Modulating photo-luminescence of Au$_{2}$Cu$_{6}$ nanoclusters via ligand-engineering†

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In this work, the luminescence of Au$_{2}$Cu$_{6}$ nanoclusters was controlled by tailoring the ligand to metal charge transfer via engineering the phosphine ligands with electron-donating or -withdrawing substituents. The fluorescence intensity was significantly enhanced from the Au$_{2}$Cu$_{6}$ nanocluster with P(Ph–F)$_{3}$ ligands (quantum yield QY = 5.7%) to that with P(Ph–OMe)$_{3}$ ligands (QY = 17.7%). In addition, the fluorescence of Au$_{2}$Cu$_{6}$ protected by P(Ph–OMe)$_{3}$ slightly red-shifts compared to that of Au$_{2}$Cu$_{6}$ protected by P(Ph–F)$_{3}$, which is similar to the trends of UV-vis spectra tendency.

Metal nanoclusters (NCs) with precise atomic number and well-defined composition (structure) have attracted intensive research interest owing to their highly promising applications in optics, catalysis and electrochemistry. In this context, photo-luminescence (PL) represents one of the most attractive properties of the metal NCs. Thanks to the advantages such as low toxicity, great photo-stability and high biocompatibility, the fluorescent NCs have recently become highly promising nanomaterials developed to enhance the luminescence of NCs. For instance, Forster and coworkers reported that the fluorescence intensity was significantly enhanced from the Au$_{24}$ nanocluster with P(Ph–F)$_{3}$ ligands (quantum yield QY = 5.7%) to that with P(Ph–OMe)$_{3}$ ligands (QY = 17.7%). In addition, the fluorescence of Au$_{2}$Cu$_{6}$ protected by P(Ph–OMe)$_{3}$ slightly red-shifts compared to that of Au$_{2}$Cu$_{6}$ protected by P(Ph–F)$_{3}$, which is similar to the trends of UV-vis spectra tendency.

In our recent study, the Au$_{2}$Cu$_{6}$(S-Adm)$_{6}$(PPh$_{2}$Py)$_{2}$ (where S-Adm = 1-adamantanethiol) NC with high fluorescence (QY = 11.7%) was synthesized via the aggregation-induced-emission method. The DFT calculations indicate that the fluorescence corresponds to the LUMO–HOMO transition, and is mainly caused by the charge transfer between the aromatic groups on the phosphine ligand and copper atoms. In other words, the luminescence originated from ligand to metal charge transfer (LMCT). Inspired by these conclusions, we tried to tailor the PL of Au$_{2}$Cu$_{6}$ NCs by engineering the phosphine ligands via functionalizing the aromatic group with electron-donating groups (EDGs) or electron-withdrawing substituents (EWGs). As summarized in Scheme 1, the EDG will hopefully strengthen the LMCT process to enhance the fluorescence. On the other hand, the fluorescence of NCs can be significantly enhanced from the Au$_{24}$ nanocluster with P(Ph–F)$_{3}$ ligands (quantum yield QY = 5.7%) to that with P(Ph–OMe)$_{3}$ ligands (QY = 17.7%). In addition, the fluorescence of Au$_{2}$Cu$_{6}$ protected by P(Ph–OMe)$_{3}$ slightly red-shifts compared to that of Au$_{2}$Cu$_{6}$ protected by P(Ph–F)$_{3}$, which is similar to the trends of UV-vis spectra tendency.

In the past decades, two main strategies have been developed to enhance the fluorescence of NCs. For instance, Bakr et al. observed a 26-fold PL QY enhancement on Ag$_{29}$ NC when doped with the central Au atom. In addition, Wu and coworkers reported that the fluorescence intensity of Au$_{24}$ NC increased in the electron-donating ability of the ligand. As the electronic structures of the organic ligands are essentially different from those of the metal atoms, the mechanistic understanding on the structure–fluorescence correlation could be more achievable. Additionally, with the structure–fluorescence relationships in hand, the target NCs with stronger PL could be easily prepared due to the synthetic similarities of NCs protected by different organic ligands.

In recent years, the ligand-engineering strategy has been successfully synthesized. Unfortunately, their practical applications have been limited due to the significantly lower quantum yield (QY) compared to the typical fluorescent nanomaterials (e.g., quantum dots). To this end, an efficient strategy to enhance the QY of weakly fluorescent NCs is highly desirable.

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the contrary, the LMCT and fluorescence could be significantly weakened when the phosphine ligand is relatively electron-deficient (in the presence of EWG).

Herein, we reported the PL modulation of Au2Cu6 NC systems via engineering the phosphine ligands with the electronic effect of the substituents. The structures and compositions of the Au2Cu6(S-Adm)2(PR3)2 (R = Ph–OMe for Au2Cu6-1; R = Ph for Au2Cu6-2; and R = Ph–F for Au2Cu6-3) NCs were verified by single crystal X-ray diffraction (SC-XRD), thermogravimetric analysis (TGA), inductively coupled plasma (ICP) and X-ray photoelectric spectroscopy (XPS) measurements. According to these characterizations, all the NCs share the same framework with the previously reported Au2Cu6(S-Adm)2(PPh2Py)2 NC. Compared with Au2Cu6-2 (QY = 12.2%), Au2Cu6-1 with EDGs exhibits enhanced PL (QY = 17.7%), while Au2Cu6-3 with EWGs shows weaker luminescence (QY = 5.7%). In addition, the emission peak on the PL spectra slightly red-shifts from Au2Cu6-1 to Au2Cu6-2 and Au2Cu6-3, consistent with the variation tendency in UV-vis spectra of different Au2Cu6 systems.

The aforementioned three Au2Cu6 NCs were prepared by the similar procedures with our previous study (see ESI† for details). Specifically, CuCl was dissolved in the mixture of acetonitrile and methanol, and AdmSH dissolved in toluene was then added to the solution. The overall solution was vigorously stirred for 15 min. Then, Au(PR3)Cl (R = Ph–OMe, Ph or Ph–F) in toluene and NaBH4 in ice-cold water were added dropwise to the flask simultaneously under vigorous stirring. The reaction was aged for 60 h under N2 atmosphere. Afterwards, the products were centrifuged to obtain the solid, which was then washed several times with toluene for further characterizations.

According to the SC-XRD characterization, the composition and total structures of the as-prepared Au2Cu6-2 and Au2Cu6-3 are similar with the overall framework of previously reported Au2Cu6(S-Adm)2(PPh2Py)2 (Fig. S1 and S2†). However, the crystal structure of Au2Cu6-1 failed to be obtained because of the relatively weak stability. Thus, TGA, XPS and ICP measurements were performed to ascertain the composition of Au2Cu6-1. The weight loss of 69.15% (Fig. S3–S5†) is consistent with the theoretical value (cal. 68.79%) of AdmSH and (Ph–OMe)2P ligands in Au2Cu6-1. In addition, the XPS and ICP results suggest that the metallic ratio of Au and Cu in Au2Cu6-1 was 1 : 3 (Fig. S6–S8 and Table S3†). Combining the TGA, XPS and ICP results with the almost identical UV-vis spectra (vide infra), we conclude that the structure of Au2Cu6-1 is similar to those of the other Au2Cu6 NCs. In other words, all these Au2Cu6 structures follow the same framework (i.e., Au2Cu6(PR3)2 axis surrounded by six Cu(S-Adm) complexes on the equatorial plane) no matter whether the electron-donating –OMe or electron-withdrawing –F substituents are introduced.

Although the point groups of Au2Cu6-2 and Au2Cu6-3 NCs are both D3h, the crystal system in space group of Au2Cu6-2 is trigonal, unlike the triclinic arrangement of Au2Cu6-3 (see Tables S1 and S2 for more details, ESI†). In addition, Au2Cu6-2 and Au2Cu6-3 exhibit some distinct structural parameters. As shown in Fig. 1, depending on the relative location around the equatorial plane, the S atoms in each NC could be categorized into two groups. The Au–Cu–S angles in Au2Cu6-3 are 85° (with upward S atoms) and 115° (with downward S atoms). This related angles in Au2Cu6-2 are significantly larger (103° or 117°). Meanwhile, the gap between the two planes constituted by the two groups of S atoms (in red planes) is 1.102 Å in Au2Cu6-2, while the gap is remarkably larger in Au2Cu6-3 (2.574 Å). The lower steric hindrance between the different thiol groups in Au2Cu6-3 results in a more regular thiolate ligands configuration (Fig. S9†). In view of the electronic effect, the weaker electron donating ability of P(Ph–F)3 results in inferior electron transfer from phosphine ligands to metallic core in Au2Cu6-3 compared to Au2Cu6-2. Accordingly, the interaction between Au and P is relatively weaker in Au2Cu6-3, and thus the Au–P bond distances Au2Cu6-3 (2.336 Å in average) are slightly longer compared with those in Au2Cu6-2 (2.325 Å in average).

The UV-vis spectra of these three Au2Cu6 NCs were compared to illustrate the ligand effect on the optical adsorption. As
shown in Fig. 2, no obvious shifts occur on the front three peaks (i.e., 325, 420 and 515 nm). In contrary, the final characteristic absorption peak slightly red-shifts from 585 nm of Au$_2$Cu$_6$-1 to 600 nm of Au$_2$Cu$_6$-3 (cal. 15 nm). Therefore, the almost maintained spectra validate the similar framework in these Au$_2$Cu$_6$ NCs, and the similar HOMO–LUMO gap suggests that the similar transition occurs in all these Au$_2$Cu$_6$ NCs. Nonetheless, the alteration of the substituents with different electronic effect induces the slight difference in the optical property. The EDGs tend to elevate both the HOMO and LUMO energies, and sensitive to the electronic effect. The PL peak of Au$_2$Cu$_6$-1 NCs, the digital photographs of the corresponding NCs under visible and UV light.

The PL spectra of Au$_2$Cu$_6$ NCs was characterized to verify the aforementioned inference of electronic effect. Comparing the different fluorescent spectra of Au$_2$Cu$_6$ NCs in Fig. 3, we find that Au$_2$Cu$_6$-1 shows the strongest fluorescence and Au$_2$Cu$_6$-3 shows the weakest one. Specifically, the QY of Au$_2$Cu$_6$-2 was 12.2%. The QY was enhanced to 17.7% when the more electron donating P(Ph–OMe)$_3$ ligands (i.e., Au$_2$Cu$_6$-1) were used. By contrast, the Au$_2$Cu$_6$-3 protected by the less electron donating P(Ph–F)$_3$ ligands shows a lower QY (5.7%). Consequently, the Au$_2$Cu$_6$-1 exhibits a brighter fluorescent response under UV light irradiation compared with the other Au$_2$Cu$_6$ NCs (Fig. 3, insets). In addition, the PL peak of Au$_2$Cu$_6$-1 centered at 656 nm slightly red-shifts to 660 nm in Au$_2$Cu$_6$-2 and 667 nm in Au$_2$Cu$_6$-3. The relatively smaller LUMO–HOMO gap induced by the electronic effect of the substituents accounts for the luminescence red-shift. This observation also correlates well with the similar red-shift tendency in the UV-vis spectra.

The relaxation dynamics of the threeAu$_2$Cu$_6$ NCs were analysed (Fig. S10†). The time constant of the Au$_2$Cu$_6$-1 NC excited-state decay (about 8.6 µs) due to the LMCT process. When the phosphine ligands were altered to PPh$_3$ or P(Ph–F)$_3$, the relaxation time constant was found to decrease to 6.4 and 5.4 µs, respectively. It has been discussed above that the replacement of P(Ph–OMe)$_3$ ligands to PPh$_3$ and P(Ph–F)$_3$ ligands reduced the HOMO–LUMO gap and weakened the LMCT process, which might be the reason of shorter relaxation time constants of Au$_2$Cu$_6$-2 and Au$_2$Cu$_6$-3 NCs.

In summary, the fluorescent intensity of Au$_2$Cu$_6$ NCs was controllable tailored by engineering the phosphine ligands with electron-donating (i.e., –OMe) or electron-withdrawing (i.e., –F) substituents. The distinct electronic effect was successfully used to modulate the LMCT process, and then control the fluorescent intensity. When protected by the electron-rich P(Ph–OMe)$_3$ ligand, the Au$_2$Cu$_6$ NC exhibits enhanced fluorescence with QY = 17.7% compared with that protected by PPh$_3$ (QY = 12.2%). On the contrary, the QY was decreased when the Au$_2$Cu$_6$ NC is protected by relatively electron-deficient ligands (i.e., P(Ph–F)$_3$). In addition, the PL spectrum of Au$_2$Cu$_6$ protected by P(Ph–F)$_3$ displays a slight red-shift compared with other Au$_2$Cu$_6$ NCs, which is similar to the observations in UV-vis spectra. This study presents a controllable strategy to enhance the PL of noble metal NCs, and also sheds lights on synthesizing new class of highly fluorescent NCs.

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