The photoluminescence of metal nanoclusters is typically low, and phosphorescence emission is rare due to ultrafast free-electron dynamics and quenching by phonons. Here, we report an electronic engineering approach to achieving very high phosphorescence (quantum yield 71.3%) from a [Au@Cu14(SPhBu)12(PPh(C2H4CN))6]+ nanocluster (abbreviated Au@Cu14) in non-degassed solution at room temperature. The structure of Au@Cu14 has a single-Au-atom kernel, which is encapsulated by a rigid Cu(I) complex cage. This core-shell structure leads to highly efficient singlet-to-triplet intersystem crossing and suppression of nonradiative energy loss. Unlike the phosphorescent organic materials and organometallic complexes—which require de-aerated conditions due to severe quenching by air (i.e., O2)—the phosphorescence from Au@Cu14 is much less sensitive to air, which is important for lighting and biomedical applications.

RESULTS AND DISCUSSION
Crystalllographic structure of Au@Cu14
The [Au@Cu14(SR)12(BCPP)6]+ NC [abbreviated Au@Cu14; counterion, SbF6−; SR, 4-tert-butyl-benzenethiolate (SPhBu); BCPP, bis(2-cyanoethyl)-phenylphosphine] was prepared by mixing NaAuBr4·3H2O, Cu(NO3)2 and PPh(C2H4CN)2, and then reduction by NaBH4 aqua tetraoctylammonium bromide, and HSPhBu. The [Au@Cu14(SPhBu)12(PPh(C2H4CN))6]+ (abbreviated Au@Cu14) via engineering the ground and excited states through atomic structure control. The cluster has a single-atom (Au) core and an exterior large Cu(I) complex cage. Such a construct drastically enhances singlet-to-triplet transfer and also suppresses the vibrational energy loss, hence, achieving an extraordinary 71.3% QY of room temperature phosphorescence in ambient solution. Because of the protection of the triplet-state wave function by a Cu14 cage, the phosphorescence of Au@Cu14 is much less sensitive to air (i.e., O2) compared to typical phosphorescent metal complexes. The strategy of single-heavy-atom core and encapsulation with a rigid cage is promising for future design of highly phosphorescent NCs for practical applications such as LEDs, high-resolution optical nanoprobes, and anticounterfeiting.

The ultimate kernel size would be a single atom, which would permit simpler yet more effective engineering of the electronic radiative and nonradiative pathways; however, NCs with single-metal-atom kernels have not been reported so far. Moreover, the mechanism for photoluminescent NCs is still not fully clear.

Here, we report a highly phosphorescent NC: [Au@Cu14(SPhBu)12(PPh(C2H4CN))6]+ (abbreviated Au@Cu14) via engineering the ground and excited states through atomic structure control. The cluster has a single-atom (Au) core and an exterior large Cu(I) complex cage. Such a construct drastically enhances singlet-to-triplet transfer and also suppresses the vibrational energy loss, hence, achieving an extraordinary 71.3% QY of room temperature phosphorescence in ambient solution. Because of the protection of the triplet-state wave function by a Cu14 cage, the phosphorescence of Au@Cu14 is much less sensitive to air (i.e., O2) compared to typical phosphorescent metal complexes. The strategy of single-heavy-atom core and encapsulation with a rigid cage is promising for future design of highly phosphorescent NCs for practical applications such as LEDs, high-resolution optical nanoprobes, and anticounterfeiting.

INTRODUCTION
Photoluminescence (PL) is one of the most important properties for molecular and nanoscale materials in many applications, such as light-emitting diodes (LEDs) and biological probes (1–3). Besides organic molecules, the PL properties of polynuclear d10 transition metal complexes, e.g., Cu(I), Ag(I), and Au(I), have been investigated widely (4), and rich photophysics was observed in cuprous complexes with different structures (5). Luminescent polynuclear complexes can form between d10 coinage metal ions and chalcogenide ligands, e.g., thiocarbamate-stabilized octahedral Cu6 complexes—which display a deep orange luminescence in solid state under ambient conditions (6)—and Cu4 complexes with S2− ligands—which show yellow-orange emission of long excited-state lifetime (7).

Compared to metal complexes, thiolate (SR)-protected metal nanoclusters (NCs) with delocalized free valence electrons (8–10) generally show lower quantum yields (QYs) in solution under ambient conditions (11). Thus, much effort has been focused on enhancing QYs of metal-SR NCs. Strategies of ligand tailoring and suppression of surface vibrations have been proved to improve the PL of NCs (12–15). Aggregation of Au(I)-SR complexes on the Au(0) kernel also led to enhanced QY of ~15% (16, 17). Alloying is an effective strategy to enhance the PL (18–22). Other than gold, copper and silver NCs have also been explored (23–26). In the research of PL materials, phosphorescence has become a recent target primarily driven by the LED industry (27–29). Compared to organics and metal complexes, phosphorescent NCs are rare (30), and the QY of room temperature phosphorescence remains to be enhanced.

We rationalize that shrinking the metal kernel size and enlarging the surface complex would be promising in achieving high QYs.
of hydrides (H\textsuperscript{−}) in the cluster; notably, the presence of hydrides is quite common in Cu NCs (24), but hydrides cannot be identified by x-ray crystallography. The \textit{Au@Cu14} NC has two free valence electrons: 1 (Au) + 14 (Cu) − 12 (SR) − 1 (charge) = 2 e. For comparison, \textit{X@Cu14} (X = mixed Au/Cl) and the \textit{Cl@Cu14} counterparts were also synthesized and structurally determined by a similar method (see fig. S2 and the Supplementary Materials) as that of \textit{Au@Cu14}. In the crystal of \textit{X@Cu14}, the central atom is partially occupied by Au or Cl. Except the central atom, \textit{X@Cu14} and \textit{Cl@Cu14} are the same as \textit{Au@Cu14} including the types and numbers of ligands and the charge state (+1, counterion = SbF\textsubscript{6}\textsuperscript{−}). Both \textit{X@Cu14} and \textit{Cl@Cu14} were characterized by ultraviolet-visible (UV-vis) and ESI-MS (fig. S1, C to F). Notably, \textit{Cl@Cu14} has no free electron: 14 (Cu) − 12 (SR) − 1 (Cl) − 1 (charge) = 0 e.

The structure of [\textit{AuCu14}((SR)\textsubscript{12}(BCPP))\textsubscript{6}]\textsuperscript{+} (Fig. 1A) can be divided into a single-Au-atom kernel and a large [\textit{Cu14}((SR)\textsubscript{12}(BCPP))\textsubscript{6}]\textsuperscript{−} exterior cage (Fig. 1B). There are two categories of Cu atoms in the \textit{Cu14} cage: a Cu\textsubscript{8} cube composed of eight inner Cu atoms (green) and a Cu\textsubscript{6} octahedron composed of six outer Cu atoms (brown). Each of the six squares of the Cu\textsubscript{6} cube is capped with a Cu(SR)\textsubscript{2}(BCPP) mount motif (Fig. 1C). The Cu(I)–Cu(I) distances between cubic Cu sites are in the range of 2.975 to 3.296 Å, much longer than the Cu–Cu bond lengths of ~2.64 Å in icosahedral or cuboctahedral Cu\textsubscript{13} kernels (24, 26) or bulk Cu. Thus, no metal-metal bond exists in the \textit{Cu14} cage [i.e., a cage of Cu(I) complex]. The Cu(I) oxidation state is further verified by x-ray photoelectron spectroscopy (XPS) analysis by comparing the Cu XPS signal from \textit{Au@Cu14} with that of Cu(I)-SR (fig. S3). The Cu\textsubscript{8} cube wraps a single-Au-atom kernel, resulting in a body-centered cubic Au@Cu\textsubscript{8} structure (Fig. 1D), in which the average Au–Cu bond length is 2.708 Å, indicating strong interactions between the central Au and Cu\textsubscript{8} cube.

**PL of \textit{Au@Cu14}**

\textit{Au@Cu14} exhibited an intense PL at ~625 nm (Fig. 2) at room temperature under ambient conditions (non-degassed), and the QY was measured to be 71.3% with rhodamine B in ethanol as the standard (31). The excitation spectrum monitored at 625-nm emission (Fig. 2A, black line) is almost identical to the absorption spectrum of \textit{Au@Cu14} (fig. S1A), and the Stokes shift is smaller than the d\textsuperscript{10} complexes of similar size (Stokes shift > 200 nm) (23, 32), indicating that the PL properties of \textit{Au@Cu14} are different from those of Cu(I), Au(I), or Cu(I)/Au(I) complexes (6, 33–35) but similar to metal NCs with free electrons, such as [\textit{Au2Cu12}((SR)\textsubscript{6}(PPh\textsubscript{2}py)\textsubscript{2}Br\textsubscript{4}])\textsuperscript{3+} (6 e) (36) and \textit{Au2Cu4}((SR)\textsubscript{6}(PPh\textsubscript{2}py)\textsubscript{2}) (2 e) (37). The emission peak position (~625 nm) of \textit{Au@Cu14} is independent of the excitation wavelengths (Fig. 2A, color lines), suggesting that the PL of \textit{Au@Cu14} originates from the same excited state (vide infra).

The \textit{Au@Cu14} powder also showed ultrabright emission (Fig. 2B, inset), and the emission peak (~630 nm; Fig. 2B) is slightly red-shifted compared to that of the solution spectrum. Temperature-dependent (300 to 80 K) measurements on the \textit{Au@Cu14} solid showed small redshifts of PL by up to 18 nm (Fig. 2C), in which the emission was enhanced by 1.3 times. The observation of small redshift from solution to solid phase and from room temperature to 80 K indicates a slight increase of energy gap between singlet state (S\textsubscript{1}) and triplet state (T\textsubscript{1}). Moreover, the small peak shifts further differentiate \textit{Au@Cu14} from metal(I) complexes; for example, the [\textit{Cu(py)}\textsubscript{14}]\textsubscript{4} complex showed emission maximum at 585 nm in solids but drastically shifted to 698 nm in toluene (38). The Au(I) complexes typically show >100-nm emission peak shifts from solution to solid (39). Such large shifts in metal(I) complexes can be explained by large structural changes that take place in solution, but the solid state often involves metal(I)–metal(I) interactions. Moreover, the Cu(I) complexes usually exhibit luminescence thermochromism due to the notably shortened Cu(I)–Cu(I) distance upon decreasing the temperature (5, 40, 41), but this is not the case in \textit{Au@Cu14}, indicating different electronic pathways.

As indicated by the small shifts in emission peak from the solution to solid state at room temperature, as well as from ambient to cryogenic temperatures, the structural change upon excitation should be rather small for \textit{Au@Cu14}. We ascribe this phenomenon to the rigid Cu\textsubscript{14} cage composed of an inner Cu\textsubscript{8} cube and an outer Cu\textsubscript{6} octahedron that are tightly combined together by the S atoms of thiolates, and the central single-Au-atom further contracts the cubic Cu\textsubscript{8} into a compact structure. For each of the cubic Cu atoms (Fig. 1B), the μ\textsubscript{4} coordination favorable to Cu(I) with complete filling of d orbital is achieved by coordinating with three S atoms and the central Au (42). Such a rigid structure greatly restricts the intramolecular motion and thus reduces the nonradiative energy loss, even in solution phase under ambient conditions. Therefore, the single-gold-atom kernel plays an important role in stabilizing the large Cu\textsubscript{14} cage.

We further provide three more perspectives for understanding the PL mechanism in \textit{Au@Cu14}, including (i) the heavy-gold-atom influence on the triplet state, (ii) singlet oxygen (O\textsubscript{2}) generation, and (iii) ultrafast electron dynamics, as discussed below.

**Single-atom kernel of \textit{Au@Cu14}**

The role of the central Au atom is elucidated by replacing Au with Cl to give rise to a Cl\textit{Cu14} complex with no free electron. As the structures of \textit{Au@Cu14} and Cl\textit{Cu14} are almost the same, the central position is occupied by Au or Cl with an atomic ratio of 0.38:0.62 in the crystal of X\textit{Cu14}. We found that the ambient QY in solution decreases from 71.3% of \textit{Au@Cu14} to 56.8% of X\textit{Cu14} and to 41.8% of Cl\textit{Cu14} (Fig. 3A). The QY is roughly proportional to the ratio of Au/(Au + Cl) as shown in Fig. 3B.

The presence of free valence electron in metal NCs often leads to PL quenching. For example, [Ag\textsubscript{62}S\textsubscript{13}(SR)\textsubscript{32}]\textsuperscript{4−} (0 e) was luminescent (43), but the one S atom less counterpart, [Ag\textsubscript{62}S\textsubscript{12}(SR)\textsubscript{32}]\textsuperscript{2+} (4 e)—which has a similar structure except the missing central S—became nonluminescent due to the PL quenching by free electrons (44). Liu et al. reported a centered cuboctahedral Cu\textsubscript{13} NC (26), and by

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**Fig. 1. Structure analysis of [\textit{AuCu14}((SR)\textsubscript{12}(BCPP))\textsubscript{6}]\textsuperscript{+}.** (A) Total structure, (B) the Cu\textit{x}(SR)\textsubscript{12}(BCPP)\textsubscript{6} cage, (C) the Cu(SR)\textsubscript{2}(BCPP) mount motif capping on the square face of the Cu\textsubscript{8} cube, and (D) the body-centered cubic Au@Cu\textsubscript{8}. Color codes: magenta, Au; brown, octahedral Cu atoms; green, cubic Cu atoms; yellow, S; orange, P; gray, C; light blue, N; white, H.
replacing the central Cu with S, Cl, or Br to break the 2 e superatom, the luminescence can be enhanced as the ionic component of the host-guest interaction is increased as Br ≈ Cl > S > Cu (45). By contrast, in our X@Cu14 NCs, the central Au atom—which leads to overall two free electrons in the cluster—instead enhances the PL of Au@Cu14 compared to Cl@Cu14. Thus, the X@Cu14 series have a previously unidentified mechanism for the role of the free electrons in the PL. Generally speaking, more free electrons decrease the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap (Eg) and, accordingly, reduce the PL. However, the 2 e Au@Cu14 and 0 e Cl@Cu14 herein show almost identical absorption spectra (fig. S1), indicating similar Eg and electron localization on Au as on the central Cl− atoms), which could be explained by the large [Cu14(TBBT)12(BCPP)2] cage observed in the three NCs. These features are different from the Ag82 and Cu13 cases (26, 44, 45). In Au@Cu14, the central Au atom plays a critical role in affecting the intersystem crossing (ISC) from the S1 to the T1 and, subsequently, giving rise to strong phosphorescence. In general, organocopper complexes are far less efficient in phosphorescence generation compared to other heavy-metal (e.g., Ir and Pt) complexes, manifested in the spin-orbit coupling parameter (ξ). The ξCu is only 857 cm−1, whereas ξIr = 3909 cm−1 and ξPt = 4481 cm−1 are much higher and hence promote ISC and enhance T1 emission. In Au@Cu14, the central Au atom greatly improves the ISC process, as Au has the highest ξAu (= 5104) among all metals, and consequently greatly enhances the phosphorescence (Fig. 3A). Moreover, metal–metal interactions between the central Au and cubic Cu4 in Au@Cu14 is favorable for electron transfer compared to the long distance of Cl–Cu (2.926, 2.899, 2.849, and 2.510 Å) in Cl@Cu14.

The emission peak positions of the three NCs are identical, indicating the energy gaps between T1 and S0 are the same for the series. However, when closely inspecting the absorption spectra (fig. S4) of Au@Cu14 and Cl@Cu14, we notice an absorption tail for the Au@Cu14, which corresponds to an S1 at lower energy. In other words, the energy gap between S1 and T1 for Au@Cu14 is smaller than that in Cl@Cu14, which contributes to a more efficient ISC process.

1O2 generation on Au@Cu14

The triplet-state emission from Au@Cu14 was further verified by observing 1O2 production over the photoexcited Au@Cu14, in which the triplet state of Au@Cu14 transfers its energy to the normal triplet state 1O2, giving rise to singlet state 1O2. In the test, an ambient CH2Cl2 solution of Au@Cu14 with PLQY = 71.3% was purged with ultrahigh-purity grade N2 for 5 min and then with O2 for 10 min. Figure 4A shows PL spectra of the N2-purged and O2-saturated solutions. The N2-purged solution of Au@Cu14 shows a higher PLQY (85.6%) than the ambient solution (with air dissolved in the solution), whereas the O2-saturated solution quenches PL to QY of ~17.9%, but this quenching is much less than typical phosphorescent metal complexes (29). Singlet 1O2 is an excited state of dioxygen and has a characteristic phosphorescence emission peak at ~1270 nm. The spectrum of the N2-purged Au@Cu14 solution was absent of 1O2 emission (Fig. 4B, black), but the O2-saturated Au@Cu14 solution showed a distinct 1O2 emission peak centered at ~1275 nm (Fig. 4B), indicating the notable generation of 1O2. To rule out the possibility that the PL quenching of the O2-saturated Au@Cu14 is resulted from the oxidation of the Cu(I) shell, we performed XPS measurements before and after O2 purging but found no obvious change in the oxidation state of Cu(I) (fig. S3). This is also confirmed by the identical UV–vis absorption spectra (Fig. 4C) and the recovery of its PL after purging with N2 (Fig. 4A). Furthermore, PL quenching upon O2 saturation and PL enhancement upon N2 purging were also observed in Cl@Cu14 solution (fig. S5), similar to the Au@Cu14 system.
Electron dynamics of Au@Cu$_{14}$

We further probed the ultrafast electron dynamics of the Au@Cu$_{14}$ by performing transient absorption (TA) measurement (46). After photoexcitation at 400 nm, one observed excited state absorption (ESA) at 490 and 550 nm together with strong net ground state bleaching (GSB) signals at 460 and 510 nm (Fig. 5, A and B). The sharp and notable net GSB peaks suggest that absorption by Au@Cu$_{14}$ is strong. Within 0.2 to 1 ps, one can observe that ESA at 560 nm decays rapidly to give rise to a flat and featureless ESA band between 520 and 750 nm. Afterward, the TA signal decays slightly from 1 ps to 1 ns and remains unchanged until 7 ns (Fig. 5A and fig. S6), i.e., there is no additional change in the profile of TA spectra. Such TA profiles and relaxation dynamics of Au@Cu$_{14}$ are consistent with the observation in Fig. 2A that the emission is independent of the excitation wavelength. The PL lifetime of Au@Cu$_{14}$ was 1.23 μs measured by time-correlated single photon counting (TCSPC) (Fig. 5C), which is reasonable for the luminescence from the spin forbidden triplet state. Furthermore, the PL lifetime of Au@Cu$_{14}$ was also measured at different excitation wavelengths (fig. S7), and no obvious change was observed. Moreover, the PL lifetimes of Cl@Cu$_{14}$ and X@Cu$_{14}$ were measured to be 0.78 and 0.92 μs (fig. S8), respectively, which are shorter than that of Au@Cu$_{14}$, consistent with the lower PLQY of Cl@Cu$_{14}$ (Fig. 3).

Together, the microsecond lifetime, the critical role of central Au atom in effecting ISC, and the effective $^{1}$O$_{2}$ generation by photoexcited Au@Cu$_{14}$ confirm that the PL emission of Au@Cu$_{14}$ is phosphorescence. The sub-picosecond decay (<1 ps) is assigned to the internal conversion (IC) from S$_{0}$ to S$_{1}$ state coupled with the ISC from S$_{1}$ to T$_{1}$ as no additional relaxation is observed, and the whole process is much shorter than the time constant of ISC measured for Cu(I) complexes (tens of picoseconds) (47). After the ultrafast IC and ISC processes, the excited electron goes from the long-lived triplet

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**Fig. 4.** $^{1}$O$_{2}$ generation. (A) Comparison of the emission spectra of CH$_{2}$Cl$_{2}$ solutions of Au@Cu$_{14}$ under ambient condition (blue), N$_{2}$-purged (black), O$_{2}$-saturated (red), and rhodamine B (magenta) as reference, $\lambda_{ex}$ = 410 nm; (B) near-infrared PL of N$_{2}$-purged (black) and O$_{2}$-saturated (red) CH$_{2}$Cl$_{2}$ solution of Au@Cu$_{14}$, $\lambda_{ex}$ = 410 nm; (C) Overlapped UV-vis spectra of N$_{2}$-purged (black) and O$_{2}$-saturated (red) CH$_{2}$Cl$_{2}$ solution of Au@Cu$_{14}$.

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**Fig. 5.** Transient absorption. (A) TA spectra of Au@Cu$_{14}$ at three different time delays (pumped at 400 nm); (B) TA kinetics decay probed at selected wavelengths; (C) the microsecond PL decay traces of Au@Cu$_{14}$. Solvent: CH$_{2}$Cl$_{2}$. (D) Schematic diagram showing the excited-state relaxation dynamics of Au@Cu$_{14}$ and energy transfer between its excited-state and triplet oxygen molecules.
excited state to the ground state and emits phosphorescence with high QY (Fig. 5D). The fluorescence emission (S1 to S0) is completely inhibited due to ultrafast ISC (≤1 ps), giving rise to phosphorescence only. The energy gap of Au@Cu14 is >1.8 eV, which is sufficient for ^1O2 generation (0.97 eV). The energy transfer between the cluster and ^3O2 in their T1 states follows the Dexter mechanism. Such a process requires a wave function overlap, and thus, it can only occur at short distances (a few angstroms).

In summary, this work reports a strategy of electronic-state engineering to achieve a highly phosphorescent Au@Cu14 NC (2 e) with a single-atom kernel encaged by a rigid Cu(I) cage, and the NC shows >70% QY (λem ~ 625 nm) in non-degassed solution at room temperature. The phosphorescence emission originates from the triplet state of Au@Cu14. The critical role of the central Au atom is illustrated by QY drop to ~40% when Au is replaced by Cl, indicating that Au enhances PL via spin-orbit coupling effect. The photoexcited Au@Cu14 can effectively transfer energy to oxygen to generate ^1O2, with PL quenching upon O2 saturation of the NC solution, whereas N2 purge increases PLQY to 85%. The analysis of electron dynamics reveals an ultrafast (<1 ps) relaxation from S1(pump). The measurements were performed in toluene or chloroform for potential application in LEDs and biomedicine.

MATERIALS AND METHODS

Synthesis of Au@Cu14

A 0.4-mL aqueous solution of NaAuBr4-H2O (0.275 g/ml) and 130 mg of tetraethylammonium bromide were mixed in 15 mL of dichloromethane and vigorously stirred (~1100 rpm) for 30 min. After that, 150 μL of 4-tert-butylanethiolate was added to the solution. After 60 min, 37 mg of Cu(NO3)2 dissolved in 5 mL of methanol was added to the above solution and stirred for 30 min. Then, 150 mg of bis(2-cyanomethyl)-phenylphosphinoxide was added to the above solution, and the solution color changed to colorless, indicating the formation of Cu(I) and Au(I) complexes. After 60 min, 5 mL of aqueous solution of NaBH4 (150 mg) was rapidly added. The reaction was allowed to proceed for ~18 hours. Last, the organic solution was evaporated and washed several times with methanol/ethanol to remove the redundant ligands and by-products. The as-prepared products were crystallized in CH2Cl2/n-hexane at room temperature (4 to 6 days). The X@Cu14 and Cl@Cu14 NCs were prepared with similar methods (see details in the Supplementary Materials).

Transient absorption

The femtosecond TA spectroscopic measurements were performed on a commercial Ti:sapphire laser system (Coherent Astrella). The ~100-fs laser pulses in the UV and near-infrared regions of the spectrum were generated by a 1.2-mJ regenerative amplifier system and optical parametric amplifier (OPA, Light Conversion). A small portion of the laser fundamental was focused into a sapphire plate to produce a supercontinuum in the visible range, which overlapped with the pump in time and space. Multiwavelength transient spectra were recorded at different pump-probe delay times (Helios Fire, Ultrafast Systems). Dilute solutions of metal clusters in 1-mm path length cuvettes were excited by the tunable output of the OPA (pump). The measurements were performed in toluene or chloroform, and the optical density was adjusted to be about 0.3 optical density at the excitation wavelength. Nanosecond emission lifetime is measured on a HORIBA FluoroMax-4P by TCSPC.

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