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Stable Cuprous Hydroxide Nanostructures by Organic Ligand Functionalization

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Abstract

Copper compounds have been extensively investigated for diverse applications. However, studies of cuprous hydroxide (CuOH) have been scarce, due to structural metastability. Herein, a facile, wet-chemistry procedure is reported for the preparation of stable CuOH nanostructures via deliberate functionalization with select organic ligands, such as acetylene and mercapto derivatives. The resulting nanostructures are found to exhibit a nanoribbon morphology consisting of small nanocrystals embedded within a largely amorphous nanosheet-like scaffold. The acetylene derivatives are found to anchor onto the CuOH forming Cu-C≡ linkages, whereas Cu-S-interfacial bonds are formed with the mercapto ligands. Effective electronic coupling occurs at the ligand-core interface in the former, in contrast to mostly non-conjugated interfacial bonds in the latter, as manifested in spectroscopic measurements and confirmed in theoretical studies based on first principles calculations. Notably, the acetylene-capped CuOH nanostructures exhibit markedly enhanced photodynamic activity in the inhibition of bacteria growth, as compared to the mercapto-capped counterparts, due to a reduced material bandgap and effective photocatalytic generation of reactive oxygen species. Results from this study demonstrate that deliberate structural engineering with select organic ligands is an effective strategy in the stabilization and functionalization of CuOH nanostructures, a critical first step in exploring their diverse applications.

Graphical Abstract

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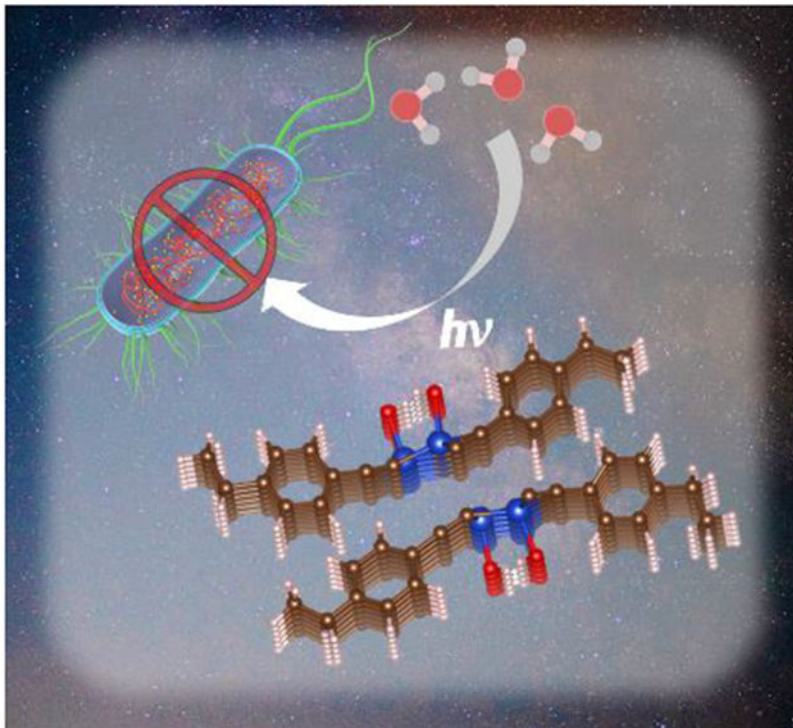
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Conflict of Interest

The authors declare no conflict of interest.

Stable CuOH nanostructures are prepared for the first time ever by a facile wet chemistry route using acetylene and mercapto derivatives as the capping ligands. Due to the conjugated interfacial linkages with the acetylene moieties, the CuOH nanostructures exhibit a reduced bandgap, new optical/electronic properties, and hence enhanced photodynamic activity towards the inhibition of bacterial growth.



Keywords

cuprous hydroxide; acetylene; mercapto ligand; interfacial electronic coupling; antimicrobial

Introduction

Copper, as a multi-valence element, can form a wide range of compounds, including oxides, [1, 2] hydroxides, [3, 4] chalcogenides, [5, 6] halides, [7, 8] and some complicated salts (e.g., Chevreul's salt), [9] which have found diverse applications, such as catalysis, [10, 11] sensing, [12, 13] energy conversion, [14, 15] and optics. [16] Amongst these, cuprous oxide (CuOH) has long been attracting extensive interest. [17, 18] Back in the early 1900s, Miller and Gillett observed that when a NaCl solution was electrolyzed with copper working electrodes at low temperatures (below 60 °C), yellow CuOH precipitates were produced. [19, 20] Subsequently, several studies were conducted to investigate the characteristic structure and properties of CuOH synthesized via various methods. [21–23] Nevertheless, in these early studies, CuOH was mostly in the bulk solid form and structurally metastable, where the yellowish precipitates would rapidly change the color appearance to dark red, signifying the formation of Cu₂O, upon exposure to the ambient or thermal treatment, due to the lack of proper

protection from oxidation and/or dehydration. Such structural instability makes it difficult to study the properties and applications of the obtained CuOH. In 2012, Korzhavyi et al.^[24] carried out theoretical studies and demonstrated that CuOH could exist in a solid form; yet the metastability led to the formation of a random mixture of various configurations in the crystal structure, such as Cu₂O and ice VII H₂O. Soroka et al.^[25] found that solid-state CuOH could indeed be produced, most likely in the hydrated form of CuOH × H₂O as an intermediate product of Cu₂O. In a combined theoretical and experimental study,^[26] Korzhavyi's group showed that the ground-state structure of CuOH(s) consisted of both one-dimensional polymeric (CuOH)_n chains and two-dimensional trilayer units, suggesting the possibility of nanosheet production. In addition, density functional theory (DFT) calculations have showed that CuOH is a semiconductor with a wide bandgap of 3.03 eV (or 2.73 eV in a cation-disorder form), suggestive of its potential optical/photocatalytic applications. However, it should be recognized that, to the best of our knowledge, thus far there has been no success in the experimental preparation of stable CuOH nanostructures.

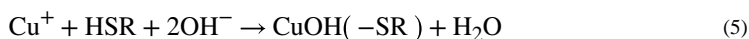
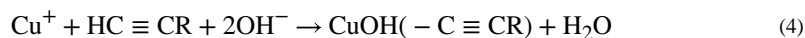
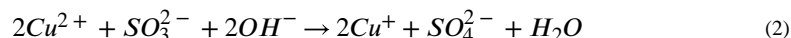
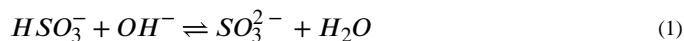
Organic ligands have been widely used in the surface functionalization and stabilization of metals and metal oxides,^[27, 28] hydroxides,^[29] and chalcogenides.^[30, 31] For their nanoparticles, select organic ligands can be exploited for the manipulation of the shape,^[32, 33] size distribution,^[34–36] and crystalline facets.^[37] Significantly, with the protection of such an organic shell, not only the structural stability can be markedly enhanced,^[38] new optical, electronic, and catalytic properties may also emerge, due to the unique interfacial interactions.^[28, 39, 40] Thus, one immediate question arises: Can stable CuOH nanostructures be obtained by deliberate functionalization with select organic ligands? This is the primary motivation of the present study, where we demonstrate an effective strategy to synthesize stable CuOH nanostructures by surface functionalization with acetylene and mercapto derivatives.^[28, 39, 40]

Specifically, for the first time ever, stable CuOH nanostructures were prepared by a facile wet-chemistry method. Experimentally, sulfite ions (SO_3^{2-}) were exploited as the reducing agent and added into a Cu²⁺ solution in a mixture of organic solvents in the presence of select acetylene and mercapto derivatives, with 4-ethylphenylacetylene (EPA), 1-hexadecyne (HC16) and 4-ethylphenylthiol (EPT) as the illustrating examples. The two acetylene derivatives were chosen, as prior studies have shown that alkyne ligands may impart unique electrical and optical properties to metal/metal oxide nanoparticles owing to the conjugated interfacial linkage that leads to intraparticle charge delocalization, which varies with the specific molecular structure of the aliphatic fragments, in contrast to mercapto derivatives like EPT that were involved in non-conjugated interfacial interactions.^[28, 39, 41] Notably, acetylene derivatives have been known to bind to Cu^I centers forming polymeric nanostructures,^[42, 43] which may be conducive to the stabilization of the CuOH units. It was found that the resulting organically capped CuOH nanostructures were readily dispersible in organic media, and stable in both solution and solid forms. Microscopic and spectroscopic studies showed that the obtained CuOH nanostructures exhibited a nanoribbon morphology and were functionalized with Cu-C≡ and Cu-S- interfacial linkages, and the photoluminescence properties varied with the surface capping ligands, due to a discrepancy of the charge transfer at the ligand-CuOH interface and hence the materials bandgap.

Consistent results were obtained in first principles calculations. Notably, the EPA-capped CuOH nanostructures manifested drastically enhanced photodynamic antibacterial activity, owing to the conjugated CuOH-EPA linkages that facilitated interfacial charge transfer and generation of reactive oxygen species (ROS) under UV and blue-light photoirradiation, in comparison to the EPT-capped counterparts.

Results and Discussion

Note that direct mixing of Cu^+ and OH^- led to the uncontrollable formation of yellow CuOH precipitates, which decayed rapidly within a day (Figure S1). Thus, to prepare stable CuOH nanostructures, a unique synthetic procedure was developed in the present study by using Cu^{2+} and SO_3^{2-} as the precursors. Briefly, a mixture of HSO_3^- and OH^- was injected into a Cu^{2+} solution in a mixed solvent of dichloromethane (DCM), N,N-dimethylformamide (DMF), and ethanol at the volumetric ratio of 1:1:1 in the presence of select organic capping ligands, producing a yellow solution that is consistent with CuOH (Figure S2).^[21–23] The experimental details are included in the Supporting information. The mixture of solvents was deliberately chosen to optimize the polarity of the solvents for good dispersion of both the copper salts and organic ligands. The production of organically capped CuOH nanostructures most likely involved the following reactions,



First, bisulfite ions were neutralized into sulfite upon the addition of KOH (eq. 1), which then reduced Cu^{2+} into Cu^+ , as the formal potential of the $\text{SO}_4^{2-}/\text{SO}_3^{2-}$ couple ($E^\circ = -0.936$ V) is far more negative than that of $\text{Cu}^{2+}/\text{Cu}^+$ (+0.159 V) (eq. 2).^[44] The resulting Cu^+ subsequently reacted with OH^- to produce cuprous hydroxide (CuOH) (eq. 3); and in the presence of select organic ligands, such as acetylene ($\text{HC} \equiv \text{CR}$) and mercapto (HSR) derivatives, stable CuOH nanostructures were produced, due to the formation of CuOH-C \equiv C- and CuOH-S- interfacial bonds (eq. 4 and 5),^[45] as manifested by the apparent color change from blue to bright yellow (Figure S2). Three samples were prepared using EPA, HC16 and EPT as the protecting ligands, and denoted as CuOH-EPA, CuOH-HC16, and CuOH-EPT, respectively. Note that in the synthesis of CuOH-EPT, the solution turned yellow upon the addition of EPT into Cu^{2+} before the addition of sulfite, likely due to

the reduction of Cu^{2+} to Cu^+ by the thiol moieties.^[46] Remarkably, all final products (CuOH) can be readily dispersed, and remain stable, in a range of organic media, such as DCM, tetrahydrofuran (THF), toluene, etc., suggesting sufficient protection by the hydrophobic organic ligands.^[39] By contrast, without the addition of any organic ligands, greenish yellow precipitates (CuOH) were formed at the bottom of the flask (Figure S3); and X-ray photoelectron spectroscopy (XPS) measurements showed the formation of CuO, which likely arose from the facile decomposition of CuOH upon exposure to the ambient, suggesting that the organic ligands played a critical role in stabilizing the formation of CuOH (Figure S1). In another control experiment without the addition of the sulfite ions, only brownish precipitates were produced (Figure S4), which was identified as CuO by XPS measurements, indicative of the critical role of sulfite ions in the reduction of Cu^{2+} into Cu^+ (eq. 2). The solution pH was also important in the formation of stable CuOH. When the solution became too acidic (Figure S5–S6) or too alkaline (Figure S7), other Cu compounds, such as CuO, Cu_2O , or cupric sulfates, would be produced instead. That is, a mildly alkaline condition is conducive to the stabilization of the ligand-capped CuOH nanostructures (Figure S8). In fact, the obtained CuOH samples could be gradually decomposed in strong acid (2 M H_2SO_4) to a colorless solution (Figure S8), consistent with the Cu(I) valence state and the formation of a hydroxide compound. In sharp contrast, the structural stability of the CuOH samples was significantly enhanced in neutral and mildly alkaline conditions, where the oxidation into Cu(II) was markedly impeded, in comparison to bare CuOH (Figure S1 and S3), as manifested in XPS measurements (Figure S9–S12).

The morphologies of the CuOH samples were first examined by transmission electron microscopic (TEM) measurements. One can see from Figure 1a that CuOH-EPA manifests a nanoribbon-like shape with a width in the range of 130 to 200 nm and micron-scale length. The CuOH-HC16 (Figure 1b) and CuOH-EPT (Figure 1c) samples also exhibit a flaky structure, but bundled into an irregular shape. High-resolution TEM measurements (Figure 1d–i) show that the samples actually consisted of ultra-small nanoclusters of less than 2 nm in diameter with well-defined lattice fringes embedded within a largely amorphous scaffold, where the interplanar spacing was estimated to be ca. 0.21 and 0.26 nm for both CuOH-EPA (Figure 1g) and CuOH-HC16 (Figure 1h) and 0.25 nm for CuOH-EPT (Figure 1i), corresponding to the (220), (210) and (0 $\bar{2}$ 2) facets of CuOH, respectively.^[26] Note that with an increasing initial feed of Cu^{2+} , larger CuOH nanoparticles were produced (dia. 5 – 10 nm, Figure S13).

Consistent results were obtained in atomic force microscopy (AFM) measurements. From the topographic images in Figure 1j and S14–S16, the three CuOH samples can all be seen to exhibit a one-dimensional nanowire-like morphology. Line scans across the nanowire actually revealed a nanoribbon structure with a width of ca. 200 nm and a thickness of ca. 45 nm (Figure 1k), in good agreement with results from TEM measurements (Figure 1a–c).

The nanoribbon structures can also be resolved in scanning electron microscopy (SEM) measurements, where CuOH-EPA can be seen to contain nanoribbons of 5 to 7 μm in length (Figure S17), whereas CuOH-HC16 (Figure S18) and CuOH-EPT (Figure S19) exhibit a mostly irregular flaky structure. Meanwhile, elemental mapping analysis based on energy dispersive X-ray (EDS) spectroscopy showed that all three CuOH samples featured

a homogeneous distribution of Cu, O, and C, with S found also in CuOH-EPT, consistent with the formation of the respective ligand-capped nanoparticles. TEM-based EDS scans in higher magnifications showed consistent results (Figure S20–S22).

Further structural insights were obtained in X-ray diffraction (XRD) measurements. Figure 11 depicts the XRD patterns of CuOH-EPA, which consists of only two sharp diffraction peaks at $2\theta = 10.18^\circ$ and 15.34° , corresponding to a d value of 0.87 and 0.58 nm, respectively. Note that such patterns are markedly different from those of “cupric” CuOH,^[26] Cu₂O (RRUFF ID: R050374.1), and Cu^I-alkyne coordination polymers reported previously (CCDC-24290, Figure S23).^[42, 43] Yet, the results are in excellent agreement with a layered structure where each layer consists of one-dimensional assembly of the CuOH-EPA moieties that is facilitated by hydrogen bonding interactions between the OH groups and π - π stacking between the phenyl rings of the EPA ligands (Figure 1m–n). In fact, the simulated XRD patterns exhibit two peaks at $2\theta = 10.69^\circ$ and 14.16° (the CIF files are included in the Supporting Information), very close to those of the CuOH-EPA sample.

Taken together, results from these characterizations suggest that the obtained samples consist of CuOH nanoclusters embedded within a CuOH-ligand nanoribbon nanostructures. Such a structure calls for a 1:1 molar ratio between CuOH and the organic ligands, which was indeed observed in XPS measurements (vide infra). Notably, the expected metal contents were also in excellent agreement with results from inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements (Table S1).

The surface structure of the obtained CuOH nanostructures was then characterized by Fourier transform infrared (FTIR) spectroscopic measurements. From Figure 1o, one can see that all three CuOH samples exhibited a broad peak around 3400 cm^{-1} (Figure S24), due to the O-H stretch.^[25] In addition, in comparison to the spectra of the monomeric ligands, the organically capped CuOH samples all exhibited vibrational peaks in the range of 2800 to 3000 cm^{-1} , as highlighted by the yellow box, due to the CH₂/CH₃ stretches of the organic ligands. For both the CuOH-EPA and CuOH-EPT, additional vibrational features can be seen in the range of 3000 to 3100 cm^{-1} (purple box), due to the aromatic C-H stretches of the aryl ligands. Consistent profiles can be found in the fingerprint region of 810 to 830 cm^{-1} (Figure S25). Meanwhile, as highlighted in the orange box, unlike their corresponding monomers, the terminal $\equiv\text{C-H}$ vibration at $3293 - 3313\text{ cm}^{-1}$ vanished with CuOH-EPA and CuOH-HC16, indicating effective cleavage of the $\equiv\text{C-H}$ bond and their anchorage onto the surface of CuOH, as observed previously.^[28, 39, 40] A similar behavior can be seen with the CuOH-EPT sample, where the S-H vibration was well-defined at 2568 cm^{-1} for the EPT monomers, but disappeared altogether in CuOH-EPT (magenta box). Since no S-O vibration could be identified around 950 - 800 or 550 cm^{-1} ,^[47] the EPT ligands were most likely bound onto the CuOH surface via the Cu-S- interfacial bonds, rather than Cu-O-S-. Notably, consistent results were obtained from DFT calculations (Table S2). Of particular notice is the contributions of the OH moiety to the vibrational bands at ca. 821.7 , 1119 , and 3583.1 cm^{-1} (Movie S1), further confirming the formation of CuOH-EPA nanostructures. In addition, the peak at 547 cm^{-1} is most likely due to the Cu-C \equiv vibration, suggesting that the alkyne ligands are bound to the Cu atomic site in CuOH (Figure 1m–n).

The interfacial bonding structure is further supported in Raman measurements. From Figure S26, both CuOH-EPA and CuOH-HC16 can be seen to exhibit multiple peaks in the range of 100 to 500 cm^{-1} , which can be attributed to Cu-C \equiv and Cu-OH vibrations. For instance, in CuOH-EPA the peaks at 120, 365, and 442 cm^{-1} may be attributed to the Cu-OH vibrations, and those at 174, 196, 287 cm^{-1} due to the Cu-C \equiv vibrations,^[48] which further confirms that the EPA ligands are indeed directly bonded to Cu instead of O. In fact, these assignments are consistent with results from DFT calculations (Table S3, Movie S2–S3). For CuOH-HC16, the Cu-OH vibrations can be found at 125, 357, and 446 cm^{-1} , with the rest of the peaks arising from Cu-C \equiv and C-C vibrations.^[48] Meanwhile, the C=C vibration can be readily resolved in both CuOH-EPA (493 cm^{-1}) and CuOH-HC16 (497 cm^{-1}), but absent in CuOH-EPT. In contrast, CuOH-EPT showed an intense peak at 110 cm^{-1} , due to Cu-S vibrations.^[49] In addition, no S-S vibrations can be identified at ca. 470 cm^{-1} for CuOH-EPT, ruling out the formation of crystalline copper sulfides.^[49]

XPS measurements were then carried out to analyze the elemental compositions and valance states of the samples (Figure S27). Figure 2a depicts the high-resolution scans of the Cu 2p electrons, where the Cu 2p_{3/2}/2p_{1/2} peaks of all samples can be found around 932.0/951.8 eV for CuOH-EPA, 932.2/952.0 eV for CuOH-EPT, and 932.3/952.0 eV for CuOH-HC16. Note that no apparent satellite peaks that are characteristic of Cu²⁺ can be discerned from the Cu 2p spectra, indicating that Cu²⁺ was indeed effectively reduced by SO_3^{2-} to Cu⁺ (eq. 2).^[50, 51] This is in sharp contrast to the control experiments where samples were prepared in the same manner but without the addition of NaHSO₃ (Figure S4). In fact, electron paramagnetic resonance (EPR) measurements (Figure 2b) show that all CuOH samples displayed only a featureless profile within the magnetic field strength of 2500 to 3500 G, in sharp contrast to CuCl₂ that exhibits a clearly-defined signal with a *g* value of 2.188. This is consistent with the diamagnetic nature of Cu⁺ and paramagnetic Cu²⁺.^[51] The corresponding high-resolution XPS spectra of the O 1s electrons were exhibited in Figure 2c. One can see that a single component was resolved in all three CuOH samples, 530.5 eV for CuOH-EPA, 531.2 eV CuOH-HC16, and 531.4 eV for CuOH-EPT, that can be ascribed to metal hydroxide.^[52] Notably, the red-shift of 0.9 eV with CuOH-EPA and 0.2 eV with CuOH-HC16, as compared to CuOH-EPT, likely arose from the different charge transfer from CuOH to the ligands (vide infra). The results are also consistent with the variation of the valence band maximum (VBM) of the three samples. From the VBM spectra in Figure 2f, CuOH-EPA can be seen to possess the lowest VBM at 0.99 eV, in comparison to 1.31 eV for CuOH-HC16 and 1.61 eV for CuOH-EPT.

As for CuOH-EPT, the S 2p spectrum shows a well-defined doublet at 162.0/163.3 eV, which can be assigned to the 2p_{3/2}/2p_{1/2} electrons of Cu-S,^[53, 54] consistent with the stabilization of CuOH by Cu-S- interfacial bonds (Figure 2d). Notably, this species was totally absent in both CuOH-HC16 and CuOH-EPA, indicating that these samples were free of metal sulfide impurities.

The C 1s spectra of the three CuOH samples are depicted in Figure 2e, which are also consistent with their respective ligand structure.^[41] For CuOH-EPA, deconvolution yields three peaks at 283.0 eV for sp-hybridized C, 283.8 eV for sp² C (aromatic rings), and

284.4 eV for sp^3 C. For CuOH-HC16, only the sp and sp^3 carbon can be resolved, and only the sp^2 and sp^3 species for CuOH-EPT. These results are also listed in Table S4, where the Cu:ligand molar ratio was indeed close to 1:1 for all samples, as suggested in the nanostructure shown in Figure 1m–n.

Notably, the XPS profiles of the three CuOH samples remained virtually invariant even after storage in ambient condition for three months (Figure S28), suggesting remarkable structural stability of the materials that was most likely endowed by the organic functionalization. This is a drastic deviation from the metastable characteristics observed with bare CuOH (Figure S3) or bulk CuOH (Figure S1).^[24, 25]

Further structural insights of CuOH-EPA were obtained from X-ray absorption spectroscopic (XAS) measurements. From the X-ray absorption near edge spectra (XANES) in Figure 3a, one can see that all three organically capped CuOH samples possessed an oxidation state close to that of Cu_2O , with the absorption edges situated between those of the Cu foil and CuO references. In fact, from the first-order derivatives of XANES (inset to Figure 3a), it can be seen that the three CuOH samples all exhibit an extremum (pre-edge peak) around 8980 eV, very close to that of Cu_2O , but apparently different from those of Cu foil (8978 eV) and CuO (8982 eV). Specifically, CuOH-EPA and CuOH-HC16 can be seen to exhibit a pre-edge peak at 8982 and 8981 eV, respectively, due to the $1s\ 4p_x/p_y$ transitions, and such transitions occurred at 8981 eV for bulk Cu_2O . By contrast, CuOH-EPT exhibited only a shoulder at 8981 eV, suggesting a different chemical environment due to the formation of Cu-S interfacial bonds (vs. Cu-C \equiv for CuOH-EPA and CuOH-HC16), whereas bulk CuO showed an even less sharp shoulder at 8984 eV, due to the $1s$ to $4p_z$ transition.^[55] From the Fourier-transform extended X-ray absorption fine spectra (FT-EXAFS) in Figure 3b, one can see that the first main peak, which arose from the Cu-O/C path, appeared at 1.72 Å for CuOH-EPA, and increased to 1.82 Å for CuOH-HC16 and CuOH-EPT. These are all larger than those of bulk CuO (1.57 Å) and bulk Cu_2O (1.47 Å). Fitting of the EXAFS data (Figure S29–S31 and Table S5–S7) shows that the bond length of Cu-O/C was rather consistent for CuOH-EPA and CuOH-HC16 at ca. 2.01 and 2.05 Å, respectively, yet longer than those of the control samples of Cu_2O (1.85 Å) and CuO (1.95 Å), indicating the absence of copper oxides in the obtained sample. Additionally, the Cu-O/C coordination numbers (5.3 for CuOH-EPA and 5.8 for CuOH-HC16) were larger than that of Cu_2O (2) but consistent with the nanoribbon structure shown in Figure 1m–n,^[56, 57] suggestive of an imperfect layered structure of the CuOH-EPA and CuOH-HC16 samples. The second main peak at 2.4 Å of CuOH-EPA and CuOH-HC16 most likely arose from the second shell interaction of Cu-C with the organic capping ligands. By contrast, the first main peak of CuOH-EPT arose from the combined contributions of Cu-O/C and Cu-S bonds (Figure S31 and Table S7), indicating successful formation of the CuOH nanostructures capped by the EPT ligands, which is significantly different from CuOH-EPA and CuOH-HC16. Taken together, these results confirm the successful production of a Cu-O/C environment around Cu with no observable Cu-Cu interactions, suggesting an amorphous structure with little to no long-range crystallinity (vide ante).

To understand the interfacial structure and properties of the organically capped CuOH nanostructures, theoretical studies were performed by using the structural models proposed

above (Figure 1m–n, and S32–S33) anchored with EPA, butyne (HC4, as a simplified representation of HC16), and EPT. Figure 4a depicts the stable configuration of CuOH-EPA after relaxing, from which one can see that the acetylene moiety formed a Cu-C≡C- interfacial structure, which is consistent with the results from FTIR, Raman, and XPS measurements (Figure 1, 2, and S26). Furthermore, one can see that the C≡C bond length increased slightly from 1.21 Å for the EPA monomer to 1.26 Å for CuOH-EPA (Figure 4a). These observations suggest effective electronic coupling at the CuOH-ligand interface, leading to elongation of the acetylene moiety.^[28] In fact, from the Bader charge profile in Figure 4a, one can see a charge transfer of ca. 0.14 |e|, relative to the pristine EPA monomer, from CuOH to the EPA ligands. Charge accumulation in the -C≡C- interfacial bond and phenyl rings in CuOH-EPA is clearly visible in the charge density isosurfaces shown in Figure 4b. CuOH-HC4 shows a similar elongation and charge accumulation of the -C≡C- bond, where ca. 0.38 |e| was transferred from CuOH to primarily -C≡C- (Figure 4c–d). Notably, the contribution of the ethyl group to interfacial charge transfer is minimal. This observation is consistent with results of our prior study of alkyne-functionalized iridium nanoparticles and alkyne-functionalized TiO₂ nanoparticles.^[28, 58] In contrast, when EPT ligands were bound onto the CuOH cores, the interfacial linkage actually consisted of non-conjugated Cu-S- bonds (Figure 4e–f). In this case, there are obvious charge depletions in the S-H and S-Cu interfacial bonds and accumulations in the S-C bond, with a net charge transfer from CuOH to the ligand being 1.38 |e|. Considering that the Cu atoms exhibit a similar valence state from the afore-mentioned XPS, XAS, and charge analysis, the depletion of electrons in Cu-OH units will render a positive shift of the O 1s binding energies, which is in excellent agreement with results from XPS measurements (Figure 2c).

Notably, such different interfacial linkages resulted in a marked variation of the optical and electronic properties of the CuOH nanostructures. As mentioned earlier, the samples can all be readily dispersed in typical organic solvents (e.g., DCM, THF, etc) and remain stable without obvious precipitation. The photographs of the suspensions are shown in Figure 5a, where the color was grey-yellow for CuOH-EPT, and dark-yellow for CuOH-EPA and CuOH-HC16. Under photoirradiation with a UV lamp (ca. 365 nm), the samples can be seen to emit orange-red, yellow, and orange photons for the CuOH-EPT, CuOH-EPA and CuOH-HC16 samples, respectively (Figure 5b). Notably, the color appearance of the DCM solutions was the same as that when they were dropcast onto a glass slide forming a solid film (Figure 5c). These observations indicated that the optical (and hence electronic) properties are different when CuOH were passivated by different organic ligands, as manifested in UV-vis and photoluminescence (PL) spectroscopic measurements (Figure 5d–i). One can see that CuOH-EPT exhibited an exponential decay profile in UV-vis measurements, without any apparent absorption features (Figure 5h),^[59] whereas two main peaks can be resolved at 492 and 406 nm for CuOH-EPA (Figure 5d), and one peak at 424 nm for CuOH-HC16 (Figure 5f). At the same excitation wavelength (λ_{ex}) of 405 nm, both CuOH-EPT and CuOH-HC16 showed a PL emission peak (λ_{em}) at 650 nm (Figure 5d and 5f), whereas the emission peak of CuOH-EPA blue-shifted to 512 nm (Figure 5h). Interestingly, for this CuOH sample series, whereas λ_{em} remains virtually unchanged when λ_{ex} was varied within the range of 360 to 445 nm, the emission intensity diminished

markedly at $\lambda_{\text{ex}} > 400$ nm for CuOH-EPT (Figure 5i) and at $\lambda_{\text{ex}} < 385$ nm for CuOH-HC16 (Figure 5g), but exhibited no clear diminishment with CuOH-EPA (Figure 5e).

To unravel the origins of the different optical properties amongst the samples, we calculated the density of states (DOS) of CuOH-EPA, CuOH-HC4, and CuOH-EPT. From Figure S34, one can clearly see that both CuOH-EPA and CuOH-HC4 exhibited a lower VBM position than CuOH-EPT, consistent with the experimental results shown in Figure 2f. To further discern the difference between CuOH-EPA and CuOH-HC4, projected local DOS (PDOS) were deconvoluted and shown in Figure 6a. It can be seen that whereas both structures showed extensive interfacial charge delocalization, the phenyl ring of EPA anchored on CuOH (CuOH-EPA) made a significant contribution to the states near the Fermi level (E_F) at the both VB and the conduction band (CB), in comparison to CuOH-HC4. A schematic illustration of PL emission is depicted in Figure 6b. For all samples, electrons are excited from the VB (contributed mainly by Cu-C \equiv C- interfacial bonds) to the CB (contributed mainly by the π electrons of the capping ligands) under appropriate photoexcitation. For the HC $_x$ ($x = 16$ for experimental and $x = 4$ for theory) capped CuOH nanostructures, the excitons relax to the CB edge and then return to the holes to emit light at around 650 nm. The situation for CuOH-EPA is different. In the recombination process, the excitons relax to the dominating states from the phenyl ring rather than the CB edge before combining with the hole states in the ring. As a result, it emits light with a higher energy (shorter wavelength at ca. 512 nm).

This emission mechanism is supported by the calculated UV-vis spectra based on time-dependent DFT (TDDFT), as depicted in Figure 6c, where the four absorption peaks of CuOH-EPA observed experimentally in Figure 5d (314, 335, 406 and 492 nm) can be clearly identified (marked with asterisks). Figure 6d presents the natural transition orbitals (NTOs) for CuOH-EPA. NTOs are unitary transformation of the ordinary molecular orbitals to enable an intuitive qualitative description of electronic excitations. The NTOs are more compact and express the excitation as pairs of NTO orbitals, with transitions occurring from excited particle (OTOs) to the empty hole (UTOs). As shown in Figure 6d, the hole states are largely localized on the ligands, whereas the particle states concentrate to the CuOH units except for 314 nm. These characteristics are manifestations of strong interactions between the ligand and the CuOH core, which enable charge transfer excitation from the ligands to the particle and is likely the origin of the intense emissions across a wide range of excitation wavelengths, as shown in Figure 5e, indicating that the optical property of CuOH-EPA was dominated by the EPA ligands, consistent with the results from PDOS analysis. In contrast, for the CuPH-HC4 sample (Figure S35), one can see that most OTOs and UTOs are localized on CuOH instead of the HC4 ligands, suggesting a diminished ligand-core interaction due to the lack of phenyl rings. Therefore, the emissions of CuOH-EPT and CuOH-HC16 are most likely dominated by the semiconducting CuOH cores.

With such unique optoelectronic properties, the ligand-capped CuOH nanostructures exhibited apparent photodynamic activity towards the inhibition of bacterial growth by using *Escherichia coli* (*E. coli*) as the illustrating example, and the antibacterial activity varied markedly among the sample series. Note that in the dark, none of the CuOH samples exhibited any antimicrobial activity (Figure S36). Yet, under UV photoirradiation for up

to 40 min (Figure 7a), the bacterial growth was significantly inhibited by CuOH-EPA and CuOH-EPT, where it took only 12 min to remove 50% of the bacterial cells with the former and 16 min for the latter, whereas virtually no inhibition was observed with CuOH-HC16, as compared to the *E. coli* control. The overall activity was diminished somewhat under blue light irradiation (465 nm). From Figure 7b, one can see that the growth of *E. coli* was significantly inhibited by CuOH-EPA only, with no survival of bacterial cells after two hours' exposure, and the antibacterial activity was minimal with CuOH-HC16 and CuOH-EPT. Taken together, these results indicate that CuOH-EPA stood out as the best antibacterial agent among the series.

Notably, no copper species were detected by ICP-OES measurements in the bacterial culture medium with CuOH-EPA (after 120 min), in comparison to 1.935 ppm with Cu₂O, signifying no leaching of Cu ions in the former. In Ellman's assay (Figure 7d), where the loss of GSH is an effective representation of oxidative stress,^[60] it can be seen that under blue light irradiation for up to 2 h, CuOH-EPA led to the most significant degradation of GSH among the series, suggesting that the high antibacterial activity of CuOH-EPA was most likely due to the substantial oxidative stress produced under photoexcitation. This was indeed confirmed in EPR measurements. From Figure 7e, one can see that after blue light photoirradiation for 10 min, the CuOH-EPA and CuOH-HC16 samples manifested a clear 1:2:2:1 hyperfine structure within the magnetic field strength of 3275-3350 G, with a *g* value of 2.005 ($a_H = a_N = 14.9$ G), which is characteristic of the DMPO-OH adducts,^[61] suggesting the formation of hydroxyl (HO•) radicals. By contrast, for CuOH-EPT and blank water, only a much weaker sextet hyperfine structure was observed within the same magnetic field range ($g = 2.006$, $a_N = 15.625$ G, and $a_H = 6.64$ G), which can be ascribed to the DMPO-OOH adduct stemming from superoxide radicals (O₂^{•-}).^[61, 62] These observations are consistent with the significantly higher bactericidal activity of CuOH-EPA and CuOH-HC16, as compared to CuOH-EPT (Figure 7a-b), as hydroxyl radicals are far more active in antibacterial action than superoxide radicals.^[63] Additionally, CuOH-EPA can be seen to exhibit the highest peak to peak intensity among the series, in excellent agreement with the greatest oxidative stress observed in Ellman's assay and the best antibacterial activity among the series.

In fact, the EPR signal intensity of CuOH-EPA exhibited a noticeable diminishment upon the addition of ethylenediaminetetraacetic acid (EDTA) and much less so with ascorbic acid (Figure S37), which are the effective scavengers for photogenerated holes and superoxide radicals, respectively.^[61] This suggests that the HO• radicals were produced mainly by the hole oxidation of water, $H_2O + h^+ \rightarrow HO\bullet + H^+$, with a minor contribution from the disproportionation reaction of O₂^{•-}.^[63]

The markedly enhanced antibacterial activity of CuOH-EPA, as compared to others in the series, can be ascribed to its low bandgap (E_g) of 2.52 eV, as compared to CuOH-HC16 (2.94 eV) and CuOH-EPT (2.96 eV) (Figure S38). This is consistent with results from DFT calculations (Figure S34), CuOH-EPA (1.02 eV) < CuOH-EPT (1.46 eV) < CuOH-HC4 (1.64 eV) — note that DFT (PBE) typically underestimates the bandgap of solids.^[64] Experimentally, the energy of the blue light photons (465 nm, 2.66 eV) is sufficiently high to excite the valence electrons of CuOH-EPA to the conduction band facilitating the generation

of ROS and the eventual antimicrobial activity, but not high enough for CuOH-HC16 and CuOH-EPT.^[60, 65]

The discrepancy of interfacial charge transfer between the organic capping ligands and CuOH cores was further evidenced in cyclic voltammetry (CV) and electrochemical impedance measurements. From the CV profiles in Figure S39, both CuOH-EPA and CuOH-HC16 can be seen to exhibit an anodic peak at ca. +0.85 V, due to the oxidation of Cu⁺ to Cu²⁺,^[66, 67] and the peak potential was substantially more positive at ca. +1.0 V with CuOH-EPT, consistent with the variation of the VBM observed in XPS measurements (Figure 2f). From the Mott–Schottky plots (Figure S40), one can see that all CuOH samples exhibited a positive slope (m), suggestive of an n-type semiconductor.^[68] The corresponding charge carrier densities (N_d) were then derived from the plots by using $N_d = \frac{2}{e\epsilon\epsilon_0 m}$, with e being the elementary charge of an electron, ϵ the dielectric constant, and ϵ_0 the vacuum permittivity, which decreased markedly in the order of CuOH-EPA ($7.54 \times 10^4 \text{ cm}^{-3}$) > CuOH-HC16 ($4.78 \times 10^4 \text{ cm}^{-3}$) > CuOH-EPT (9.58×10^3). The markedly higher charge carrier density of CuOH-EPA and CuOH-HC16 can be ascribed to the conjugated CuOH-ligand interfacial linkages that facilitated intraparticle charge delocalization and hence interfacial charge transfer, a critical step in the photocatalytic generation of ROS, in comparison to the CuOH-EPT sample that involved nonconjugated interfacial bonds instead.^[69, 70]

Conclusions

In summary, for the first time ever, a facile wet-chemistry procedure was developed for the preparation of stable CuOH nanostructures in the presence of select organic ligands, such as acetylene and mercapto derivatives, where sulfite ions were exploited as the reducing agent. Electron microscopic study showed that the resulting CuOH nanostructures exhibited a nanoribbon morphology, and spectroscopic measurements confirmed the anchoring of the acetylene moieties onto the CuOH surface forming Cu-C \equiv interfacial linkage, whereas for the mercapto ligands, Cu-S- bonds. The former was found to lead to effective electronic coupling between the ligand π electrons and CuOH cores, in contrast to the latter which entailed mostly non-conjugated interfacial bonding interactions, as manifested in optical measurements and confirmed in theoretical studies based on DFT calculations. Significantly, with such unique optoelectronic properties, the CuOH-EPA stood out as the best antibacterial agent among the sample series under both UV and blue light irradiation, due to the effective production of hydroxyl radicals. This was largely ascribed to hole oxidation of water that was facilitated by the conjugated core-ligand linkages and a narrowed bandgap. Results from this study suggest that functionalization by select organic ligands may be an effective strategy in the stabilization and functionalization of CuOH nanostructures, a key step towards their practical applications.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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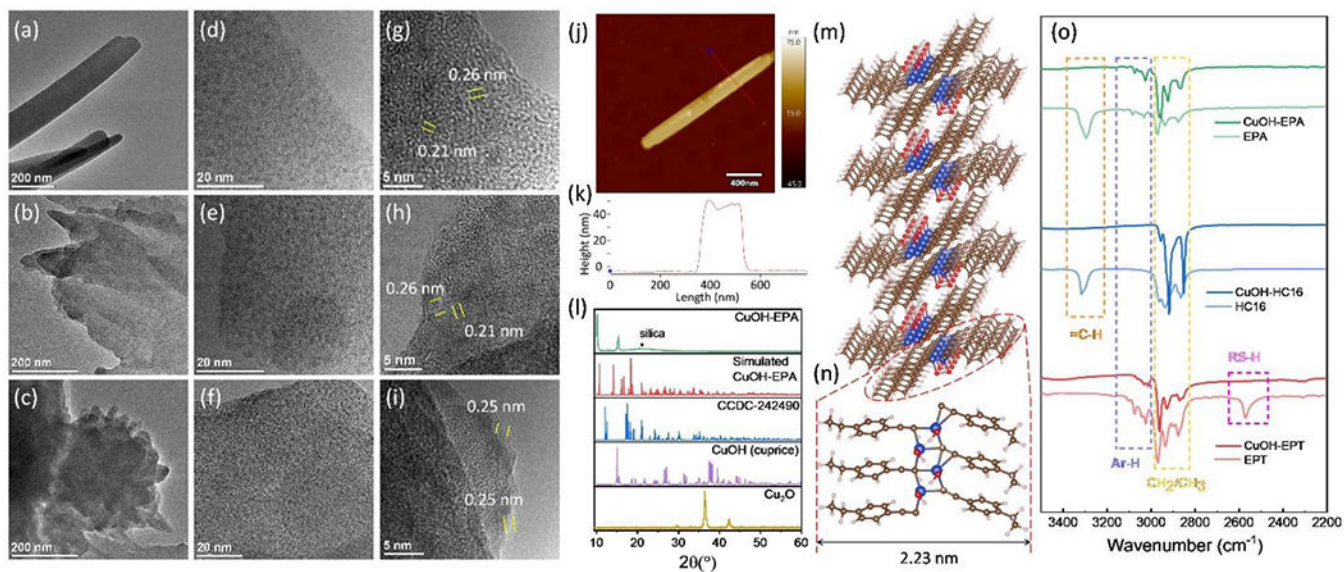


Figure 1.

Representative TEM images of the organically capped CuOH samples: (a, d, g) CuOH-EPA, (b, e, h) CuOH-HC16, (c, f, i) CuOH-EPT. Scale bars are (a-c) 200 nm, (d-f) 20 nm, and (g-i) 5 nm. (j) AFM topograph of CuOH-EPA and (k) the corresponding height profile along the red line in panel (j). (l) XRD patterns of CuOH-EPA, simulated CuOH-EPA, traditional Cu-alkyne polymer (CCDC-242490), CuOH (cuprice), and Cu₂O. (m and n) Simulated CuOH-EPA structure. (o) FTIR spectra of CuOH-EPA, CuOH-HC16, and CuOH-EPT nanostructures, and the corresponding ligand monomers (light-colored curves).

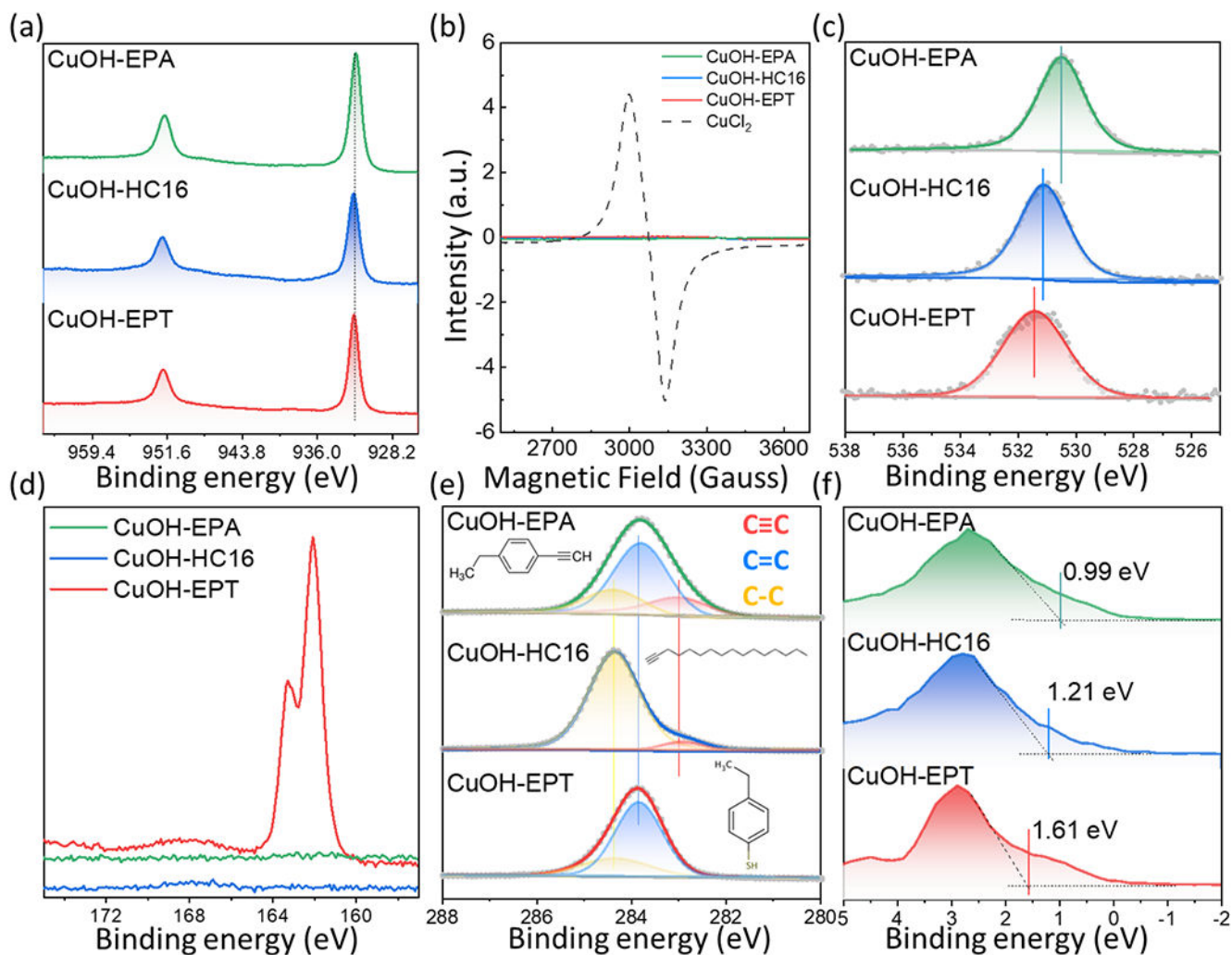


Figure 2. High-resolution XPS spectra of the (a) Cu 2p, (c) O 1s, (d) S 2p, and (e) C 1s electrons of the CuOH-EPT, CuOH-EPA, and CuOH-HC16 samples (from bottom to top). The corresponding (b) EPR and (f) VBM spectra.

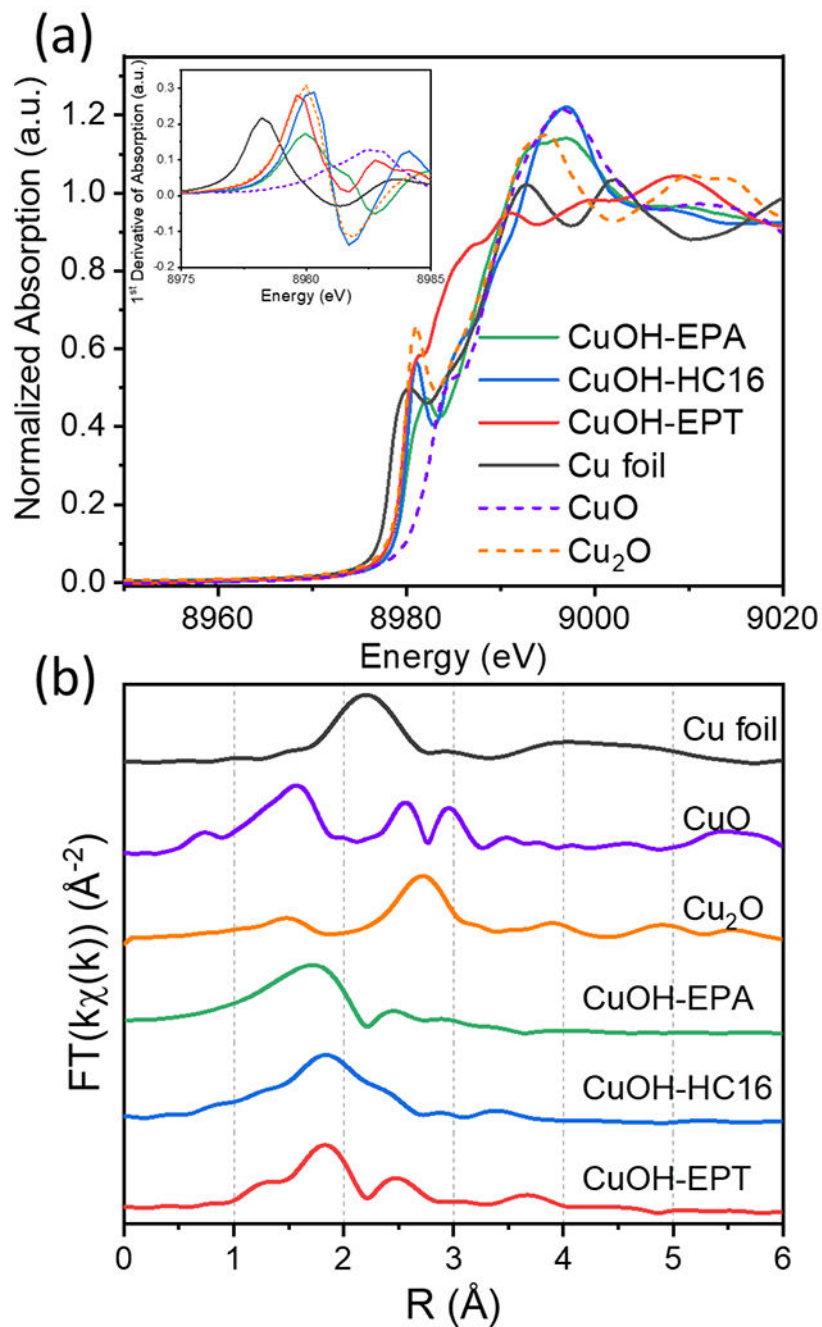


Figure 3. (a) Cu K-edge normalized XANES profiles of CuOH-EPA, CuOH-HC16, CuOH-EPT, Cu foil, Cu₂O, and CuO, and (b) their corresponding FT-EXAFS spectra. Inset to panel (a) is the corresponding first-order derivative of the pre-edge region.

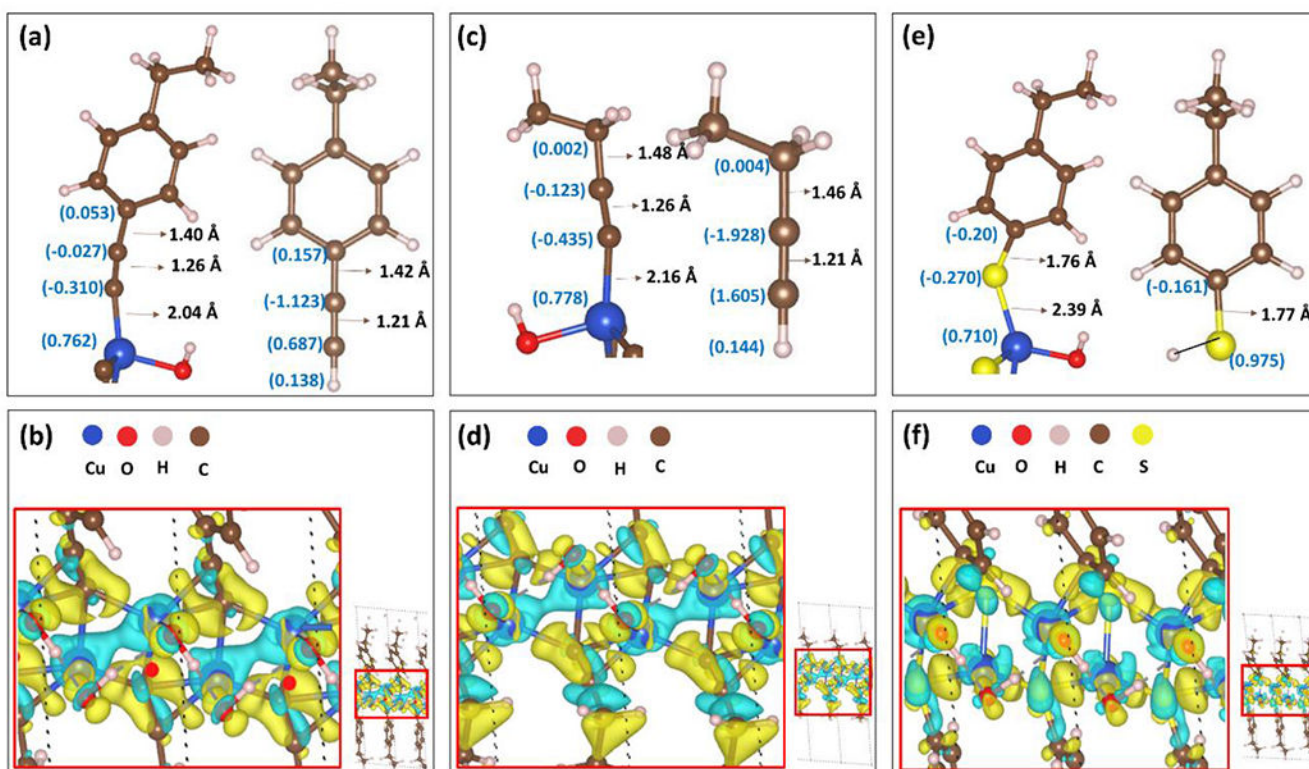


Figure 4. Optimized structure of (a) CuOH-EPA and EPA ligand, (c) CuOH-HC4 and HC4, (e) CuOH-EPT and EPT with corresponding bond distances (black) and Bader charges in $|e|$ (blue). Charge density difference isosurfaces of (b) CuOH-EPA, (d) CuOH-HC4, and (f) CuOH-EPT ($\pm 0.0016|e|$). Yellow, positive representing electron gains; cyan, negative for electron loss.

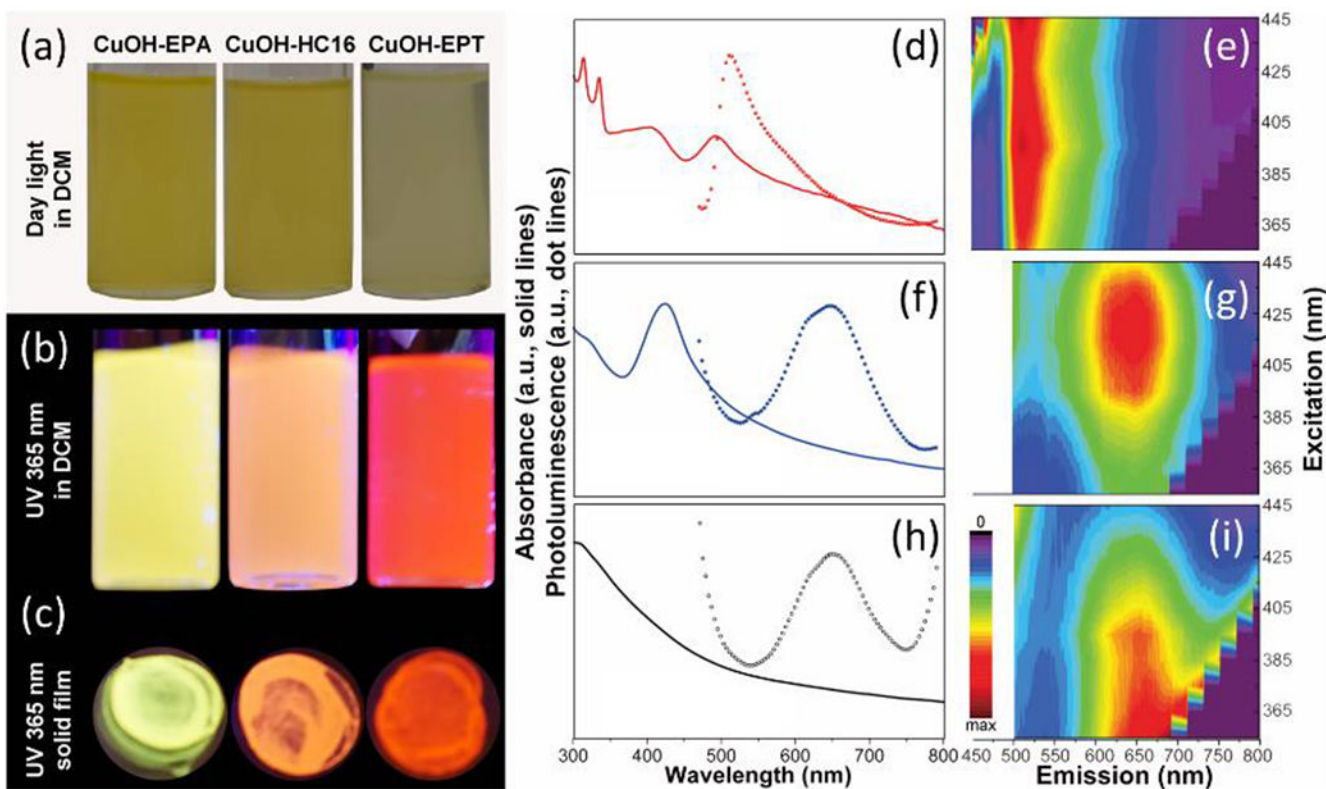


Figure 5.

Photographs of different organically capped CuOH nanostructures (a) in ambient light (dispersed in DCM) and under 365 nm photoirradiation (b) when dispersed in DCM and (c) as solid films). The colors of the CuOH-EPA, CuOH-HC16 and CuOH-EPT dispersions in DCM are all yellowish, while the photoluminescence is red, yellow, and orange, respectively when dispersed in DCM or solid films. (d, f, h) UV-vis (solid curves) and PL spectra (dotted curves) of the ligands-functionalized CuOH nanostructures at the excitation at 395 nm, and (e, g, i) the excitation-dependent PL profiles of (e) CuOH-EPA, (g) CuOH-HC16, and (i) CuOH-EPT.

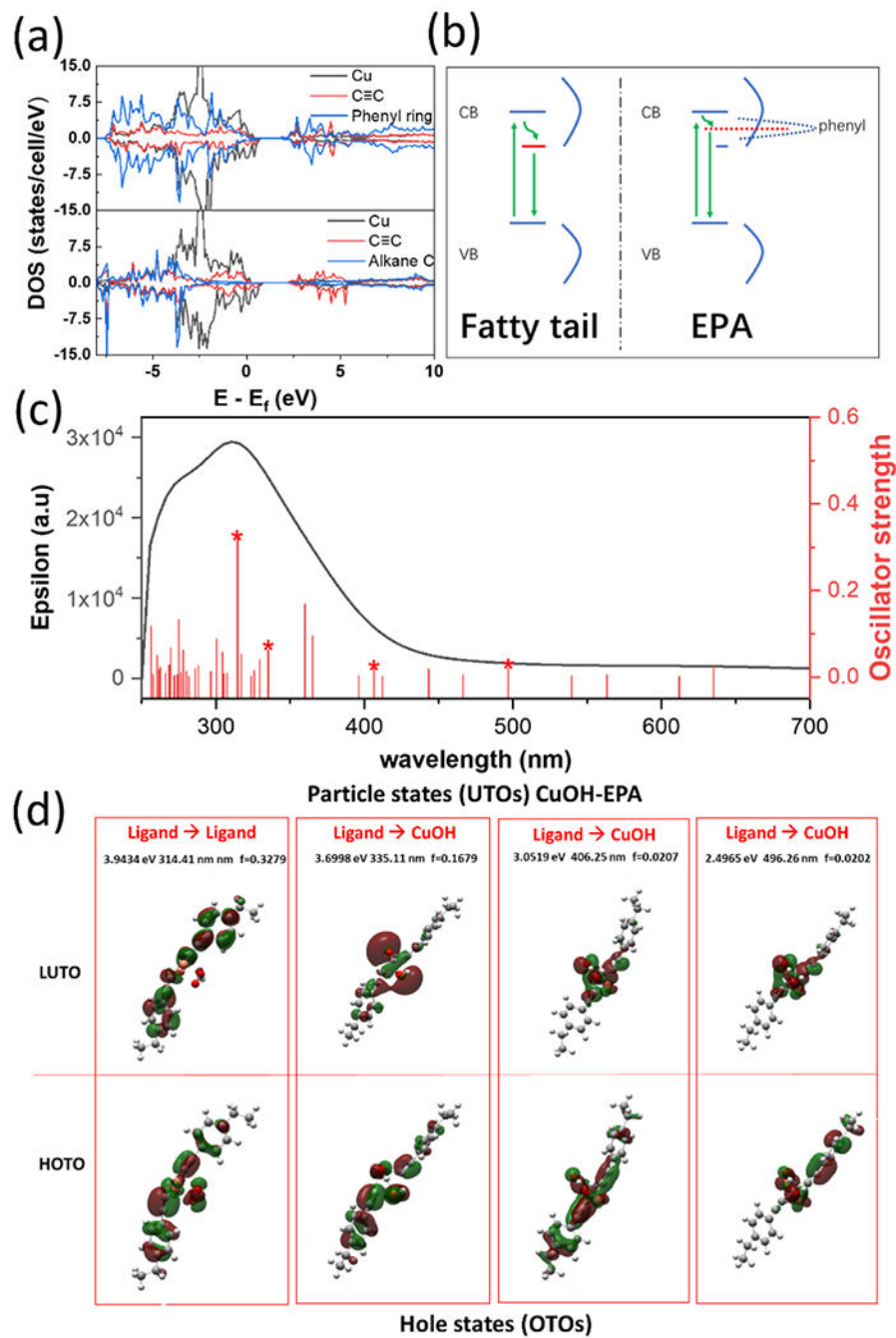


Figure 6. (a) Projected local density of states of CuOH-EPA (top) and CuOH-HC4 (bottom). (b) Proposed PL mechanism. (c) TDDFT-based UV-vis spectrum of CuOH-EPA, where the asterisks denote experimental values. (d) Natural transition orbitals (NTO) analysis of CuOH-EPA.

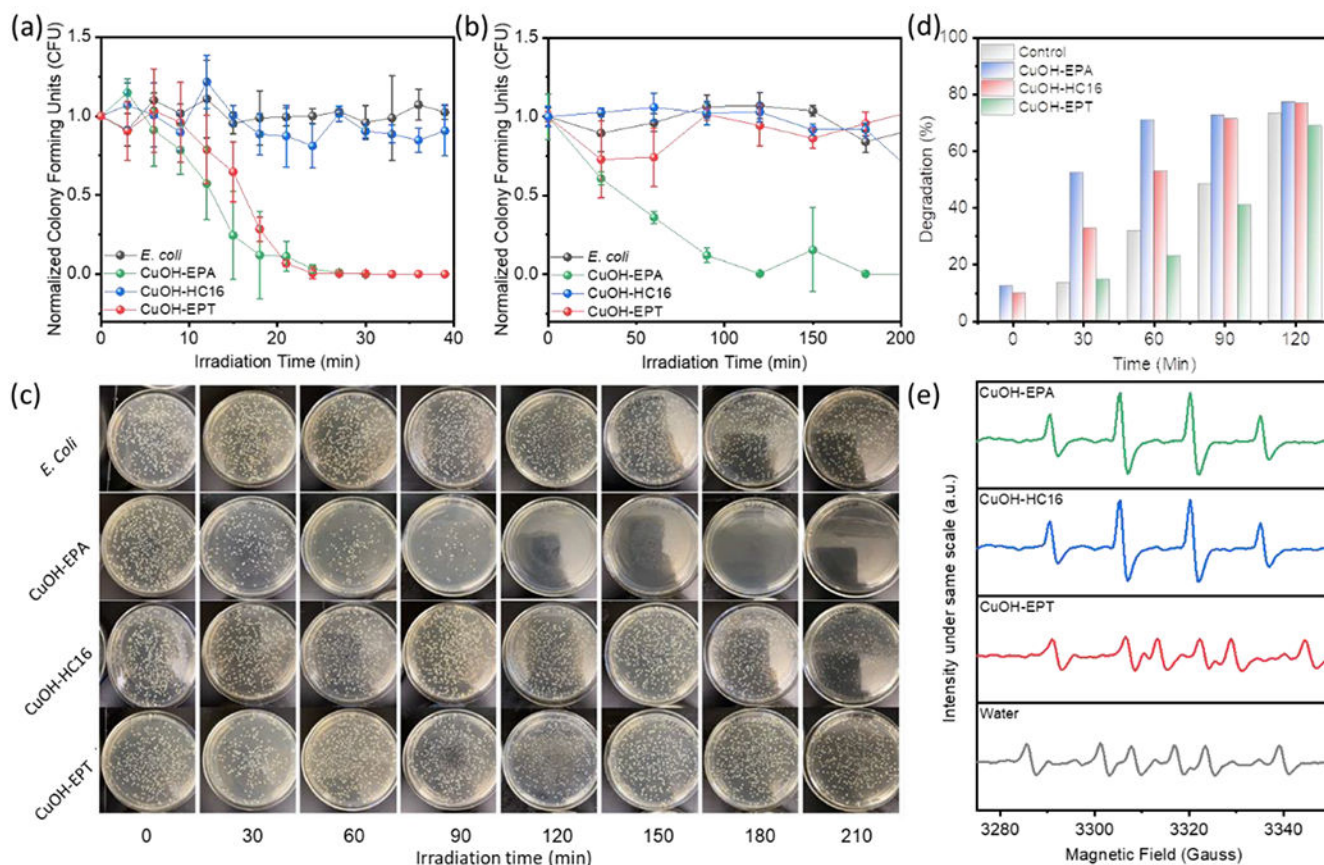


Figure 7. Antibacterial study of CuOH samples series. (a) Study under UV photoirradiation for 40min. Gram negative bacteria *E. coli* is a control for comparison with CuOH containing samples. (b) Study under blue Light (465 nm) for 200 min. Antibacterial studies under blue light photoirradiation. *E. coli* in PBS 1X (black line) is a control. Error bars are included as the study was done in triplicate. (c) Photographs depicting *E. coli* grown on LB agar plates at different photoirradiation time points (i.e., 0, 30, 60, 90, 120, 150, 180 and 210 min) under blue light (465 nm) in the absence of CuOH and the presence of CuOH-EPA, CuOH-HC16, and CuOH-EPT. (d) Loss of GSH after treatment by materials at different time points. (e) EPR hyperfine splitting patterns in the presence of DMPO after 10 minutes of photoirradiation at 465 nm.