

Supporting Information for:

**Efficient non-halogenated solvent for template-free solution
synthesis of ultralong copper octaethylporphyrin nanowires network
with strong photoswitching properties**

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Experimental Section:

The copper octaethylporphyrin (CuOEP) powder (product number was 257540, purity>95%) was purchased from Sigma-Aldrich. The solvent chloroform, m-xylene, THF and anisole were purchased from Sinopharm Chemical Reagent Co., Ltd. All the chemicals were of analytical grade and were not purified further before use.

The CuOEP nanowires were produced by slowly self-assembling from m-xylene solution under a certain solvent pressure in a closed container. Figure S2 illustrates the setup and the procedures. The CuOEP solution was directly deposited onto the substrate (glass, SiO₂/Si or PET) and the solvent was allowed to evaporation at room temperature. The vapor pressure of the solvent atmosphere could guarantee the free movement of the CuOEP molecules and then induced them to assemble together leading to the growth of nanowire. The morphology and crystalline structures were then characterized by scanning electron microscope (SEM, Quanta 400 FEG), transmission electron microscope (TEM, Tecnai G2 F20 S-Twin), X-ray diffraction (XRD, Bruker D8 Advance powder X-ray diffractometer), and Fourier-transform infrared (FTIR, Thermo Fisher Scientific FTIR 6700).

The photodetector was constructed in a bottom-connected configuration. The finger electrodes with lengths of 200 μm, widths of 20 μm, and distances of 20 μm were fabricated using photolithography and electron beam deposition of Au on SiO₂/Si. The pre-patterned electrodes were cleaned using acetone, ethanol, and de-ionized water. The 30 μL CuOEP solution (0.8 mg/mL) was deposited on the Au electrodes. The solution was allowed to evaporate slowly in solvent atmosphere. To remove the solvent thoroughly and enhance the contact between the nanowire and Au electrodes, the device was post-annealed at 150°C for 30min. The current–voltage characteristics of the devices were recorded with a Keithley 4200 SCS and SUSS PM8 probe station in a clean and shielded box at room temperature. A xenon lamp was used as the white light source with different intensities. All measurements were carried out at ambient conditions.

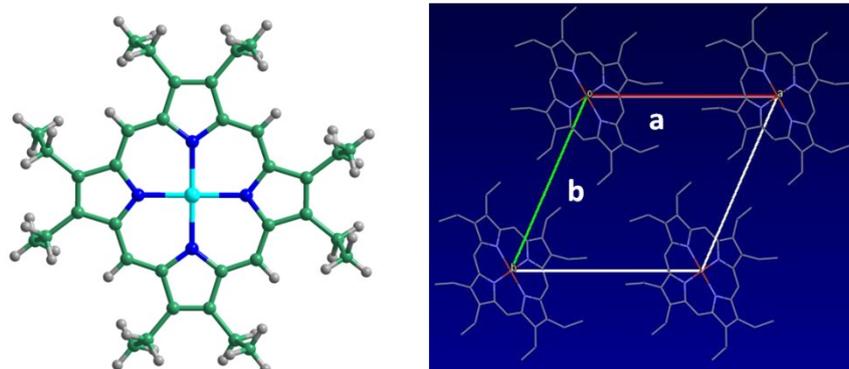


Fig.S1. The molecular structure of CuOEP, comprised of a copper-centered porphyrin macrocycle and eighty ethyl moieties (left) and the view of the crystal packing arrangement CuOEP molecules at c-axis (right).

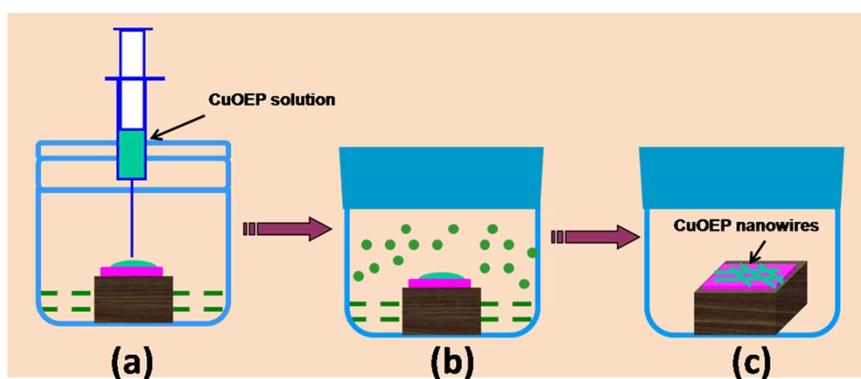


Fig.S2. Schematic for the preparation of CuOEP nanowires: (a) injecting a drop of CuOEP solution onto the substrate, which is in the beaker with solvent in the bottom, (b) CuOEP molecules self-assembled into nanowires in the solvent atmosphere, (c) large-area CuOEP nanowires was obtained on the substrate.

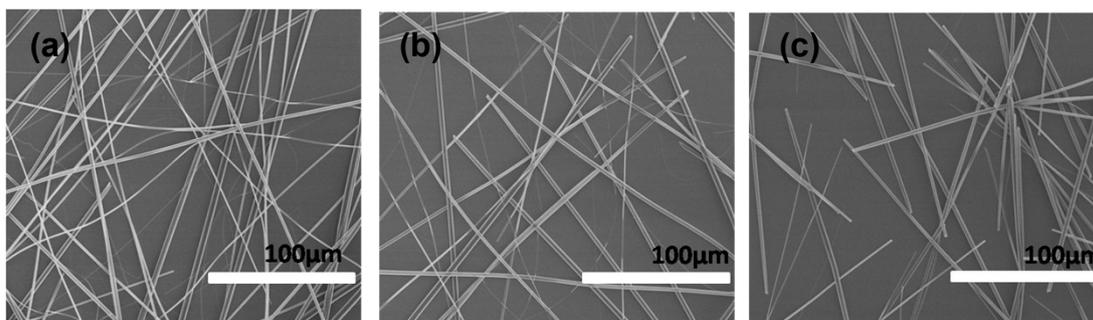


Fig.S3. SEM images of the self-assembled CuOEP nanowires on (a) glass, (b) quartz wafers, and (c) flexible polyethylene terephthalate (PET) substrate from m-xylene solution.

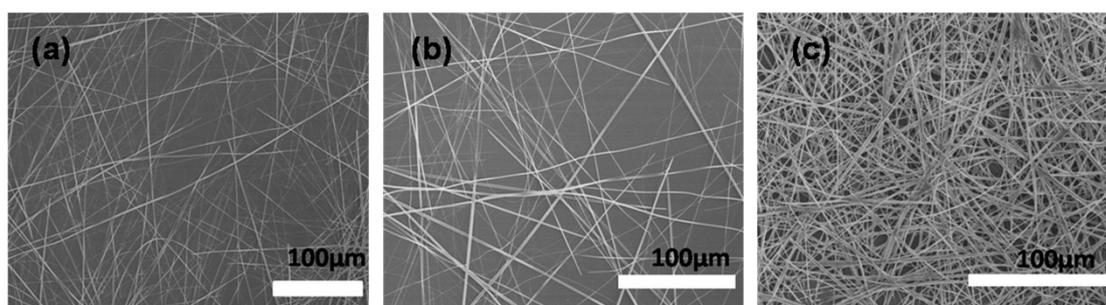


Fig.S4. SEM images of the self-assembled CuOEP nanowires on Si/SiO₂ substrates from m-xylene solution: (a) 0.4 mg/mL, (b) 0.6mg/mL, (c) 1.2mg/mL.

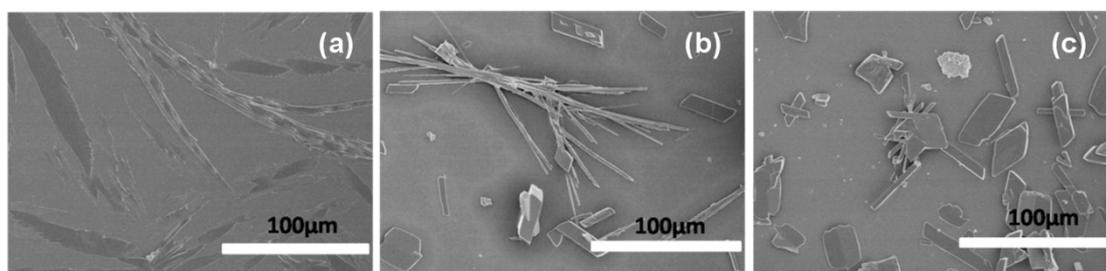


Fig.S5 SEM images of the resulting CuOEP assemblies fabricated using different solvents: (a) chloroform; (b) anisole; (c) THF.

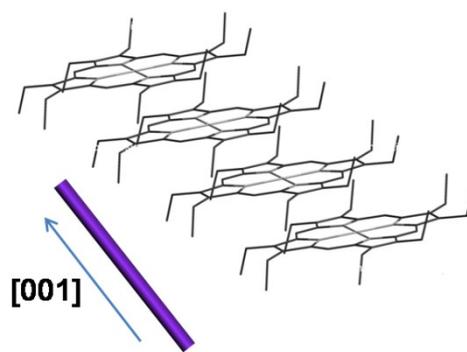


Fig.S6 View of stacking of CuOEP molecules along c-axis ([001] direction) showing clearly intermolecular π - π interaction along c-axis to assemble the nanowires.

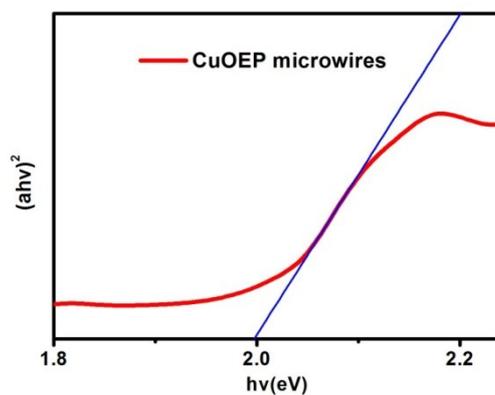


Fig.S7 The curve of $(\alpha h\nu)^2$ versus $h\nu$ to extract the optical band of CuOEP nanowires. The α and $h\nu$ represent the absorption coefficient and band gap, respectively.

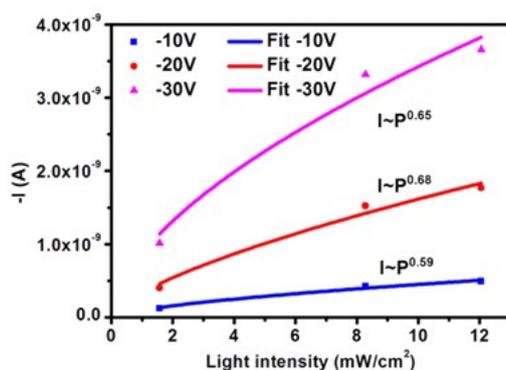


Fig.S8. Curve of the photocurrent *versus* incident optical densities measured at bias voltages of -10V, -20V and -30V.

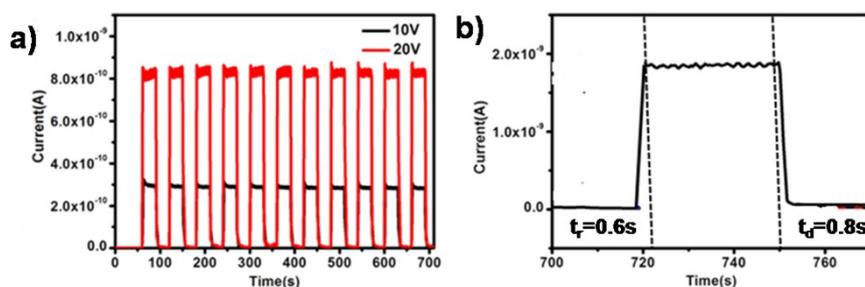


Fig.S9. (a) The photoswitching properties of CuOEP nanowires photoswitches at a constant bias voltage of 10V or 20V, the incident light intensity for all the devices was kept constant at 12.05mW/cm². b) The enlarged portions of the rise and decay processes of the current response.