Supporting Information

Copper Inter-Nanoclusters Distance-Modulated Chromism of Self-Assembly Induced Emission

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Figure S1. EDX composition analysis of the Cu NSAMs prepared in LP (a) and BE (b), which reveals the Cu-to-S molar ratio of 1.2/1 and 1.5/1, respectively. Cu LMM XAES spectra of the Cu NSAMs prepared in LP (c) and BE (d), which indicates the Cu(I)/Cu(0) molar ratio of 1/0.2 and 1/0.5, respectively. TGA curves of the Cu NSAMs prepared in LP (e) and BE (f) heated under N_2 atmosphere from 25 to 900ºC, which shows the organic proportion of 71.3% and 66.5%, respectively. The Cu NSAMs are prepared at 50ºC.
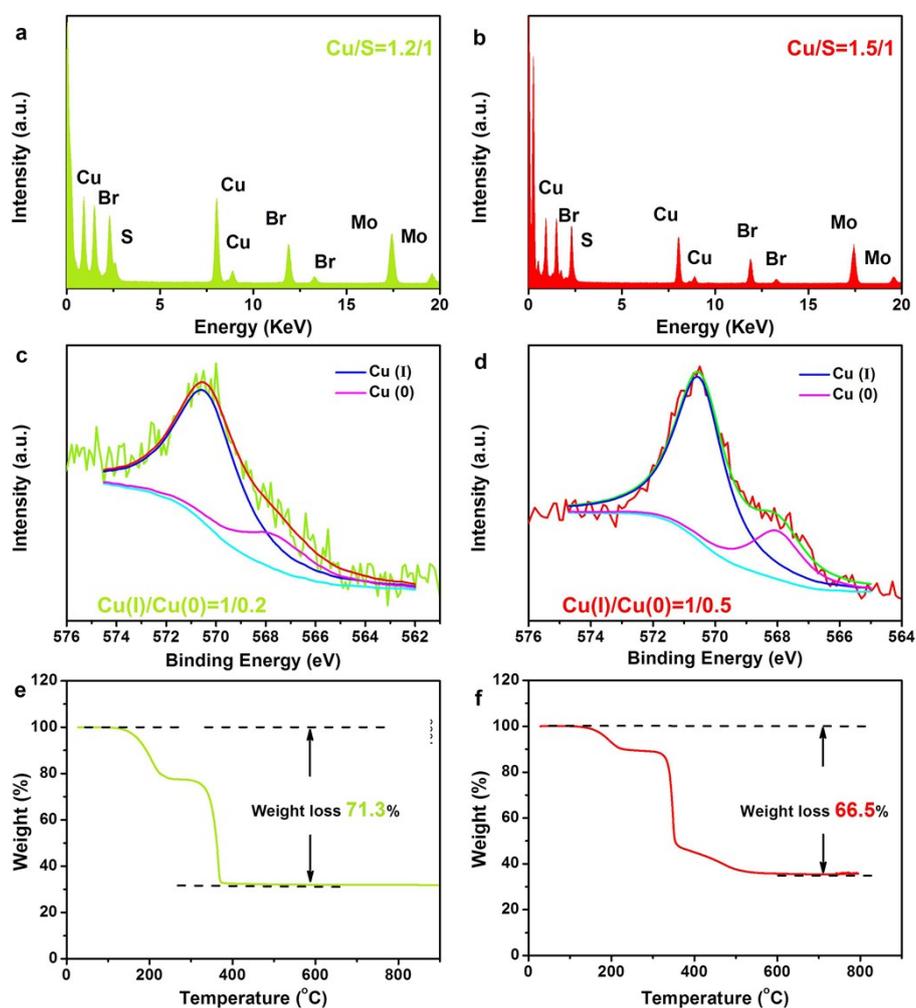
Figure S2. Room-temperature luminescence lifetimes of Cu NSAMs with 365 nm excitation, which exhibit long excited-state lifetime of 7.8, 8.5, 8.6, 8.8, and 9.9 μs. The luminescence lifetime fit parameter is fit = $B_1 exp(-t/\tau_1)$ + $B_2 exp(-t/\tau_2)$. $\tau_{ave} = \dfrac{\Sigma_i B_i \tau_i^2}{\Sigma_i B_i \tau}$.
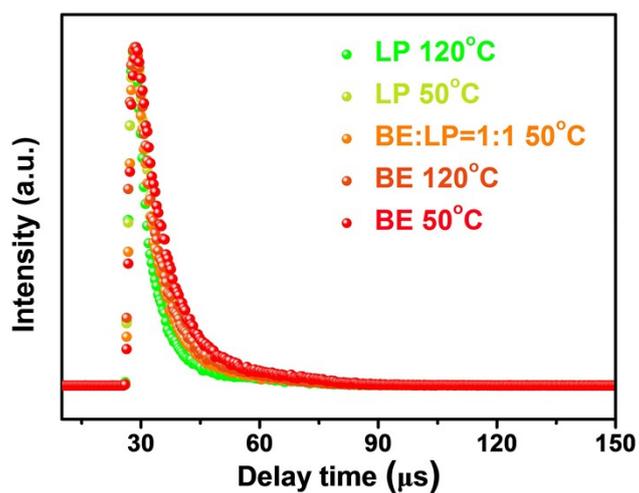
Figure S3. The emission lifetimes of the Cu NSAMs prepared in LP (a) and BE (b) at different PL wavelength. TRES of the Cu NSAMs prepared in LP (c) and BE (d) with various delay times. In all experiments, a 365 nm excitation is adopted.
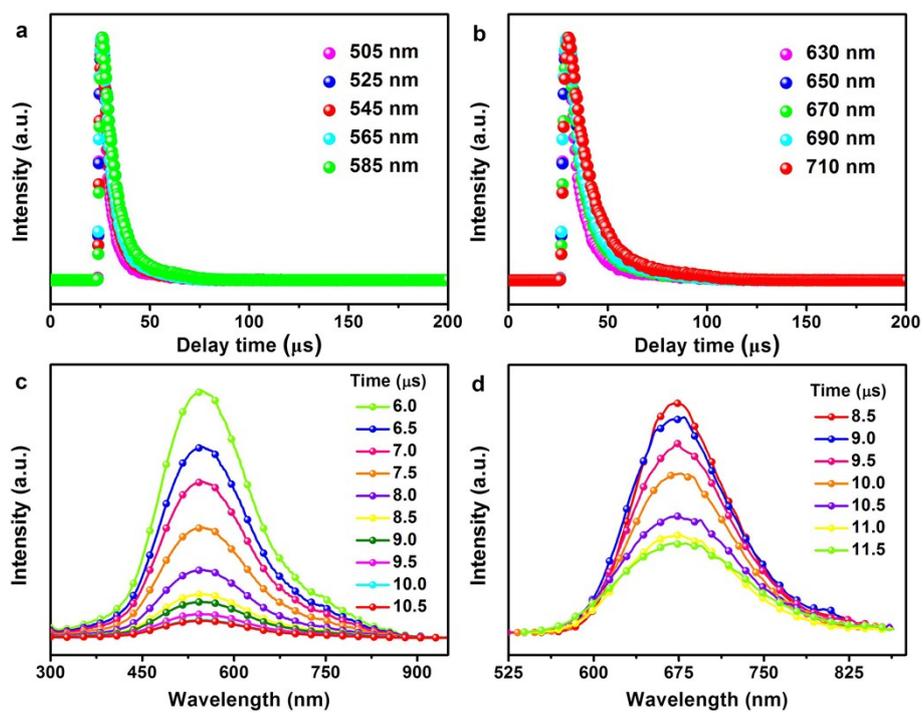
Figure S4. Concentration dependent UV-vis absorption spectra of the Cu NSAMs dispersed in CHCl$_3$ that are originally prepared in LP (a) and BE (b) at 50ºC.
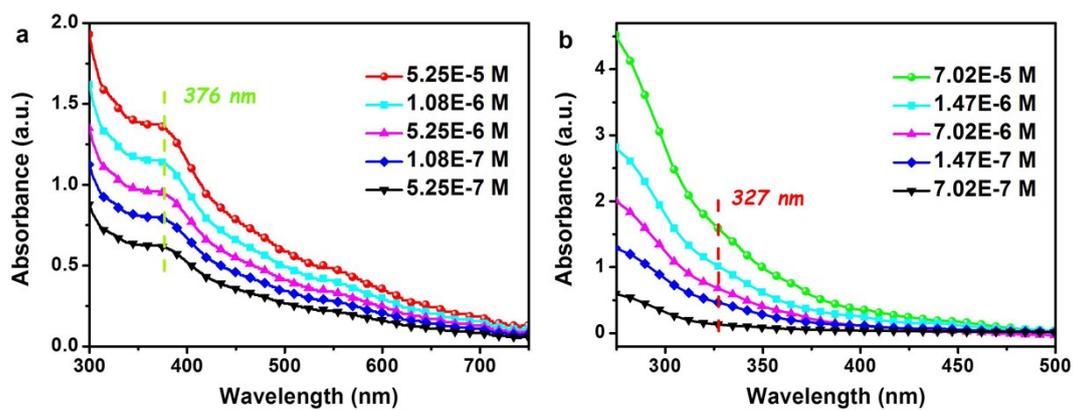
Figure S5. FTIR spectra of the Cu NSAMs prepared in different solvents at 50ºC and the capping ligand of BTP. The disappeared -SH peak indicates the formation of Cu-S bond. The peak around 3000 cm^{-1} attributes to BE residue in the Cu NSAMs.
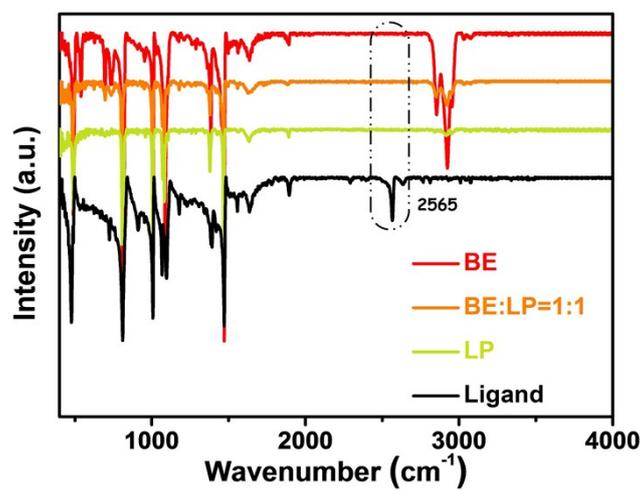
Figure S6. Two kinds of Cu NCs composed of Cu_3BTP_2 and Cu_6BTP_5 are sketched by GaussView 5.0.8 and optimized by VAMP module in Material Studio version 5.0. For the specific arrangement of Cu atoms in the NCs and the distinct ligand conformation together with their distribution on the NCs, the dipole moment of Cu_3BTP_2 and Cu_6BTP_5 is calculated as 3.11 and 0.87 D. The calculations are conducted using AM1 semi-empirical method.[1] The stable Cu_3 and Cu_6 cluster structures shown in (a) and (c) are adopted from [2]. The Cu_3BTP_2 and Cu_6BTP_5 clusters are optimized by AM1 method and the equilibrium structures are shown in (b) and (d).
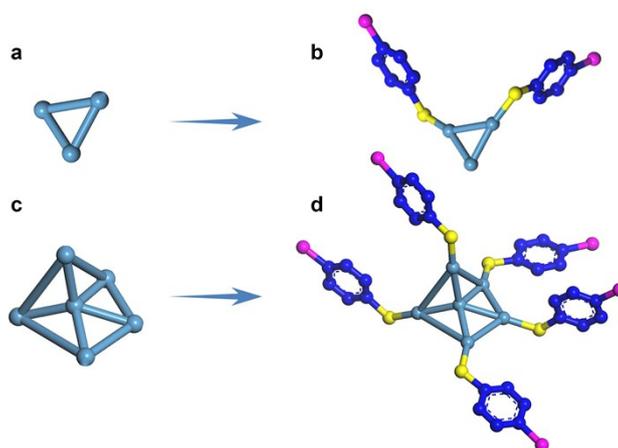
[1] T. Clark, A. Alex, B. Beck, F. Burkhardt, J. Chandrasekhar, P. Gedeck, A. Horn, M. Hutter, B. Martin, G. Rauhut and et al, *VAMP 10.0,* University of Erlangen: Germany, 2003.

[2] P. Calaminici, M. Pérez-Romero, J. M. Vásquez-Pérez and A. M. Köester, *Comput. Theor. Chem.,* 2013, **1021**, 41.

Calculation S1. The conversion of the energy of dipolar attraction. In detail, the energy of dipolar attraction between Cu NCs is calculated according to the classical formula for aligned dipoles $E = -\mu^2/2\pi\varepsilon_0 r(r^2-d_{NC}^2)$, where ε_0 is 8.85×10^{-12} $C^2J^{-1}m^{-1}$. As to the dipole moment $\mu = 0.87$ D of Cu_6BTP_5, estimating the center-to-center interdipolar separation r to be 1.67 nm for diameter $d_{NC} = 0.7$ nm, the energy of dipolar attraction is equal to 0.02 kJ/mole. By estimating the center-to-center interdipolar separation r to be 1.26 nm for diameter $d_{NC} = 0.4$ nm, the energy of dipolar attraction afforded by 3.11 D of Cu_3BTP_2 is 0.64 kJ/mole.

Figure S7. Small angle XRD pattern of the Cu NSAMs prepared in the mixture of LP:BE (v/v=1:1).
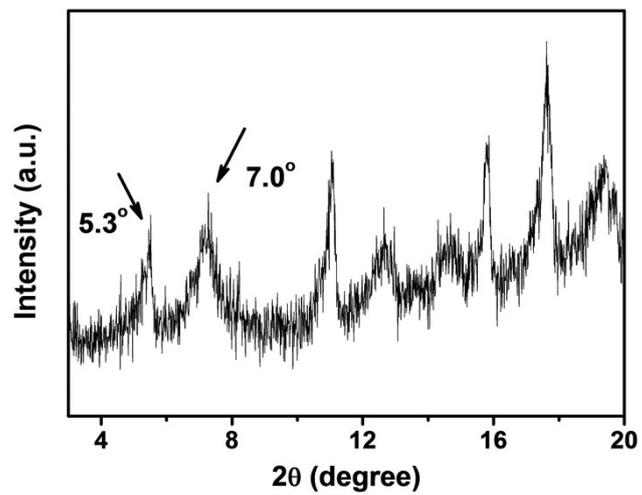
Figure S8. PL excitation spectra of the Cu NSAMs prepared in different solvents at 50ºC.
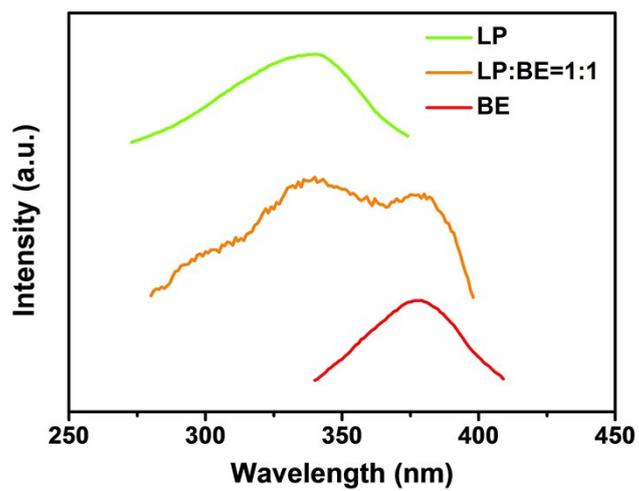
Figure S9. SEM (a, c) and AFM (b, d) images of the Cu NSAMs prepared in LP (a, b) and BE (c, d).
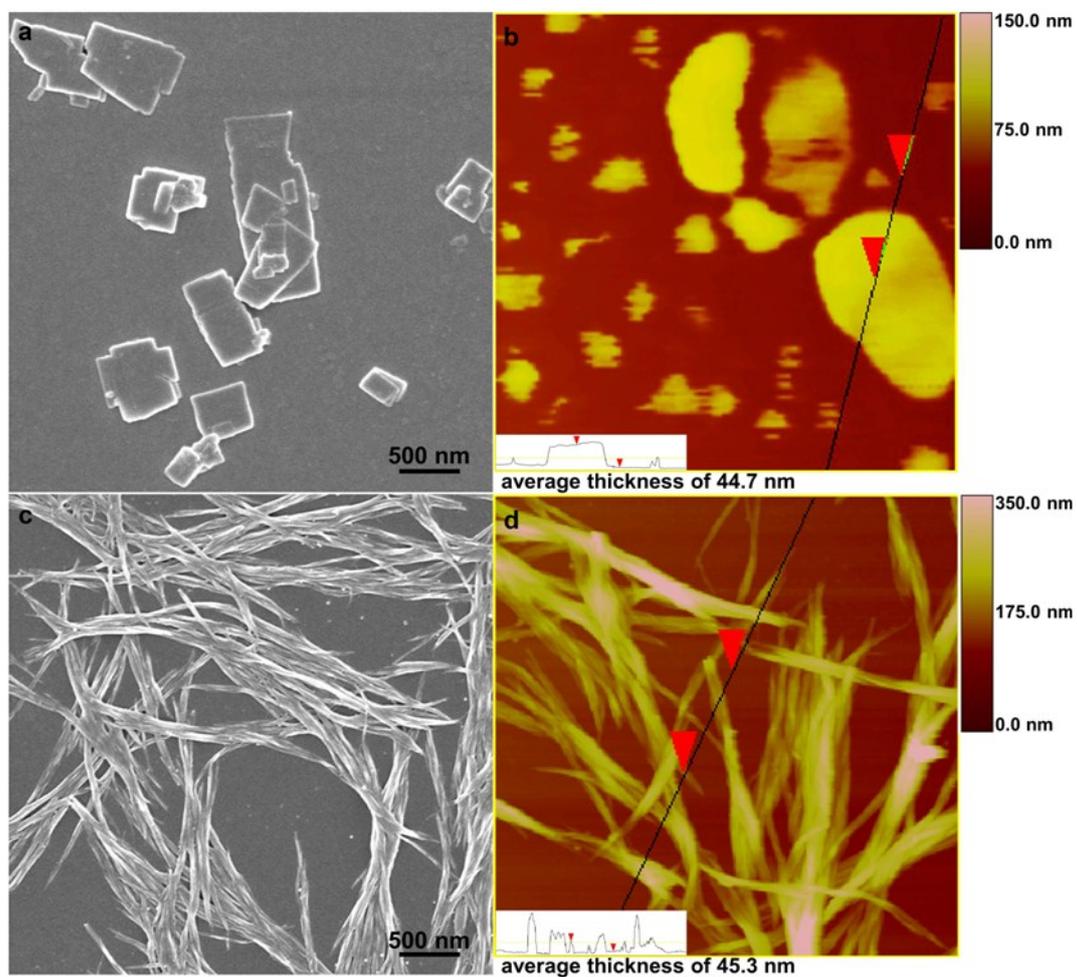
Figure S10. Photographs for the solubility of BTP in LP (a) and BE (b) at 50ºC, indicating that LP is a poor solvent for BTP. Optical (c, d) and PL (e, f) images of the reaction mixtures in LP (c, e) and BE (d, f) after ultrasonication for 5 min at 50ºC. In BE, the reaction mixture already shows weak reddish orange emission. Whereas in LP, the reaction mixture is not luminescent. The PL images are obtained under 365 nm UV lamp irradiation.
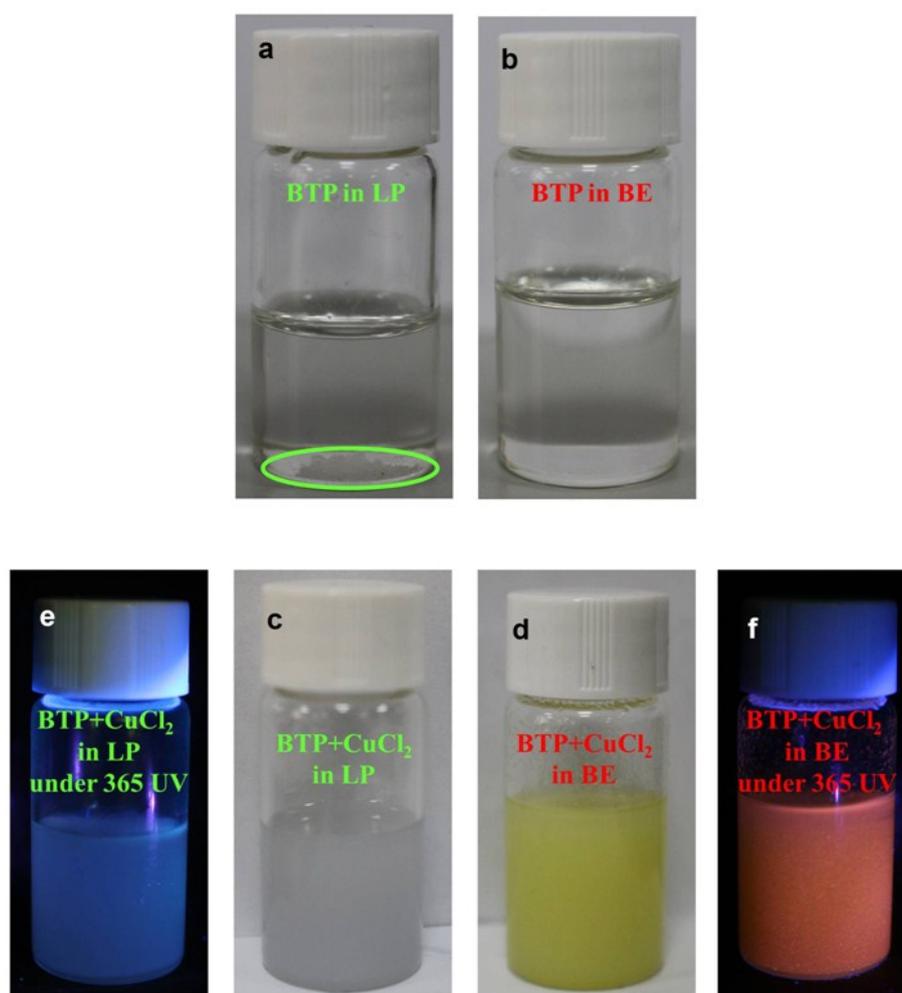
Calculation S2. The calculation of vdW attraction between neighboring Cu NCs composed of Cu_6BTP_5 and Cu_3BTP_2 in the NSAMs, which is 13.7 k_BT and 5.5 k_BT, respectively.

In detail, the vdW interaction between atoms and/or molecules is expressed as the well-known formula:

$$U_{vdw}(r) = -C_{vdw}/r^6$$

where C_{vdw} is a constant characterizing the interacting species and the surrounding medium, r is the distance between atom and/or molecule center. The simplest approach to estimate the macroscopic vdW attraction between two nano-objects composed of many atoms/molecules is a pairwise summation (or integration) of these molecular interactions throughout the volume of two bodies, which results in the following approximation for two spheres with radii a_1 and a_2 separated by a center-to-center distance r:

$$U_{vdw}(r) = \frac{A}{3}\left[\frac{a_1 a_2}{r^2-(a_1+a_2)^2} + \frac{a_1 a_2}{r^2-(a_1-a_2)^2} + \frac{1}{2}\ln\left(\frac{r^2-(a_1+a_2)^2}{r^2-(a_1-a_2)^2}\right)\right]$$

here, A is the Hamaker coefficient and can be estimated according to the Hamaker integral approximation of $A = C_{vdw}\pi^2/v_1 v_2$, where v_i is the molar volume of material i. For -CH-group, $A \approx 5\times10^{-20}$ J ($C_{vdw} \approx 50\times10^{-79}$ Jm^{-6}, $v \approx 30$ Å^3), r is 0.44 nm corresponding to the center-to-center distance for slip parallel benzene dimer.[3, 4] Cylinder diameter (2^a) composed of -CH- is 0.40 nm. With the consideration of hexagonal alignment of the clusters inner NSAMs, the vdW attraction between neighboring Cu_6BTP_5 is calculated as 13.7 k_BT. Whereas the vdW attraction between neighboring Cu_3BTP_2 is calculated as 5.5 k_BT.

[3] S. Grimme, *J. Comput.Chem.,* 2004, **25**, 1463.

[4] A. Puzder, M. Dion and D. C. Langreth, *J. Chem. Phys.,* 2006, **124**, 164105.

Figure S11. TEM image (a), PL image with 365 nm excitation (b), PL emission spectrum (c) and Small angle XRD pattern (d) of the Cu NSAMs prepared in ODE at 50ºC.
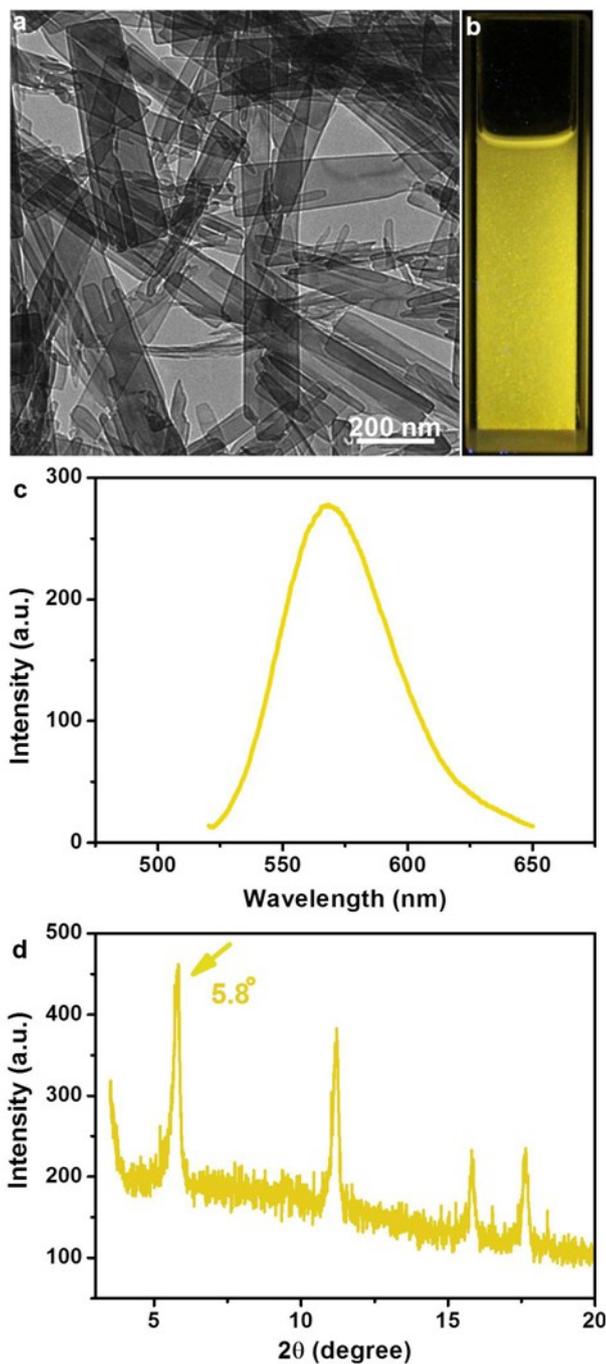
Figure S12. Small angle XRD patterns of the Cu NSAMs prepared in LP (a) and BE (b) respectively at 50 and 120ºC. (c) The relation between inter-NC distance and the position of PL peak. The inter-NC distance is calculated according to the position of XRD diffraction peak.
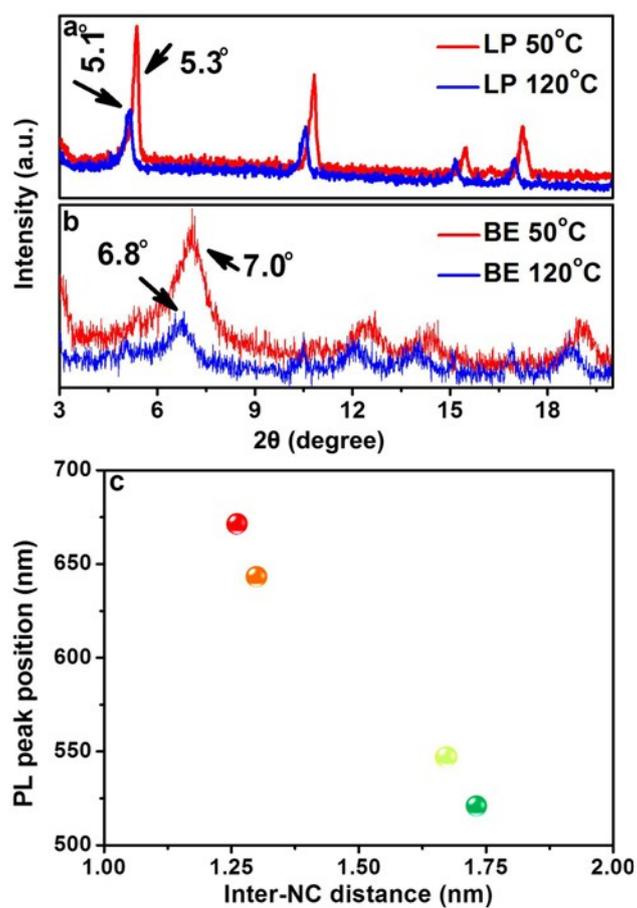
Figure S13. Fluorescent images of the Cu NSAMs prepared in BE (a, b) and LP (c, d) at 120ºC before (a, c) and after grinding (b, d). PL emission spectra of the Cu NSAMs prepared in BE (e) and LP (f) before and after grinding with 365 nm excitation. (g) The comparison of the Small angle XRD patterns of the Cu NSAMs prepared in BE and LP before and after grinding.
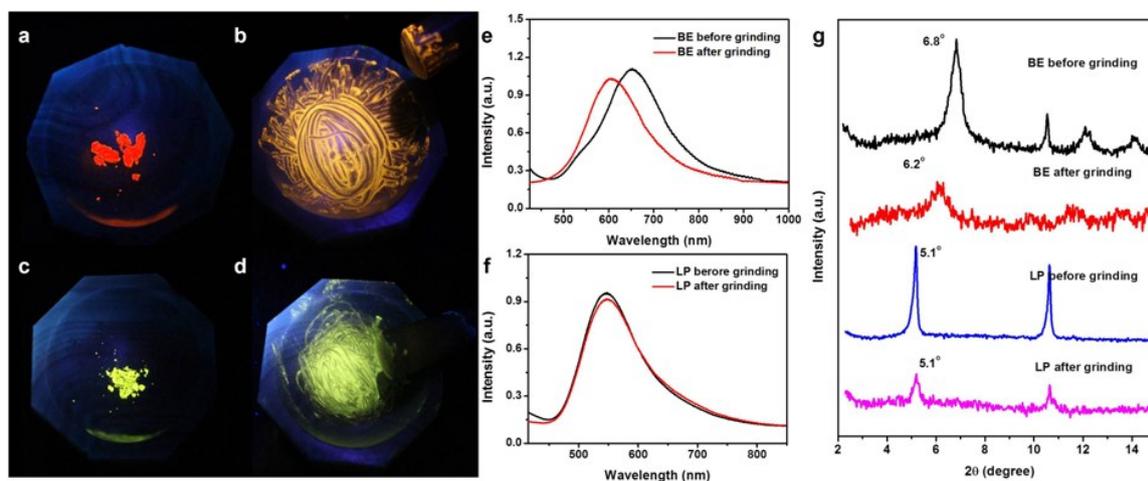
Figure S14. Temporal evolution of the UV-vis absorption spectra of Cu NSAMs prepared in

BE at room temperature.
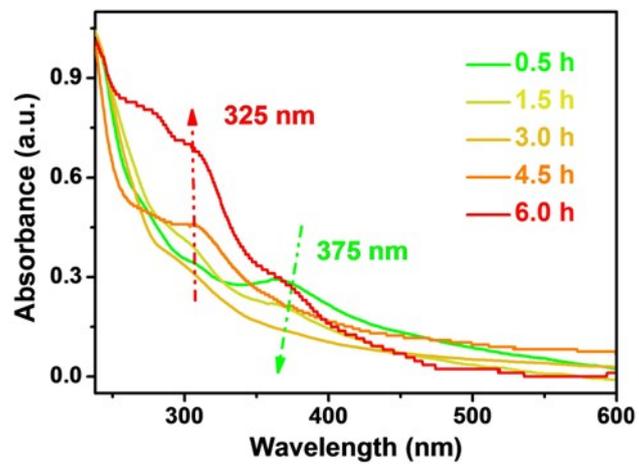
Figure S15. (a) The PL emission spectra of the Cu NSAMs which are prepared in BE with different BTP concentration. (b) The dependence of the PL emission peak position and the appearance time on the concentration of BTP. (c-f) TEM images of the Cu NSAMs which are prepared in BE with BTP concentration of 0.03 (c), 0.11 (d), 0.12 (e) and 0.42 mol/L (f). The concentration of $CuCl_2$ is fixed at 0.06 mol/L. As the concentration of BTP is lower than 0.12 mol/L, the Cu NSAMs are disordered and non-fluorescent.
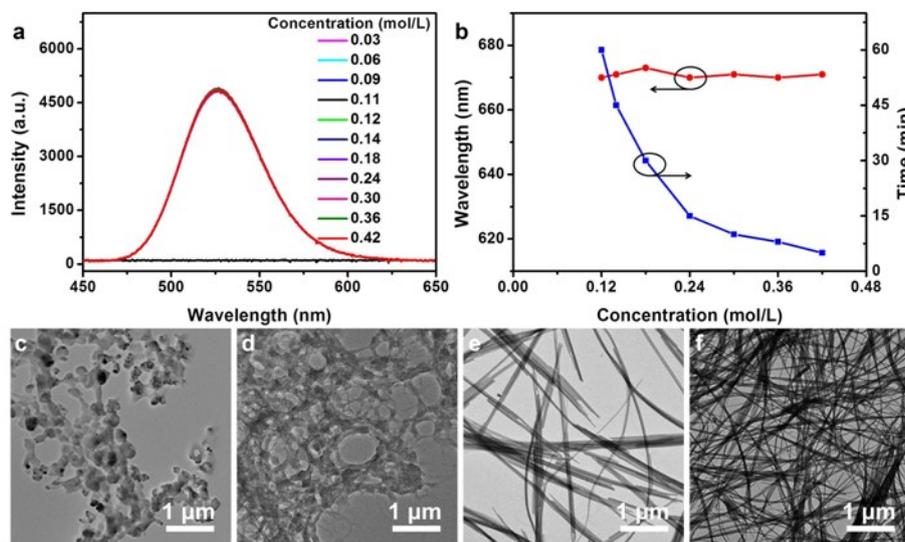
Figure S16. Low (a, c) and high (b, d) magnification TEM images of the Cu NSAMs prepared in BE at 50 ºC as prolonging the reaction duration to 12 (a, b) and 24 h (c, d). Insets in (b, d): TEM size distribution of the NCs.
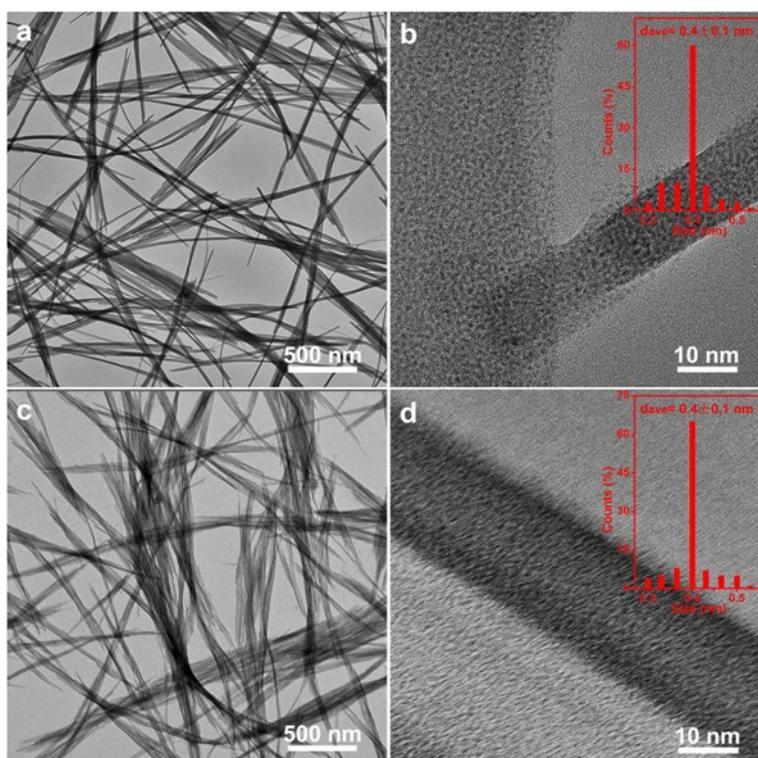
Figure S17. The variation of the PLQYs of Cu NSAMs prepared in LP (a) and BE (b) within 6 months.
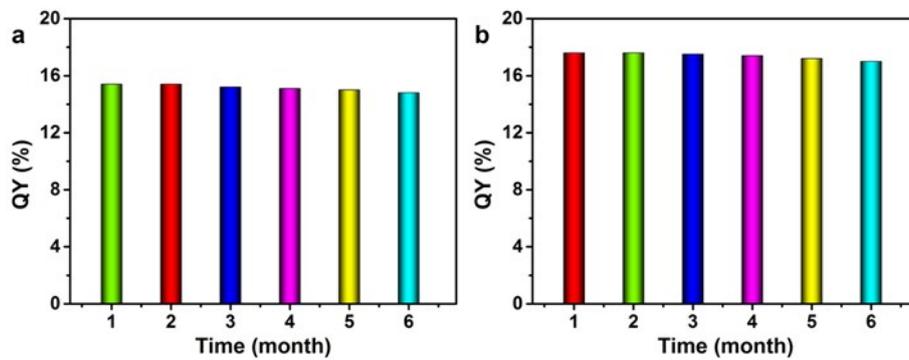
Figure S18. The relation between inter-NC distance and the position of PL emission peaks. The inter-NC distance is calculated according to the position of Small angle XRD patterns. Insets: the corresponding PL images of self-assembled materials prepared in different reaction condition with 365 nm excitation.