Supplementary materials

Title: Aggregation and conductivity in hot-grown petroporphyrin films
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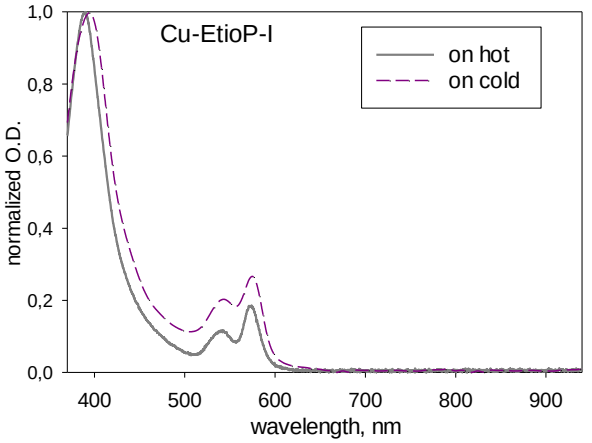
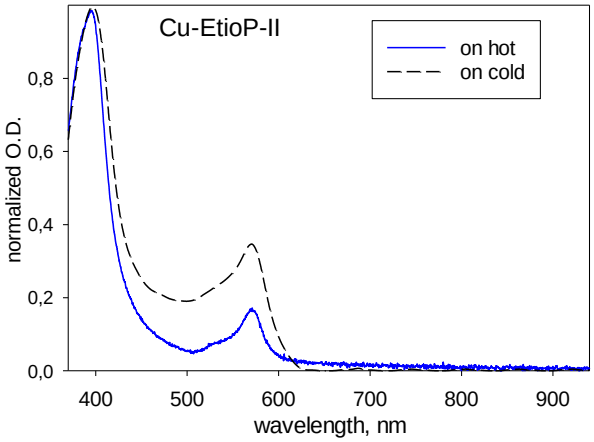
Figure S1
EAS of copper etioporphyrin films deposited on cold/hot substrate (standard ITO coated glass slides from Sigma-Aldrich)





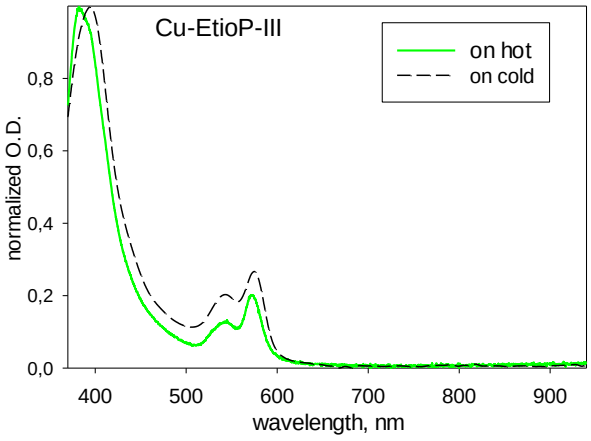


Figure S2

Comparison of SEM (top b/w panels, see Fig. 2) and AFM (bottom color panels) images of the surface of hot-grown Cu-etioporphyrin films on silicon wafer

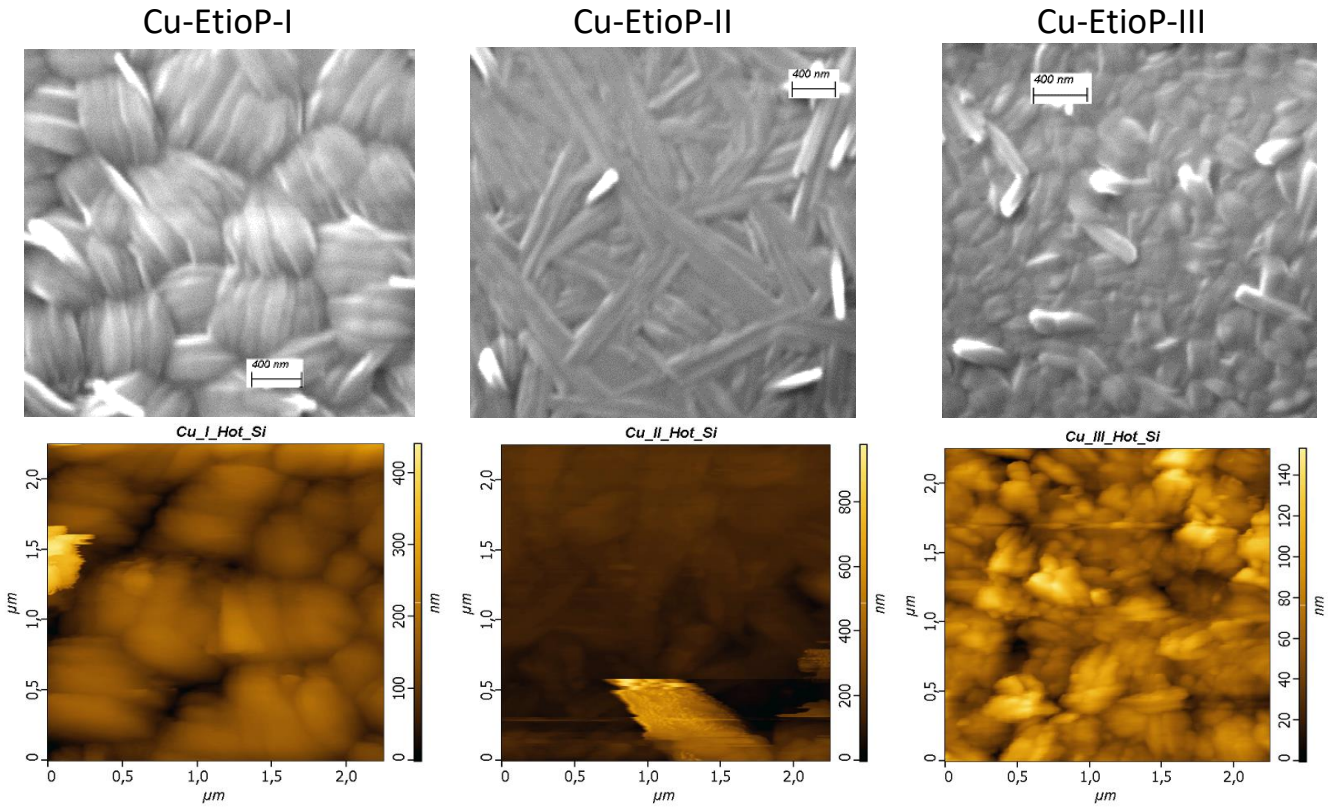
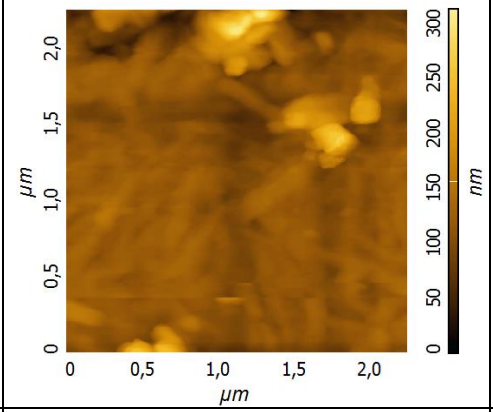
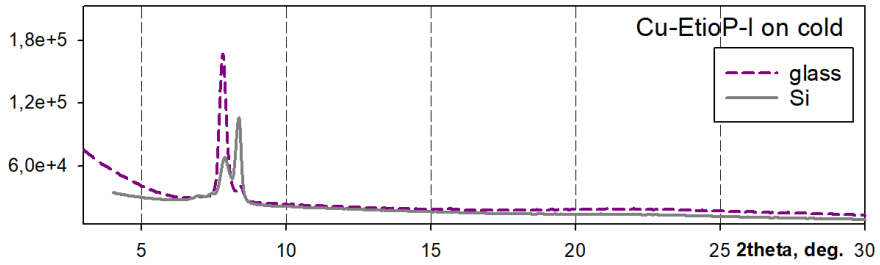
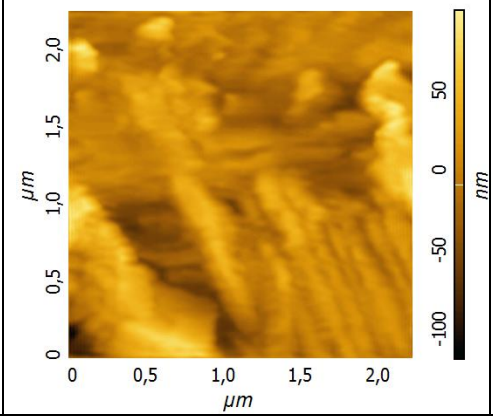
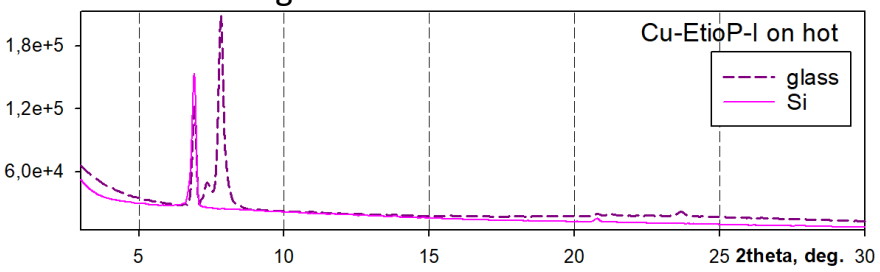
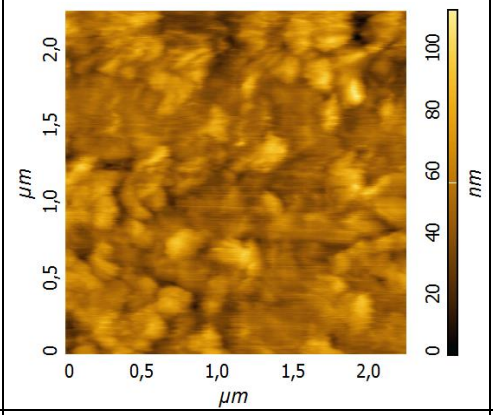
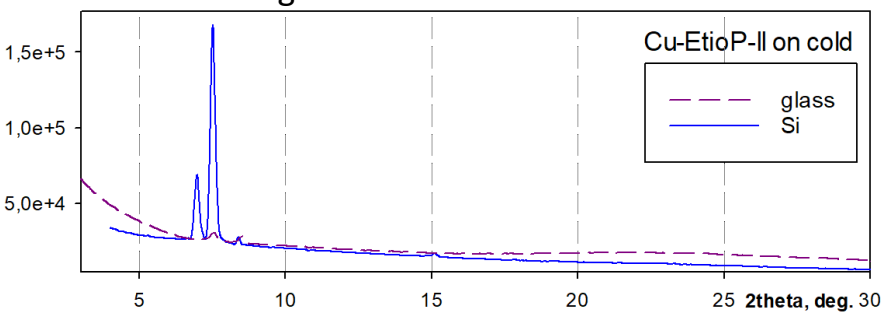
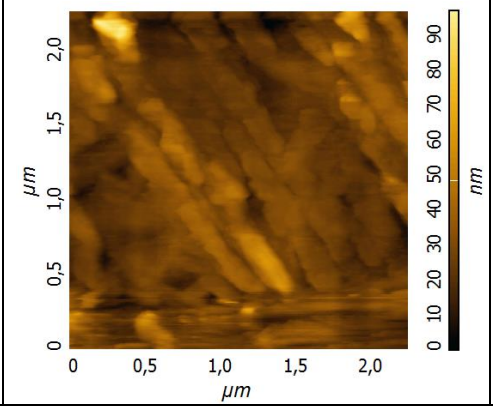
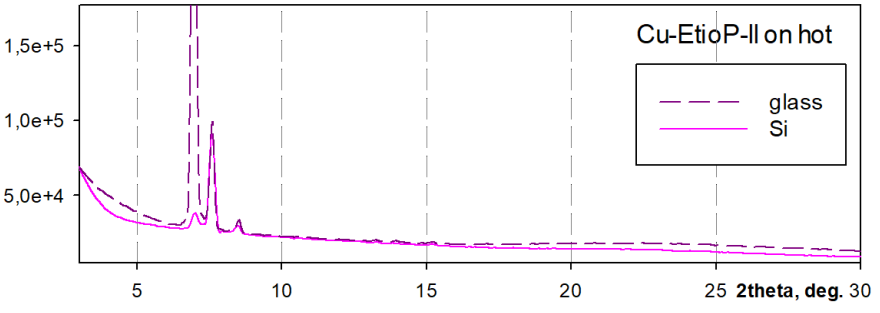


Figure S3

	AFM images of Cu-EtioPs deposited on cold/hot glass substrate	XRD patters of Cu-EtioPs deposited on glass slide and silicon wafer
(a) Cu-EtioP-I		
cold		Gray curve from Fig. 3. 
hot		Pink curve from Fig. 3. 
(b) Cu-EtioP-II		
cold		Blue curve from Fig. 3. 
hot		Pink curve from Fig. 3. 

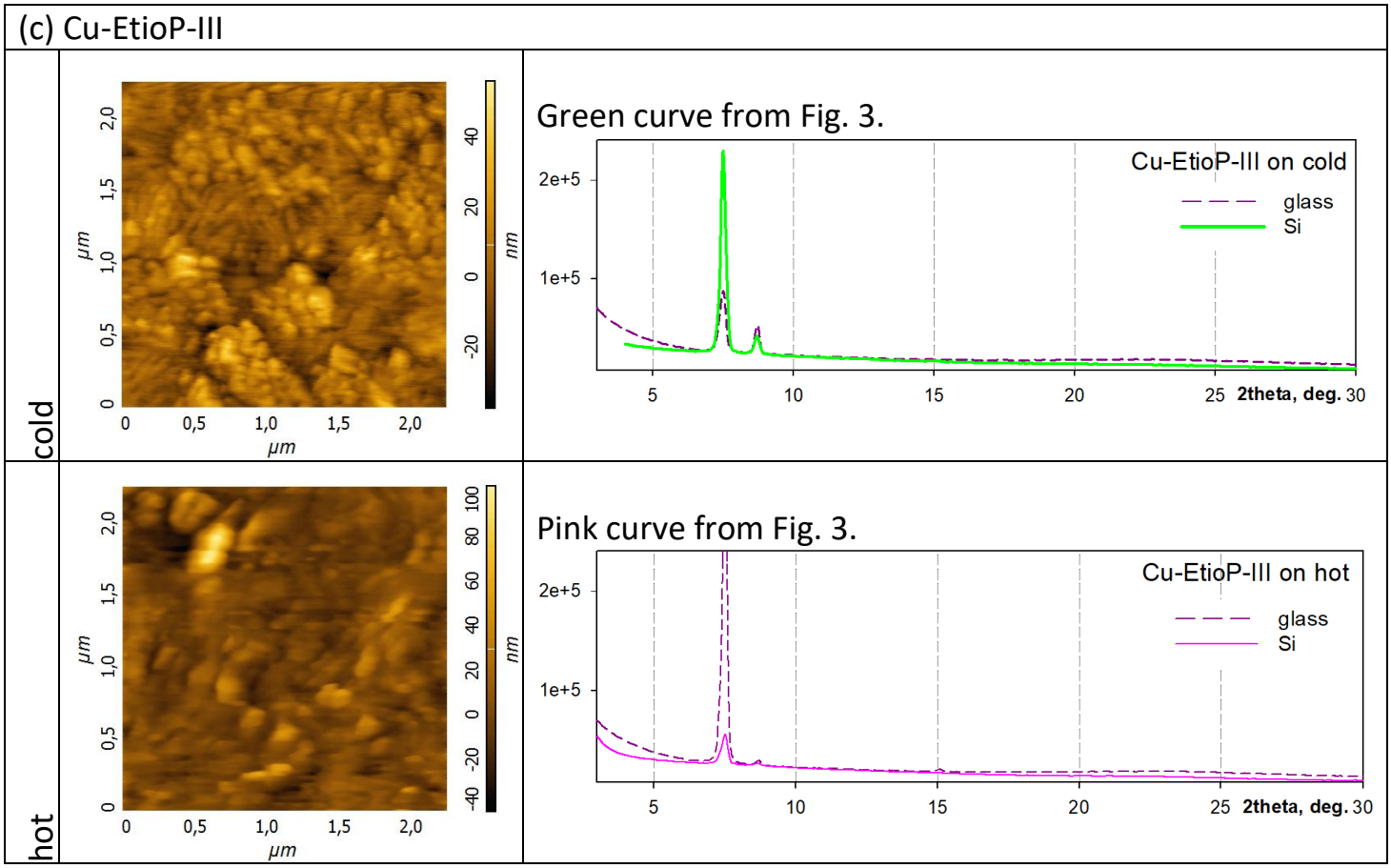
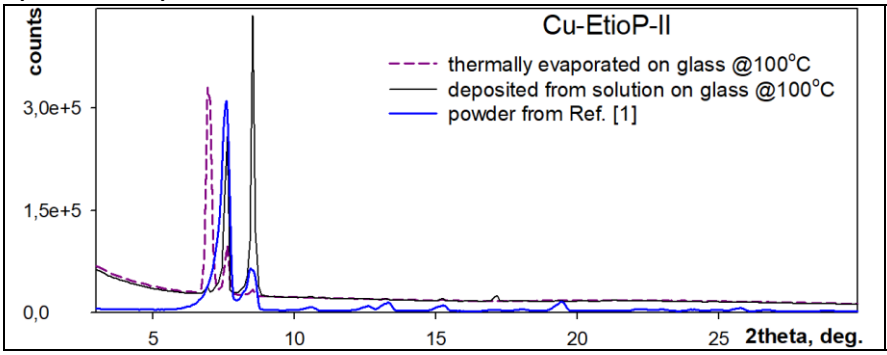


Figure S4

The XRD-patterns of Cu-EtioP-II films deposited either by drop-casting from the binary solution (toluene+DMF) or by vacuum evaporation on hot substrate, compared to the powder spectrum

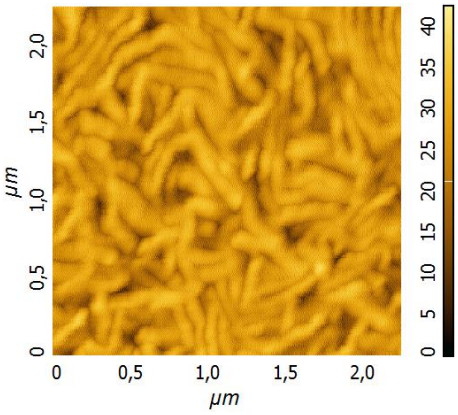


This Figure illustrates that "hot" films deposited from solution (gray curve) are closer in their crystalline structure to the original powder (blue) than the films grown in vacuum (dashed, pink). For instance, the low-angle peak at 6.98 deg. is a distinct feature of the vacuum-sublimed thin-film phase.

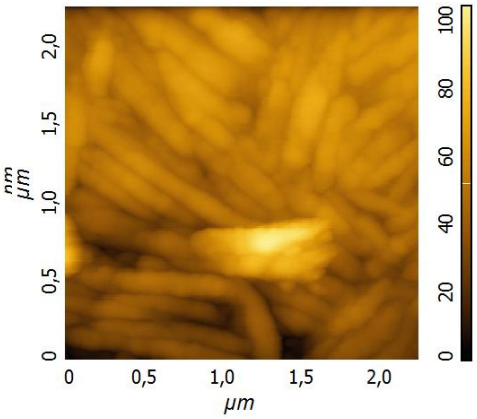
Figure S5

AFM images of the surface of Cu-etioporphyrin-I films grown on various substrates at T_g = **cold**

silicon wafer



Ni-metallized ceramics



ceramics (p-Al_2O_3)

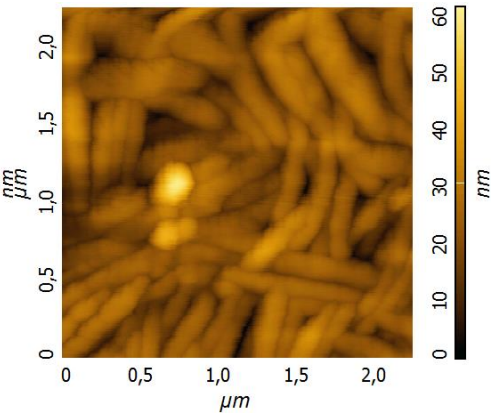


Figure S6

Photo of Cu-EtioP-I film vacuum-deposited on the IDE substrate

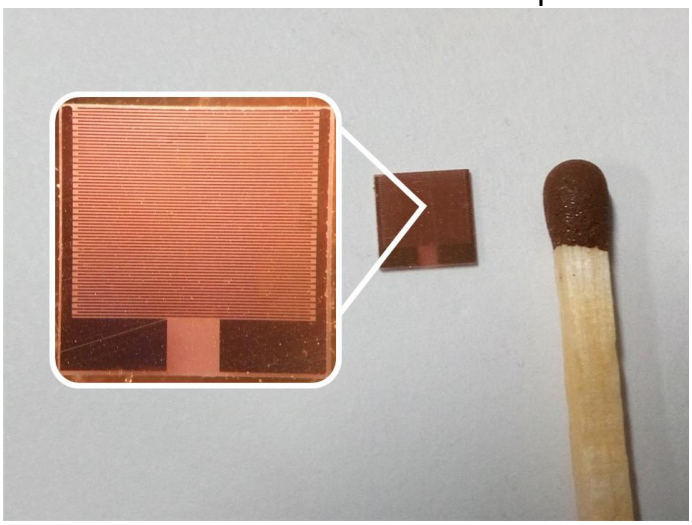
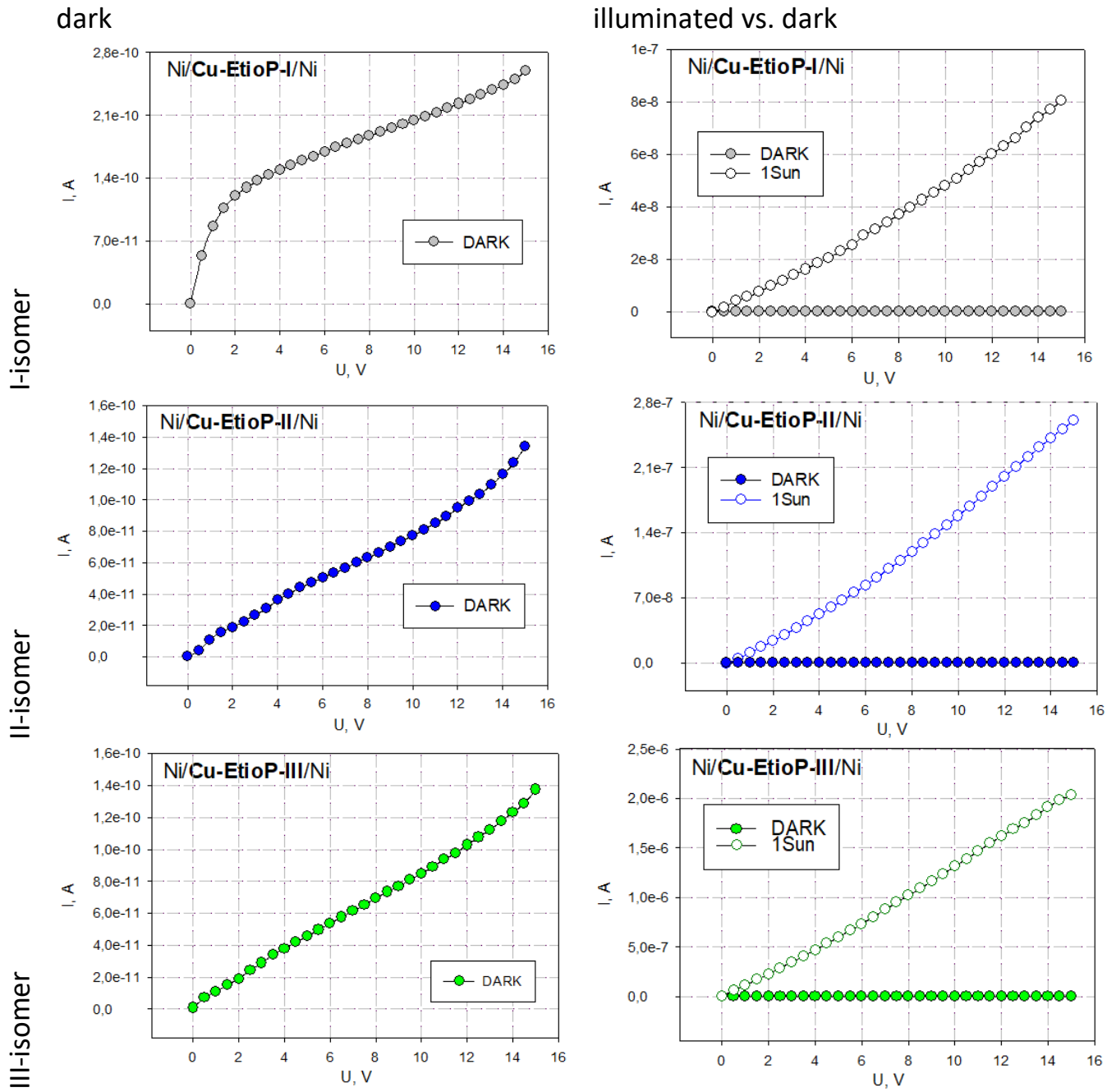
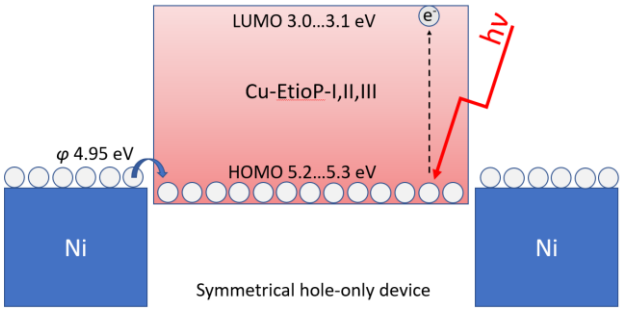


Figure S7

Dark and illuminated I-V dependences measured at room temperature in air-free conditions for three Cu-EtioP isomers vacuum-deposited on the substrates with IDE contacts shown in Fig. S6.



The tentative band diagram of the device, the HOMO-LUMO values are estimated from CV (to be published elsewhere)



Example of an Arrhenius plot for the Cu-EtioP-II film →

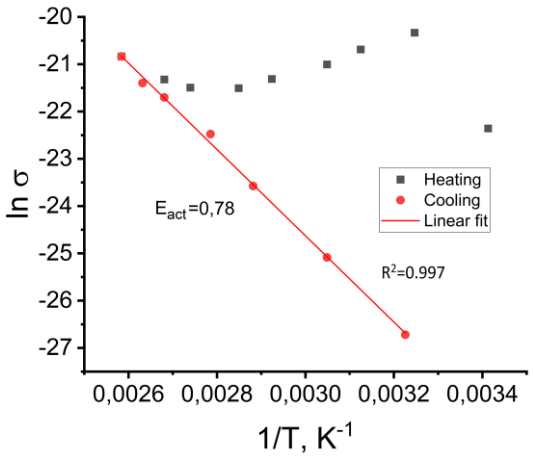


Table S1
Crystal data, details of data collection, and parameters of structure refinement

Parameter	Value
Formula	$C_{32}H_{34}CuN_4$
CCDC	2201607
M	538.17
System, Z	monoclinic, 2
Space group	P $2_1/c$
T, K	100(2)
a, Å	4.6803(6)
b, Å	20.039(2)
c, Å	14.846(2)
α, °	90
β, °	108.483(14)
γ, °	90
V, Å^3	1320.6(3)
D_x, g·cm^{-3}	1.353
μ, mm^{-1}	0.855
Absorption T T_{min}/T_{max}	0.443 / 1.000
Absorption correction	Gaussian
F(000)	566
Size, mm	0.514 × 0.065 × 0.044
Diffractometer / Radiation / Monochromator / Scan	Rigaku XtaLab, MM003, P200K / MoKα, λ= 0.71073 Å / MicroMax-003 / ω scans
Range of θ, °	4.318 - 26.371
Range of indices	-5 ≤ h ≤ 5 -25 ≤ k ≤ 25 -18 ≤ l ≤ 18
Measured reflections, all / independent / with I > 2σ(I) / R_{int}	10915 / 2546 / 1230 / 0.1626
Parameters	185
GOOF	0.956
R-factors for $F^2 > 2\ \sigma(F^2)$	R_1 = 0.0929 wR_2 = 0.1935
R-factors for all reflexes	R_1 = 0.1807 wR_2 = 0.2254
Δρ(min/max), e·Å^{-3}	-0.494 / 1.223

Table S2
The atom list for $C_{32}H_{34}CuN_4$

Atom	x	y	z	Occupancy	Ueq, Å²
C1	0.8358(16)	0.4550(4)	0.2929(5)	1	0.0435(18)
C2	0.6471(16)	0.4055(3)	0.3054(5)	1	0.049(2)
C3	0.5892(14)	0.3906(3)	0.3891(5)	1	0.0402(18)
C4	0.3894(16)	0.3387(3)	0.3987(5)	1	0.047(2)
C5	0.3883(15)	0.3400(4)	0.4889(6)	1	0.047(2)
C6	0.5868(15)	0.3927(3)	0.5367(5)	1	0.0422(18)
C7	0.6521(15)	0.4108(3)	0.6306(5)	1	0.0425(18)
C8	0.8454(16)	0.4613(4)	0.6779(5)	1	0.0417(18)
C9	0.9123(18)	0.4779(4)	0.7771(5)	1	0.052(2)
C10	1.1054(18)	0.5294(4)	0.7949(5)	1	0.051(2)
C11	1.236(2)	0.5670(4)	0.8882(5)	1	0.076(3)
C12	0.789(2)	0.4414(4)	0.8457(5)	1	0.064(2)

C13	0.955(3)	0.3817(6)	0.8854(7)	0.833(3)	0.093(4)
C14	0.2243(16)	0.2945(4)	0.5361(5)	1	0.053(2)
C15	0.418(3)	0.2372(6)	0.5794(9)	0.658(3)	0.068(4)
C16	0.2266(17)	0.2894(3)	0.3221(5)	1	0.053(2)
C17	0.379(4)	0.2288(10)	0.3160(13)	0.509(3)	0.101(7)
Cu1	1.000000	0.500000	0.500000	1	0.0413(4)
H2	0.547209	0.379077	0.251482	1	0.059
H7	0.554435	0.386088	0.666942	1	0.051
H11A	1.452215	0.573814	0.900826	1	0.113
H11B	1.203025	0.541021	0.940024	1	0.113
H11C	1.135560	0.610408	0.883878	1	0.113
H12A	0.790378	0.472004	0.898233	1	0.077
H12B	0.576340	0.429127	0.812441	1	0.077
H13A	0.829286	0.353012	0.911070	0.833(3)	0.139
H13B	1.138231	0.393971	0.936429	0.833(3)	0.139
H13C	1.008543	0.357623	0.835669	0.833(3)	0.139
H14A	0.168591	0.319323	0.585686	1	0.063
H14B	0.036913	0.278231	0.488609	1	0.063
H15A	0.301861	0.204937	0.603017	0.658(3)	0.102
H15B	0.590088	0.252909	0.632177	0.658(3)	0.102
H15C	0.491780	0.215786	0.531552	0.658(3)	0.102
H16A	0.033061	0.277750	0.331916	1	0.064
H16B	0.177958	0.312317	0.259955	1	0.064
H17A	0.290638	0.209330	0.252679	0.509(3)	0.152
H17B	0.357833	0.197412	0.364069	0.509(3)	0.152
H17C	0.592844	0.238099	0.327009	0.509(3)	0.152
N1	0.7100(12)	0.4241(3)	0.4729(4)	1	0.0410(15)
N2	1.0016(11)	0.5018(3)	0.6357(4)	1	0.0444(14)

Table S3

Interatomic distances for $C_{32}H_{34}CuN_4$

Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Distance, Å
Cu1 – N1	1.993(5)	C6 – C5	1.437(10)	C14 – C15	1.479(12)
Cu1 – N1$^{(I)}$	1.993(5)	C8 – N2	1.370(9)	C14 – C5	1.500(10)
Cu1 – N2	2.013(6)	C8 – C7	1.390(9)	C9 – C10	1.342(10)
Cu1 – N2$^{(I)}$	2.013(6)	C8 – C9	1.444(9)	C9 – C12	1.511(10)
C3 – N1	1.368(8)	C1 – C2	1.379(10)	C10 – C11	1.525(10)
C3 – C2	1.386(10)	C1$^{(I)}$ – N2	1.392(8)	C12 – C13	1.446(12)
C3 – C4	1.434(10)	C1 – C10$^{(I)}$	1.449(10)	C16 – C17	1.425(19)
C6 – C7	1.377(9)	C4 – C5	1.341(10)		
C6 – N1	1.405(9)	C4 – C16	1.518(9)		

Symmetry codes: I) -x+2, -y+1, -z+1;

Table S4

Valence angles for $C_{32}H_{34}CuN_4$

Atoms	Angle, °	Atoms	Angle, °	Atoms	Angle, °
N1$^{(I)}$ – Cu1 – N2	89.9(2)	C2 – C1 – C10$^{(I)}$	126.1(7)	N2 – C8 – C7	123.8(7)
N1 – Cu1 – N2$^{(I)}$	89.9(2)	N1 – C3 – C4	111.1(7)	C7 – C8 – C9	125.4(7)
N1 – Cu1 – N2	90.1(2)	C2 – C3 – C4	124.3(7)	C10 – C9 – C8	107.0(7)
N1$^{(I)}$ – Cu1 – N2$^{(I)}$	90.1(2)	N1 – C3 – C2	124.5(7)	C8 – C9 – C12	124.8(8)
N1 – Cu1 – N1$^{(I)}$	180.0(2)	C5 – C4 – C3	107.1(6)	C10 – C9 – C12	128.1(7)
N2 – Cu1 – N2$^{(I)}$	180.0	C3 – C4 – C16	125.9(7)	C9 – C10 – C1$^{(I)}$	107.3(7)
C3 – N1 – C6	104.6(6)	C5 – C4 – C16	126.9(7)	C1$^{(I)}$ – C10 – C11	125.1(8)
C6 – N1 – Cu1	127.2(5)	C4 – C5 – C6	107.5(7)	C9 – C10 – C11	127.6(8)

C3 – N1 – Cu1	128.1(5)	C6 – C5 – C14	124.2(7)	C1 – C2 – C3	126.3(6)
C8 – N2 – C1$^{(I)}$	105.3(6)	C4 – C5 – C14	128.3(7)	C6 – C7 – C8	127.1(7)
C1$^{(I)}$ – N2 – Cu1	126.9(5)	N1 – C6 – C5	109.6(6)	C13 – C12 – C9	113.8(8)
C8 – N2 – Cu1	127.8(5)	C7 – C6 – N1	123.9(7)	C15 – C14 – C5	109.9(7)
N2$^{(I)}$ – C1 – C10$^{(I)}$	109.6(7)	C7 – C6 – C5	126.5(7)	C17 – C16 – C4	117.4(9)
C2 – C1 – N2$^{(I)}$	124.3(7)	N2 – C8 – C9	110.8(7)		

Symmetry codes: I) -x+2, -y+1, -z+1;