Two-Dimensional and Subnanometer-Thin Quasi-Copper-Sulfide Semiconductor Formed upon Copper-Copper Bonding

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ABSTRACT: Ultrathin two-dimensional (2D) semiconductors exhibit outstanding properties, but it remains challenging to obtain monolayer-structured inorganic semiconductors naturally occurring as nonlayered crystals. Copper sulfides are a class of widely studied nonlayered metal chalcogenide semiconductors. Although 2D copper sulfides can provide extraordinary physical and chemical applications, investigations of 2D copper sulfides in the extreme quantum limit are constrained by the difficulty in preparing monolayered copper sulfides. Here, we report a subnanometer-thin quasi-copper-sulfide (q-CS) semiconductor formed upon self-assembly of copper(I)– dodecanethiol complexes. Extended X-ray absorption fine structure analysis revealed that the existence of Cu–Cu bonding endowed the



layer-structured q-CS with semiconductor properties, such as appreciable interband photoluminescence. Theoretical studies on the band structure demonstrated that the optical properties of copper-dodecanethiol assemblies were dominated by the q-CS layer and the photoluminescence originated from exciton radiative recombination across an indirect band gap, borne out by experimental observation at higher temperatures, but with the onset of a direct emission process at cryogenic temperatures. The following studies revealed that the metal-metal bonding occurred not only in copper-alkanethiolate complex assemblies with variable alkyl chain length but also in silver-alkanethiolate and cadmium-alkanethiolate assemblies. Therefore, the current studies may herald a class of 2D semiconductors with extremely thin thickness out of nonlayered metal sulfides to bridge the gap between conventional inorganic semiconductors and organic semiconductors.

KEYWORDS: ultrathin semiconductor, two-dimensional, metal-metal bonding, organic-inorganic hybrid structure, metal-alkanethiolate

ltrathin two-dimensional (2D) semiconductors have rapidly emerged as a fascinating family of materials showing outstanding electronic, optical, and mechanical properties for diverse optoelectronic and biomedical applications.¹ The electronic structure of 2D semiconductors, such as graphene and layered transition metal dichalcogenides (TMDs), strongly depends on the thickness of the 2D structures. It will be obviously changed especially when the thickness is approaching the dimension of a single unit cell.^{2–6} For instance, for layered TMD semiconductors such as MoS₂, WS₂, and WSe₂, the variation in electronic structures will lead to a crossover from an indirect to direct band gap transition when the thickness of the TMDs is thinned to one monolayer,^{5,7} accompanied by a thickness dependency for the photoluminescence.⁶ It is also reported that monolayer MoS₂ with broken inversion symmetry has a strong intrinsic piezoelectric response, potentially useful for electromechanical sensing, wearable and implanted devices, whereas the

centrosymmetric bilayers and bulk counterparts have no piezoelectric responses at all.⁸

Copper sulfides $(Cu_{2-x}S, 0 \le x \le 1)$ belong to one of the most commonly studied nonlayered transition metal chalcogenides with various stoichiometries and rich physical properties.⁹ Benefiting from its tunable band gap and excellent p-type conductivity, copper sulfides hold promise for diverse optoelectronic applications. In addition, off-stoichiometric $Cu_{2-x}S$ nanomaterials (x > 0) also show a strong localized surface plasmon resonance (LSPR) in the near-infrared (NIR)

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Figure 1. (a) Schematic drawing of the preparative procedures for obtaining q-CS nanosheets, accompanied by observations under ambient light and UV light, (b) PL spectrum (λ_{ex} = 380 nm) together with corresponding PL excitation (PLE) spectrum (λ_{em} = 665 nm), (c) PL spectra recorded by excitation at different wavelengths, (d) Time-resolved PL decay curve together with its multiexponential fitting (solid line), (e) MALDI-TOF-MS result, (f) SEM image, and (g) TEM image (inset is the fast Fourier transform analysis of the circled area) of q-CS nanosheets.

region, arising from excess holes in the top of the valence band originating from the intrinsic copper vacancy.^{9,10} The LSPR quenches the fluorescence due to the coupling between the plasmonic and excitonic modes.^{11,12} By modulating the degree of the copper deficiency, the NIR fluorescence of stoichiometric Cu₂S nanocrystals of 5 nm size was successfully observed by different research groups.^{11,13} However, the stoichiometric Cu₂S nanocrystals are prone to oxidation into Cu_{2-x}S under ambient conditions, which will switch the nanocrystals from fluorescent back to plasmonic again.

The crystal structures of the $Cu_{2-x}S$ family are strongly dependent on the stoichiometry, but none of them display a layered structure.^{14,15} Regarding the layer-structured semiconductors, such as graphene and TMDs in which a van der Waals force holds the atomic layer structures together, ultrathin 2D materials can be readily prepared by direct exfoliation of their bulk crystals.^{4,16} In contrast, it remains very challenging for nonlayered metal chalcogenides such as Cu_{2-x}S to form free-standing ultrathin layer structures.^{17,18} Therefore, there have only been a few studies on the physical properties of 2D copper sulfide nanomaterials until now. 19-23 For example, 3.2 nm thick CuS nanosheets exhibited a large capacity and good cycling stability when used as an electrode in a lithiumion battery,²¹ and 1.8 nm thick β -Cu₂S nanotriangles presented good ohmic contact and high conductivity,²² while 1.2 nm thick thin Cu₂S nanosheets exhibited high photocatalytic ability.²³ All of these experimental results suggest that 2D copper sulfide materials can fulfill extraordinary physical and chemical applications. Nevertheless, there is no report on truly

monolayered copper sulfide to our best knowledge; therefore, the electronic and optical properties in the extreme 2D quantum limit remain unexplored.

Herein, we report a type of subnanometer-thin quasi-coppersulfide (hereafter denoted as q-CS) nanosheets, with a crystalline cell unit formed by two linear $(Cu-S)_n$ subunits interconnected perpendicularly via a Cu-Cu bond and four alkanethiol molecules at the outside as a stabilizing agent. Theoretical simulations of electronic band structures were performed using density functional theory (DFT). The results predicted a semiconductor-type set of electronic band structures with an indirect band gap of 1.84 eV, which found supportive evidence in temperature-dependent photoluminescence. Moreover, the molecular orbital analysis revealed that the electronic structures are dominated by Cu and S orbitals, suggesting the inorganic copper sulfide component is exclusively responsible for the semiconductor nature of the resulting nanosheets and thus forms truly the thinnest, and a type of, 2D copper sulfide semiconductor, which has not been previously reported. Further studies were carried out to show the ubiquity of the metal-metal bonding in the other layerstructured metal-alkanethiolate complexes.

RESULTS AND DISCUSSION

Preparation and Optical Properties of q-CS Nanosheets. The preparative procedures for q-CS nanosheets are given in Figure 1a. Briefly, a powder of copper(I) iodide was dissolved in excess 1-dodecanethiol at 40 $^{\circ}$ C to form a colorless solution of copper-dodecanethiol coordination

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Figure 2. (a) PXRD pattern overlaid with a Le Bail fitting, (b) 13 C NMR spectrum, (c) Fourier transform magnitudes of the Cu K-edge EXAFS of copper-alkanethiol assemblies and Cu₂S, CuS, and Cu together with (d) molecular packing model of copper-dodecanethiol assemblies (the difference between two top views in the middle is that carbon atoms at the bottom are hidden to better show the (Cu-S)_n central plane).

polymers. Upon the introduction of ethanol, the yellowish precipitates obtained exhibit an unexpected red emission under UV excitation, as shown in Figure 1a, whereas the initial colorless coordination polymer solution presents no fluorescence at all. At room temperature, the photoluminescence (PL) is characterized by a single peak emission centered at 665 nm with absolute PL quantum yield (PLQY) around 1% and a wide excitation band, as well (Figure 1b). According to the emissions recorded at different excitation positions, as given in Figure 1c, the PL emission remains nearly unchanged with respect to the peak position, which indicates that there is only one type of emissive center in the hybrid structures at room temperature. The time-resolved PL was recorded (Figure 1d) and is generally characterized by a multiexponential decay process. The best decay fit was obtained by a triexponential function, as displayed in Figure S1, from which the average PL lifetime was calculated to be 5.38 μ s.

The elemental composition of the precipitates was comprehensively analyzed. According to the matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) result in Figure 1e, the precipitates are presumably formed by self-assembled $CuSC_{12}H_{25}$ molecular complexes as the strong signals at m/z = 273.01 and 287.08 can be assigned to $[CuSC_{12}H_{25} + Na]^+$ and its fragment

 $[CuSC_{11}H_{23} + Na]^+$, respectively (the appearance of Na⁺, which combines with electrically neutral CuSC₁₂H₂₅ complexes to form a positive fragment, may come from the system pipeline or glass containers).^{24,25} This is also supported by the thermogravimetric (TG) behavior (Figure S2) and the elemental composition obtained through inductively coupled plasma mass spectroscopy (ICP-MS) and organic elemental quantitative analysis (Table S3). In addition, the X-ray photoelectron spectroscopy (XPS) results in Figure S3 show that the dodecanethiol moieties are coordinated to copper atoms with an oxidation state of +1. According to the hardsoft acid-base theory, both RS⁻ and I⁻ are soft bases which are expected to have strong affinity for the soft acid Cu⁺. However, the bond dissociation energy of Cu-S is higher than that of Cu–I (*i.e.*, 285 vs 197 kJ/mol),²⁶ thus the copper– dodecanethiol complexes are formed by substituting I⁻ of CuI with 1-dodecanethiol.

In fact, the introduction of ethanol not only gave rise to photoluminescence but also triggered the precipitation of copper-dodecanethiol coordination polymers owing to its strong polarity. A representative scanning electron microscopy (SEM) image given in Figure 1f reveals that the resulting precipitates have brick-like morphologies, whereas the transmission electron microcopy (TEM) results given in Figure 1g show that each brick comprises periodic stripes with an interstripe spacing of \sim 3.19 nm. This indicates that the precipitates have a long-range ordered structure, which was previously observed from metal–alkanethiolate complexes as solids, as well.²⁷

Molecular Packing Structure of Copper-Dodecanethiol Assemblies. Systematic characterizations were carried out to show the detailed atomic packing structures within the self-assembled copper-dodecanethiol complexes. Powder Xray diffraction (PXRD) of the yellowish precipitates exhibits a series of intense signals in the low-angle region peaking at 2.6, 5.2, 7.8, 10.4, and 13.1°, as shown in Figure 2a and Figure S4, which can reasonably be assigned to (00l) (l = 2n, n = 1-5)planes with a *d* spacing of 3.34 nm, consistent with the periodic stripes in the TEM image (Figure 1f). In fact, the *d* spacing of 3.34 nm is comparable to twice the length of a stretched alkyl chain of 1-dodecanethiol (Figure S5),^{28,29} indicating that the alkyl chains are most likely stretched out and form a layered structure. To prove this, a solid-state ¹³C nuclear magnetic resonance ($^{13}\hat{C}$ NMR) study was conducted to disclose the conformation of the alkyl ligands in the self-assembled structures. As displayed in Figure 2b, the chemical shift of midchain C3-C9 methylenes is around 34.5 ppm, suggesting that the alkyl ligands are highly ordered, showing a transconformation, as given in the inset.^{30,31} This can also be evidenced by Fourier transform infrared (FTIR) spectra of the assemblies shown in Figure S6. Additionally, the chemical shift of C1 and C2 is 42.9 ppm, obviously higher than those of the corresponding carbon atoms in 1-alkylthiol (i.e., 24.5 and 33.9 ppm),³² owing to the formation of the Cu(I)–S bond. From the PXRD pattern, peaks can also be seen in the higher-angle region, which belong to high-order Miller planes, but more information is needed to unveil their precise origin.

The coordination environment of the copper atoms in the molecular packing structure of the copper-dodecanethiol assemblies was studied by X-ray absorption spectroscopy. The X-ray absorption near-edge structure (XANES) of the Cu Kedge in Figure S7 suggests the copper atoms in the assemblies have a different coordination environment contrasting those in Cu, CuS, and Cu₂S reference materials, with an oxidation state of +1, which is consistent with the XPS result. The extended Xray absorption fine structure (EXAFS) of the Cu K-edge exhibits two distinct peaks at 1.81 and 2.54 Å, as shown in Figure 2c, which can be attributed to the scattering paths of the first-coordinated S atom and the second-coordinated Cu atom in comparison with the reference samples. Then, the local atom arrangement was analyzed by EXAFS fitting, showing that it was best fitted with 2.4 S atoms and 0.8 Cu atoms from the central Cu atom at the distance of 2.25 and 2.79 Å, respectively (Figure S8). The distance between two adjacent Cu atoms of 2.79 Å indicates the existence of Cu–Cu bonding apart from the Cu-S bonds of 2.25 Å in the assembled structure. The Cu-Cu bonding has been largely considered as a type of closed-shell interaction, the length of which ranges from 2.6 to 3.9 Å. $^{33-35}$ In fact, there is an enormous body of work on the transition metal-alkanethiolate complexes, and long-range ordered structures were often observed from those complexes in the solid state.^{31,36-42} It is usually considered that the orderly packed alkyl chains form the interlayer structure, whereas a central slab connected by metal-sulfur coordination bonds forms the intralayer structure.^{31,36,37} However, no evidence for the existence of metal-metal interactions inside these metal-alkanethiolate complexes was

reported before. Therefore, it can be concluded that ethanol superficially acts as a bad solvent for precipitating $CuSC_{12}H_{25}$ molecular complexes out of the solution, and it indeed induces the formation of Cu–Cu bonds within the self-assembled 2D structures, which then explains the appearance of the yellowish color and red fluorescence that were not observed before in molecular complexes formed into self-assembled structures. In other words, ethanol not only acts as a precipitant but also catalyzes the formation of an unusual and distinct Cu–Cu bonding.

Finally, a crystalline structure model was constructed based on the PXRD and EXAFS results. The parameters of the unit cell with orthorhombic symmetry were derived upon simulation of the PXRD pattern using the X-Cell package in the Material Studio software. Then, a layered crystal structure, as displayed in Figure 2d and Figure S9, was constructed with space group of I222 upon geometry optimization, with the detailed data being shown in Table S4. In this layered model structure, the central plane consists of two $(Cu-S)_n$ layers perpendicularly aligned in-plane and interconnected through two adjacent copper atoms from the two $(Cu-S)_n$ layers. This central plane is sandwiched by two layers of closely packed alkyl chains extended outward from the central plane on both sides. To verify this crystalline structure, a simulated XRD pattern is provided in Figure 2a for comparison with the experimental XRD pattern. The perfect match between them strongly supports the rationality of the crystal structure model in which the distance between two adjacent copper atoms is also 2.79 Å. Thus, the assignment of XRD peaks in the higherangle region of Figure 2a can be obtained (Figure S10). Moreover, it can be observed that the copper-dodecanethiolate assemblies tend to form stacks from the atomic force microscopy (AFM) images shown in Figure S11. The thickness of the assembly ranges from approximately 30 to 130 nm, suggesting the existence of stacked multilayers, consistent with the TEM image in Figure 1g.

Electronic Band Structure and Optical Properties of q-CS Nanosheets. To show the optical properties involving Cu-Cu bonding, the electronic structures and molecular orbitals of the copper-dodecanethiol assemblies were simulated based on DFT using the Vienna Ab Initio Simulation Package (VASP). As shown in Figure 3a, it is obvious that the copper-dodecanethiol assemblies behave like a semiconducting material showing a low-lying indirect band gap of 1.84 eV from the Γ point of the conduction band to the M point of the valence band, very close to the PL emission peak at 665 nm (1.86 eV) in Figure 1d (the coordinates of the high symmetry points in the Brillouin zone are provided in Table S6). Based on Kasha's rule,⁴³ it is reasonable to attribute the above PL emission to exciton radiative recombination from the conduction band minimum (CBM) to the valence band maximum (VBM). The projected density of states (DOS) in Figure 3a and the partial density of states (PDOS) in Figure 3b provide the detailed compositions of the valence band and conduction band of the copper-dodecanethiol assemblies. It can be observed that the valence bands between -3.0 and -1.8eV primarily originate from the d oribitals of Cu, whereas the valence bands between -1.8 and 0 eV mainly stem from the hybridization of the p orbitals of S and the d orbitals of Cu. Moreover, the high similarity between the state profiles of Cu and S from -1.8 to 0 eV indicates that σ bonds are formed between Cu and S atoms.⁴⁴ It should be noted that the conduction bands between 1.8 and 2.6 eV are formed upon the

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Figure 3. (a) DFT-computed band structure with projected DOS, (b) PDOS of Cu, S, and C states, (c) Partial charge density isosurfaces of CBM and VBM, (d) UV–Vis absorption spectrum overlaid with a simulated absorption curve of q-CS nanosheets.

hybridization of Cu orbitals (s, p, d) and S orbitals (s, p). This can be visualized in a more intuitive way in Figure 3c. The VBM and CBM are mainly distributed on the Cu and S atoms, indicating that the optical properties of the copperdodecanethiol assemblies are solely determined by the inorganic $(Cu-S)_n$ thin layer (*i.e.*, the q-CS). The electronic distribution patterns of the VBM and CBM on the central $(Cu-S)_n$ slab together with the calculated effective mass of the charge carriers (Table S7) suggest that the carrier motion is restrained within the q-CS slab and is energetically impossible along the z-direction due to the insulating nature of the adjacent alkyl chains.

The UV-Vis absorption spectrum in Figure 3d and Figure S12 reveals that q-CS nanosheets exhibit a broad multiband absorption with an absorption tail extended into the red, which is typical for an indirect band gap transition.^{45,46} Based on the electronic structure given in Figure 3a, the absorption curve of the q-CS nanosheets was simulated in Figure 3d. Apparently, the theoretical one highly resembles the experimentally determined one (the residual discrepancies between simulated and experimental curves probably result from unexpected lattice defects in the real samples that inevitably formed during the synthesis process), suggesting that the simulated electronic band structure can well reflect the actual electronic energy levels and optical transition behaviors of this subnanometerthin 2D semiconducting q-CS structure. From the NIR absorption spectrum shown in Figure S13, it can also be observed that no LSPR absorption appears to quench the fluorescence, owing to the stoichiometric structure of the current q-CS. In addition, the orderly packed structures of the alkyl chains will suppress the molecular rotation and vibration that can depopulate the excited state via nonradiative relaxation.47,48 Therefore, the excitonic energy in the excited state of the q-CS layer is released via a radiative recombination pathway to give rise to the fluorescence shown in Figure 1b.

Contrasting from inorganic semiconductors, organic semiconductors largely rely on $\pi-\pi$ conjugated structures that

enable the intramolecular delocalization of electrons apart from the intermolecular overlapping of π electron clouds.^{49,50} The layered network of CuSC12H25 molecular complexes interconnected with Cu-Cu bonds can also promote the electron delocalization along the central plane, although no π conjugation structure is present in the system. In this respect, q-CS nanosheets represent a type of semiconductor different in its fundamental electronic nature from the conventional inorganic and organic ones. This can also be illustrated from the average PL lifetime of the q-CS nanosheets (Figure 1d), which is close not only to that of copper-containing semiconductor nanocrystals⁵¹ but to that of multinuclear copper compounds.^{52,53} In addition, the projected band structure of the q-CS (Figure S14) shows that the CBM is largely dominated by Cu states, while the VBM is mainly composed of Cu and S states, indicating that the electronic transition from CBM to VBM can in some respects be viewed as the combination of a metal-to-ligand charge transfer and a Cu-centered transition of multinuclear copper complexes.⁴² These results imply that the q-CS nanosheets can be a type of semiconductor bridging conventional inorganic semiconductors and metal-organic complexes.

Temperature-Dependent Photoluminescence of q-CS Nanosheets. As shown in Figure 4a, the PL intensity of the 665 nm emission of q-CS nanosheets is dramatically increased when the temperature is decreased from 280 to 140 K, which is a common phenomenon as the nonradiative recombination process is more sensitive to temperature than the radiative recombination process.^{54,55} However, a higher-energy emission peak centered at 560 nm appears when the temperature is further brought below 140 K, and its intensity quickly increases when the temperature is decreased from 140 to 80 K. As shown in Figure 3a, the theoretical indirect band gap between the Γ and M point is about 1.86 eV for q-CS nanosheets, much lower than the direct band gap referring to the vertical transition at the Γ point (2.26 eV). Therefore, it is reasonable to attribute the former lower-energy emission to the indirect

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Figure 4. Temperature-dependent (a) PL spectra, (b) integrated PL emission, (c) PL peak position (top) and PL emission line widths (bottom) overlaid with fitted lines (the few strongly deviated points were excluded from the fits), and (d) relative radiative rates of q-CS nanosheets.

band gap transition and the higher-energy emission at 560 nm (2.21 eV) to the direct band gap transition. These two transitions begin to compete against each other when the temperature is below 100 K, which can be clearly seen after multiple Gaussian peak fittings given in Figure S15. According to the fitting results, the temperature dependencies of the relative PLQYs (expressed as plots of the relative integrated PL peak areas) of these two transitions were extracted and are provided in Figure 4b.

To further verify the attribution of 560 and 665 nm emissions to the direct and indirect band gap transitions, respectively, the temperature-dependent PL peak positions were recorded and then simulated with the well-known Varshni empirical expression showing the temperature dependence of the band gap energies.⁵⁶ As shown in Figure 4c, the indirect process strictly follows the curve described by the empirical expression, whereas the direct process exhibits a departure from the empirical law close to the onset around 140 K, and the points at 120-80 K could well follow a separate fitted curve. However, apart from this step-like jump in the direct process, both trends are relatively flat when compared with the dependences usually exhibited by other bulk semiconductors.⁵⁶ The flatter response reflects the weaker temperature dependence of lattice expansion in q-CS nanosheets, owing to Cu-Cu bonding that firmly holds the subnanometer-thin 2D q-CS structures together.

To understand the temperature-dependent band gap transition behaviors, the temperature dependencies of the line widths of indirect and direct transition processes are also plotted in the lower frame of Figure 4c. The total line width $\Gamma_{\text{Tot}}(T)$ of emissive transitions in semiconductors is a sum of three contributions: the inhomogeneous line width (Γ_{inh}) and the broadenings from acoustic and from optical phonon interactions (Γ_{Ac} and Γ_{LO} , respectively) as described below:

$$\Gamma_{\text{Tot}}(T) = \Gamma_{\text{inh}} + \Gamma_{\text{Ac}}T + \Gamma_{\text{LO}}(e^{E_{\text{LO}}/kT} - 1)^{-1}$$
(1)

where T refers to temperature, $E_{\rm LO}$ refers to the energy of longitudinal optical phonons, and k is the Boltzmann constant. As shown in Figure 4c, both indirect and direct points determined above 160 K exhibit linear trends and extrapolate to relatively similar line widths at T = 0 K. According to eq 1, these linear trends suggest that the temperature dependence of the band gap transition is mostly dominated by interactions between the exciton and acoustic phonons. However, the indirect points show a rising trend as the temperature drops over the 120–80 K range, and the direct points show a strong deviation from the otherwise linear trend over the 140–120 K region. These deviations may originate from the crossover from almost completely indirect to a mixture of indirect and direct emission mechanisms occurring when the temperature is decreased.

The competition between the direct and indirect processes was further investigated *via* temperature-dependent transient fluorescence spectroscopy. As shown in Figure S16, the PL decay curves of two emission peaks recorded at different temperatures could be well fitted using a triple exponential function, and the details are given in Tables S8 and S9. In combination with the relative PLQYs derived from Figure 4b, the relative radiative recombination rates of indirect and direct transition pathways were obtained and compared in Figure 4d. Even though the integrated PL peak area of the indirect process is increasing upon cooling, as shown in Figure 4b, the relative radiative rate is actually decreasing, while the direct recombination process is becoming more favorable below T =150 K, competing progressively and more aggressively against the indirect process.

As discussed before, the direct band gap of q-CS nanosheets at the Γ point is much larger than the indirect band gap from the Γ to M point, so the indirect-to-direct band gap crossover



Figure 5. (a) PXRD patterns and (b) normalized PL spectra (λ_{ex} = 410 nm) of q-CS nanosheets with variable alkyl chain lengths, (c) PXRD patterns, (d) Raman patterns, and (e) UV–Vis absorption (dashed lines) and PL spectra (solid lines) of the AgSR and Cd(SR)₂ assemblies.

cannot be achieved at room temperature. As the radiative recombination of excitons through the indirect band gap transition requires additional momentum compensation from phonons to obey momentum conservation,^{45,57} the influence of temperature on the intensity of an indirect emission is an additive result of phonon momentum and a thermal quenching effect. When the temperature decreases below 140 K, it is too low to provide momentum compensation from phonons for the indirect emission, thus the exciton recombination through the direct band gap transition is more likely to happen, leading to the indirect-to-direct band gap crossover for the q-CS nanosheets.

Ubiquity of Metal–Metal Bonding in Metal–Alkanethiolate Complexes. To show the existence of Cu–Cu bonding in similar systems, $C_xH_{2x+1}SH$ ligands with different alkyl lengths (*i.e.*, x = 4, 6, 8, and 10) were chosen to repeat the preparation and the resulting copper–alkanethiolate complex (CuSR) assemblies are labeled as C4, C6, C8, and C10, respectively, for comparison with the one synthesized with 1dodecanethiol (denoted as C12). The PXRD patterns shown in Figure 5a reveal that all of the resulting samples exhibit similar long-range-ordered structures. In addition, the interplanar distance of the q-CS nanosheets is directly associated with the length of the alkyl chains following the linear relationship given below:

$$y = 7.47 + 2.17x \tag{2}$$

where *y* refers to the layer spacing (Å) and *x* is the number of $-CH_2$ units ranging from 4 to 10. According to the fitting results given in Figure S17, a goodness-of-fit, R^2 , of 0.998 leads to a reliable intercept of 7.47 Å that can reasonably be attributed to the q-CS central slab. Most importantly, C4–C10 also present very similar photoluminescence apart from the fact that the thickness of the q-CS layer extracted from C4–C10 is very comparable to that extracted from C12. It is therefore highly reasonable to infer that the Cu–Cu bonding exists in all of these systems irrespective of the carbon chain lengths.

To further show the ubiquity of metal-metal bonding in other metal-alkanethiolate complexes, silver-dodecanethiol (AgSR) and cadmium-dodecanethiol $(Cd(SR)_2)$ assemblies were also prepared. The chemical structures of the resulting complexes were confirmed by XPS analysis. According to the XPS results given in Figure S18, the atomic ratios of Ag/S and Cd/S were determined to be very close to 1 and 0.5, respectively, for AgSR and in Cd(SR)₂. The PXRD results shown in Figure 5c reveal that both the AgSR and $Cd(SR)_2$ assemblies display the characteristic diffraction peaks of longrange ordered structures with nearly identical d spacing of 3.38 nm, quite close to 3.34 nm for copper-dodecanethiol complexes. Actually, apart from EXAFS, Raman spectroscopy offers a convenient approach to identify metal-metal bonds.^{33,58-61} According to the results given in Figure S19, the Cu-Cu bonding within q-CS nanosheets is characterized by a single Raman peak at $63 \text{ cm}^{-1.33}$ As shown in Figure 5d, AgSR and Cd(SR)₂ assemblies exhibit similar Raman signals peaking at 71 and 59 cm⁻¹, respectively, which can be assigned to a Ag–Ag stretching vibration^{59,60} and a Cd–Cd stretching vibration.⁶¹ These preliminary Raman results support the existence of metal-metal bonding in the layer-structured metal-alkanethiolate complexes. As a consequence, both the AgSR and Cd(SR)₂ complex assemblies exhibit broad band photoluminescence, as shown in Figure 5e, similar to that of the CuSR complexes, although there are no conjugated π electrons in these two systems either.

CONCLUSIONS

In conclusion, the 2D subnanometer-thin luminescent q-CS semiconductor was obtained upon self-assembly of CuSR complexes. The Cu–Cu bonding has been discovered in the CuSR assemblies through systematic studies. It interconnects two layers of $(CuSR)_n$ perpendicularly, leading to the formation of layer-structured q-CS semiconductors, independent of the chain length of the alkylthiols used. Further studies indicate that similar metal–metal bonding occurs not only in copper–alkanethiolate complexes but also in the analogous

assemblies of silver-dodecanethiol and cadmium-dodecanethiol complexes, which leads to the formation of a class of subnanometer-thin 2D semiconductors, bridging the gap between conventional inorganic semiconductors and organic semiconductors, although their physical properties remain to be further explored.

METHODS

Chemicals. The following materials were purchased from Aladdin, *i.e.*, cuprous iodide (98%), 1-dodecanethiol (98%), 1-decanethiol (96%), 1-hexanethiol (96%), 1-octanethiol (98%), butanethiol (97%). Other analytical grade chemicals, such as ethanol and cyclohexane, were purchased from Sinopharm Chemical Reagent Beijing, Co., Ltd. All reagents were used as received without further purification.

Preparation of Quasi-Copper-Sulfide Nanosheets. To prepare the quasi-copper-sulfide (q-CS) nanosheets, a solution of copper-alkanethiolate complexes was prepared first. Typically, a mixture of 0.4 mmol of CuI and 12 mL of 1-dodecanethiol was kept under magnetic stirring at room temperature for about 60 min until a clear and colorless solution was formed. It was found that this reaction process can be accelerated by raising the reaction temperature, that is, from room temperature to 70 °C. Other copper-alkanethiolate complexes (CuSR, SR = $-SC_4H_{9}$, $-SC_6H_{13}$, $-SC_8H_{17}$, $-SC_{10}H_{21}$) were prepared by the same method except that 1-dodecanethiol was replaced by the other 1-alkanethiol homologues. It was found that the shorter the carbon chain of the 1-alkanethiol reagent, the faster the reaction occurred. Then, ethanol of 3-fold the volume of the reaction solution was rapidly added into the colorless solution, and yellowish q-CS nanosheets were immediately generated. The q-CS nanosheets were separated from the solution by centrifugation and purified by washing several times with ethanol.

Preparation of Silver–Alkanethiolate and Cadmium–Alkanethiolate Assemblies. To prepare the silver–alkanethiolate assemblies, 10 mL of an acetonitrile solution of $AgNO_3$ (0.02 M) was added dropwise into 12 mL of 1-dodecanethiol, and the AgSR assemblies were immediately formed as yellowish precipitates. Then, 20 mL of ethanol was added into the mixture and kept stirring for 30 min. The AgSR assemblies were separated from the solution by centrifugation and purified by washing several times with ethanol. The cadmium–alkanethiolate assemblies were prepared in a very similar way. Typically, 10 mL of ethanol solution of Cd(CH₃COO)₂·2H₂O (0.02 M) was added dropwise into 12 mL of 1-dodecanethiol to generate the Cd(SR)₂ assemblies. The subsequent procedures were the same as those for AgSR.

Structural and Compositional Characterization. The SEM images were obtained by a Hitachi S4800 scanning electron microscope operating at beam energy of 10 kV. The TEM images were obtained by a JEM-2100F electron microscope operating at an accelerating voltage of 200 kV. AFM images were obtained on a Bruker Dimension FastScan system. XPS measurements were carried out on a Thermo Scientific ESCALab 250Xi using 200 W monochromated Al K α radiation, and the X-ray beam size was 500 μ m. The MALDI-TOF-MS data were collected in positive-ion mode with 2,5-dihydroxybenzoic acid as the matrix on a Bruker Autoflex III mass spectrometer. TG analysis was carried out on a TG209 F3 Tarsus thermal gravimetric analyzer operated under N2 atmosphere from room temperature to 800 °C. The solid-state ¹³C NMR spectra were obtained using a Bruker AVANCE 400 MHz WB solid-state NMR spectrometer. The FTIR spectra were recorded on Bruker FTIR Tensor 27 spectrometer. The PXRD patterns were recorded on a Rigaku D/Max-2500 diffractometer with Cu K α radiation. The Raman spectra were recorded on a Horiba Labram HR Evolution Raman spectrometer with 633 nm excitation. The elemental composition of the copper-dodecanethiol assemblies was determined by ICP-MS on a Thermo iCAP RQ spectrometer for Cu and I and organic elemental quantitative analysis on a Thermo Flash Smart elemental analyzer for C, H, and S.

Spectroscopic Characterization. The steady-state PL spectra were obtained from a NanoLog FL3-2iHR infrared fluorescence

spectrometer. The PL decay curves were recorded on a Delta flex UltraFast lifetime spectrofluorometer. The UV–vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer. The absolute PLQY was determined on an Edinburgh FLS980 fluorescence spectrometer equipped with an OXFORD Microstat temperature-controlling system.

Methods for PL Lifetime Fitting. The PL decay curves were fitted using a triexponential function (eq 3):

$$I(t) = \sum_{i=1}^{n} B_i \exp(-t/\tau_i), \quad \sum_{i=1}^{n} B_i = 1$$
(3)

In this expression, τ_i represents the decay time constants, B_i represents the normalized amplitudes of each component, and n is the number of decay terms (usually three).

The average PL lifetime was calculated using eq 4

$$\tau_{\text{avg}} = \left(\sum_{i=1}^{n} B_{i} \tau_{i}^{2}\right) / \left(\sum_{i=1}^{n} B_{i} \tau_{i}\right)$$

$$\tag{4}$$

In the case where emission from the direct and indirect processes overlapped, the measured average decay rate was assumed to result from a combination of the two true average decay rates weighted according to the relative numbers of photons emitted by each process. In this manner, the separated average decay time for each process was recovered, with the main influence or correction being upon the direct decay times measured at temperatures of 120 K and below and 560 nm emission wavelength.

Structure Modeling Methods. The PXRD patterns for structure modeling were collected on a PANalytical X-Pert Pro diffractometer operated with the capillary mode and step size of $0.001^{\circ}/s$ (Cu K α radiation of $\lambda = 1.5418$ Å at 40 kV and 40 mA). During the data collection, the capillary with the sample was spinning to eliminate the effect of any preferred orientation as much as possible. The molecular packing structure model of the copper-alkanethiol assemblies was built by Material Studio software. The unit cell parameters with orthorhombic symmetry were derived directly using the X-Cell package in the Material Studio software. After the reflection condition was carefully analyzed by Le Bail fitting, the possible space group could be chosen from I222, I2121, Imm2, and Immm. The simulated annealing parallel tempering algorithm in the Material Studio software was used to find a starting molecular arrangement according to the PXRD results. Finally, the crystal structure of the q-CS nanosheets was solved with the space group of I222.

X-ray Absorption Spectroscopy Methods. The Cu K-edge Xray absorption spectra were recorded at Beamline 1W1B of the Beijing Synchrotron Radiation Facility. Background subtraction and EXAFS shell fitting were conducted using Athena and Artemis programs in IFEFFIT software packages^{62,63} (fitting range: $3.00 \le k$ (Å) ≤ 12.46 and $1.25 \le R$ (Å) ≤ 2.88).

Density Functional Theory Simulation. All of the calculations are based on DFT implemented in the VASP.⁶⁴ Both the lattice parameters and molecular geometry optimization were performed by the projector-augmented wave (PAW) method with the Perdew–Burke–Ernzerhof functional including a dispersion (PBE-D3) exchange correlation function.^{65,66} The cutoff energy for the planewave basis set was adjusted to be 400 eV. The *k*-mesh of $5 \times 5 \times 1$ was used during the optimization. Based on the optimized crystal structure, the accurate electronic and optical properties were calculated by means of DFT+U at PBE-D3 level with 11 × 11 × 1 k-point sampling in reciprocal space. In the DFT+U calculations, the effective U and J values are 1 and 5 eV for Cu 3d, respectively, according to a previous study.⁶⁷

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c07388.

Additional figures and tables: TG curve, XPS spectra, FTIR spectra, XANES spectra, EXAFS fitting results, AFM image, NIR absorption spectrum, temperature-

dependent PL decay curves and Raman spectrum of the q-CS nanosheets, XPS spectra of AgSR and $Cd(SR)_2$ assemblies, fitting results of PL decay curves, elemental composition analysis results, additional data obtained from PXRD refinement, and DFT calculation (PDF)

X-ray crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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