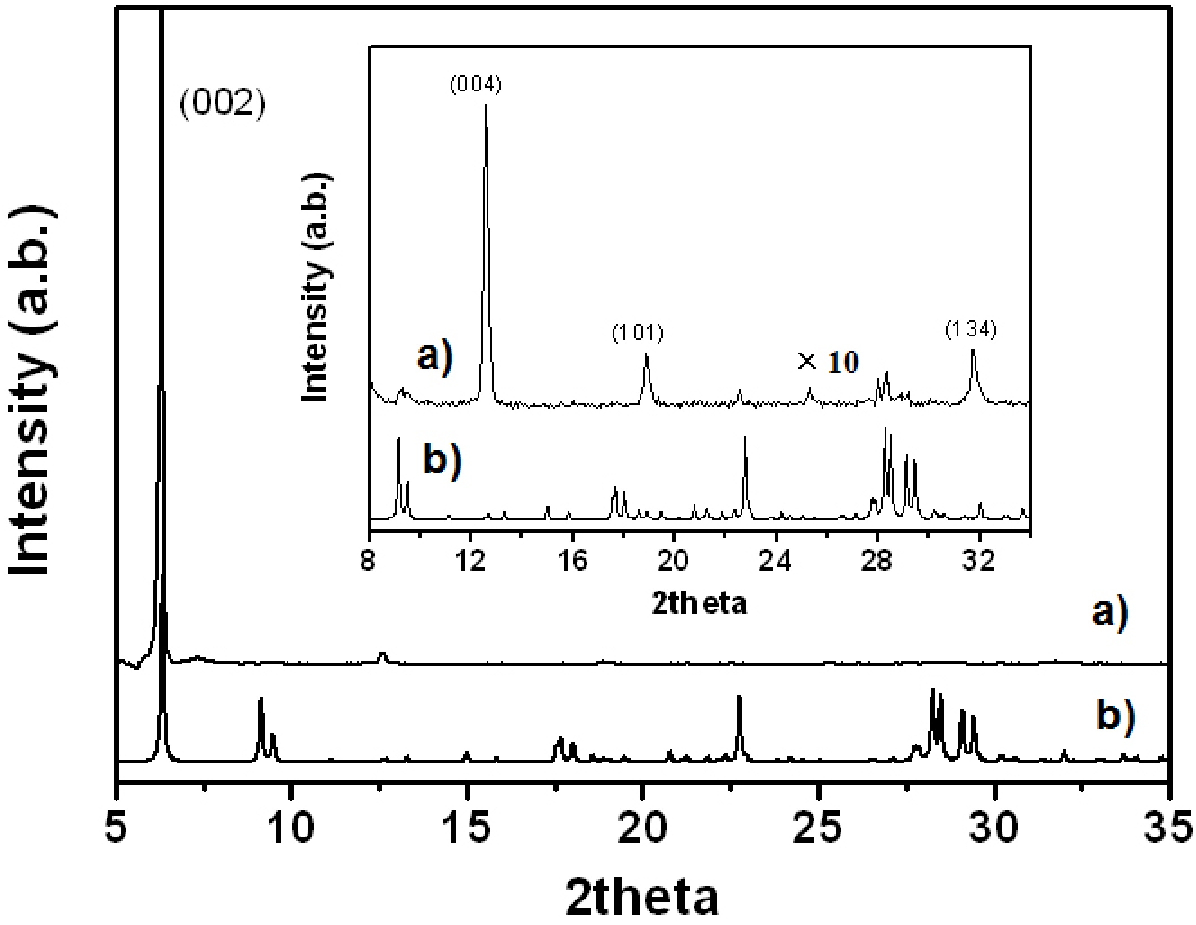

Fig. S2 (a) Powder X-ray diffraction pattern of $F_{16}CuPc$ ribbon. (b) Simulated XRD pattern converted from the single crystal data of $F_{16}CuPc$ ribbon. Inset patterns are magnified ones to show detail peaks from 8° to 34° of 2 theta.

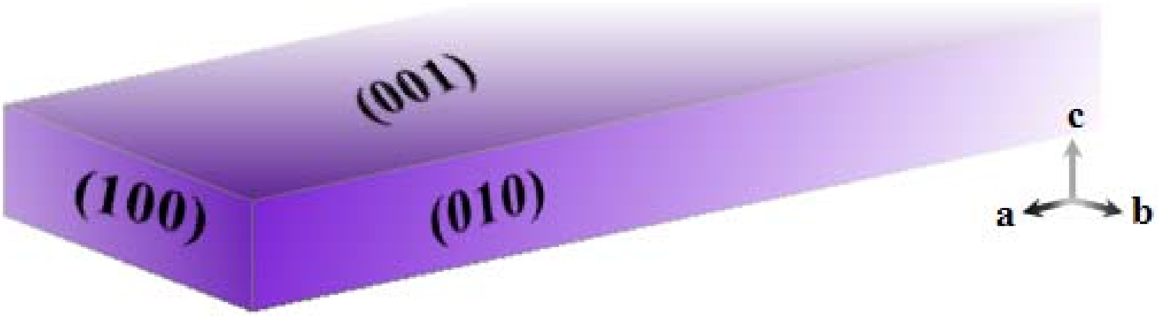

Fig. S3 Perspective view of F_{16}CuPc ribbon.

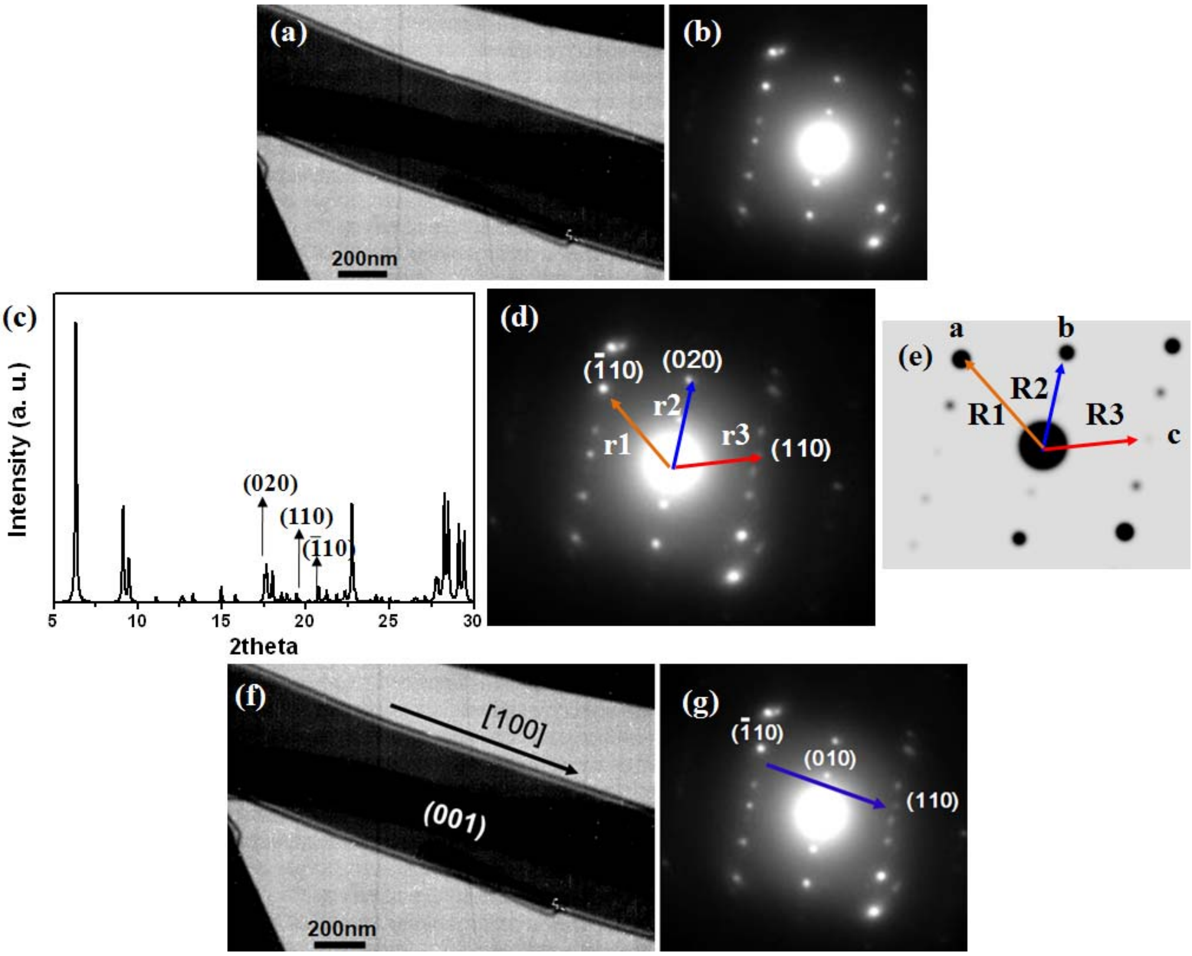

Fig. S4 XRD, TEM image and electron diffraction patterns for the determination of growth direction and crystallographic planes of F_{16}CuPc ribbon.

Procedure for the determination of growth direction and crystallographic planes:

1. TEM image and SAED pattern of a nanoscale F_{16}CuPC ribbon was obtained (Fig. S3a and b).
2. Powder XRD pattern from the single crystal data of the F_{16}CuPc ribbon was retrieved by simulation (Fig. S3c)[2].
3. The crystal planes corresponding electron diffraction spots in the SAED pattern were assigned by directly comparing the distance ratios of r1/r2 and r2/r3 in Fig. S3d with the possible ratios of known d values in Fig. S3c. As a result, we found that the ratio r1/r2 ≈ d(020)/d(-110), and r2/r3 ≈ d(110)/d(020). Considering that the electron diffraction spots in the SAED pattern are in the reciprocal space, the crystal planes of the spots at the end of arrows of r1, r2, and r3 are (-110), (020), and (110), respectively.
4. Since three electron diffraction spots were indexed, a zone plane could be determined to be (001) plane because the zone plane should be normal to all the spots in the SAED.
5. The assignment of the electron diffraction spots were further confirmed by the simulated SAED pattern.[3] The simulated electron diffraction patterns were same as the experimentally observed SAED patterns by showing r1: r2: r3 = R1: R2: R3, and the

same angles: (-110)-(000)-(020) = a-(000)-b, (020)-(000)-(110) = b-(000)-c (Fig. S2e).

6. The broad face of the $F_{16}CuPc$ ribbon was determined to be (001) because the zone plane was (001) (Fig. S3f).
7. As shown in Fig. S2f and g, the growth axis was determined to be [100] since the direction from (-110) to (110) (blue arrow) matched well with the growth direction (black arrow). Consequently, the plane corresponding to the thickness could be determined as (010).

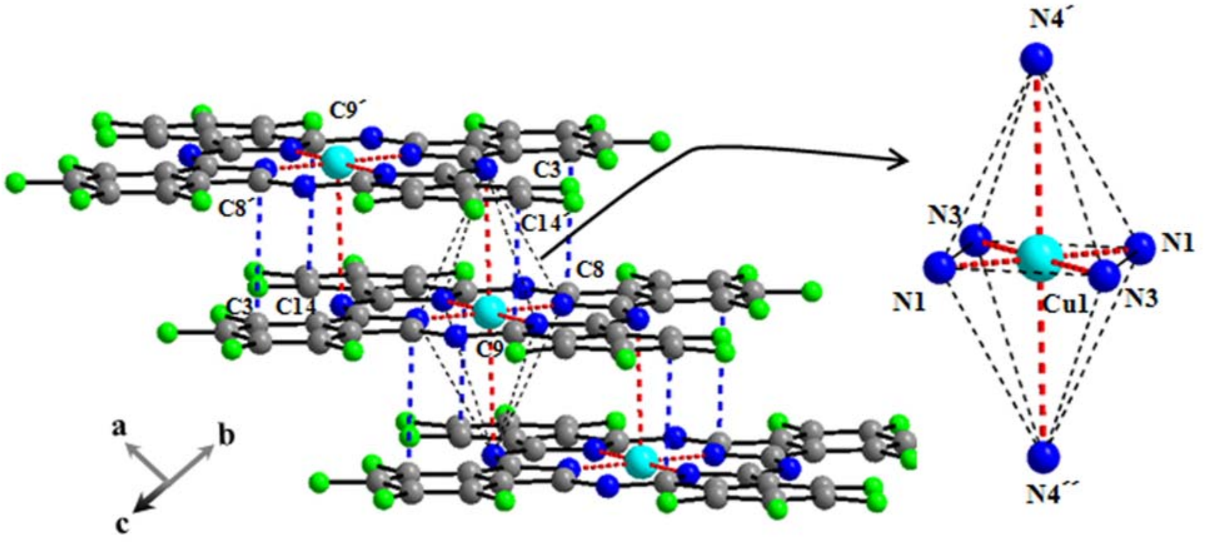

Fig. S5 Intermolecular interactions along the a-axis. The red dashed lines indicate Cu···N interactions which constitute a pseudo-octahedral geometry. The blue dashed lines indicate π-π intermolecular interactions between the $F_{16}CuPc$ molecules.

References

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1. G. Sheldrick, Program for Crystal Structure Solution, Universität Göttingen, 1986.; G. Sheldrick, Program for Crystal Structure Refinement, Universität Göttingen, 1993.
2. Mercury 1.4.2. Cambridge Crystallographic Data Centre.
3. Single crystal 1.2.0. Crystal Maker Software Ltd.