New Journal of Chemistry

Supporting Information

pH-Induced Fragmentation of Colloids based on Responsive Self-Assembled Copper(II) Metallopolymers

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Table of Contents

- 1. Absorbance spectrum of (LCu$_2$)$_n$ polymer in methanol.

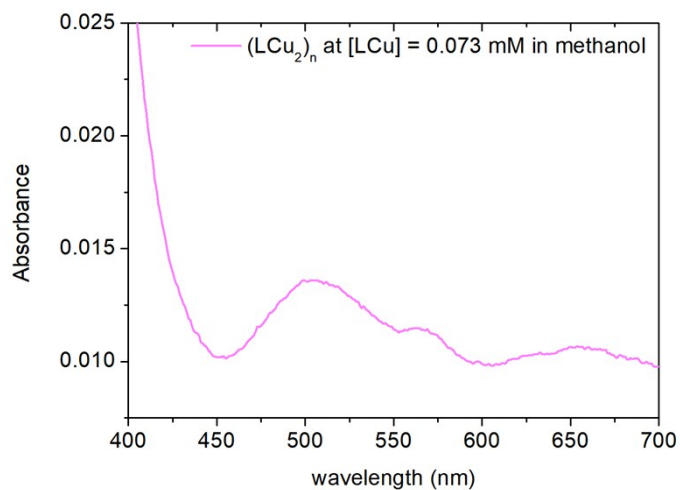**Fig. S1.** Absorbance spectrum of **(LCu$_2$)$_n$** polymer at [**LCu**] = 0.073 mM in methanol.

Fig. S1 shows the UV-vis absorbance spectrum of **(LCu$_2$)$_n$** polymer at [**LCu**] = 0.073 mM in methanol. The absorbance peak at 510 nm is characteristic of the presence of dioxocyclam-Cu^{2+} complex and gives a pink color to **(LCu$_2$)$_n$** polymer in solution. A secondary band is identified at 570 nm. Finally, a broad signal is present at 680 nm. The Absorbance spectrum is in good agreement with previous work.[1]

- 2. Distribution in size of $(LCu_2)_n$ particles characterized by DLS

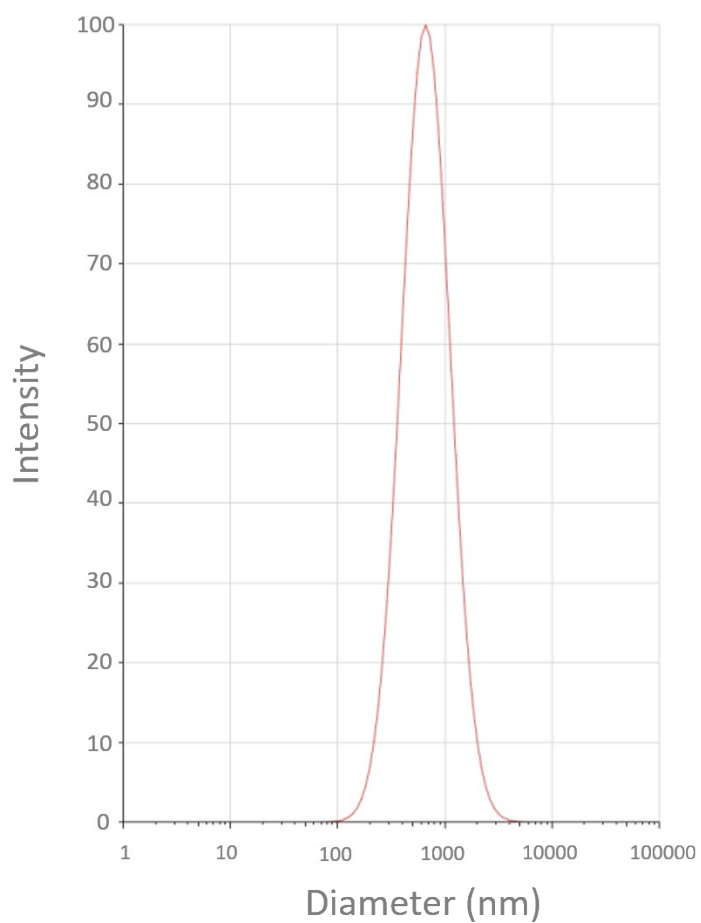**Fig. S2.** Light scattered intensity as function of the diameter of **$(LCu_2)_n$** particles synthesized in 90/10 water / methanol mixture at [**LCu_2**] = 2 μM. Measurement was preformed 16 h after synthesis. The average hydrodynamic diameter is D_H = 664 nm and the polydispersity index is PDI = 0.307.

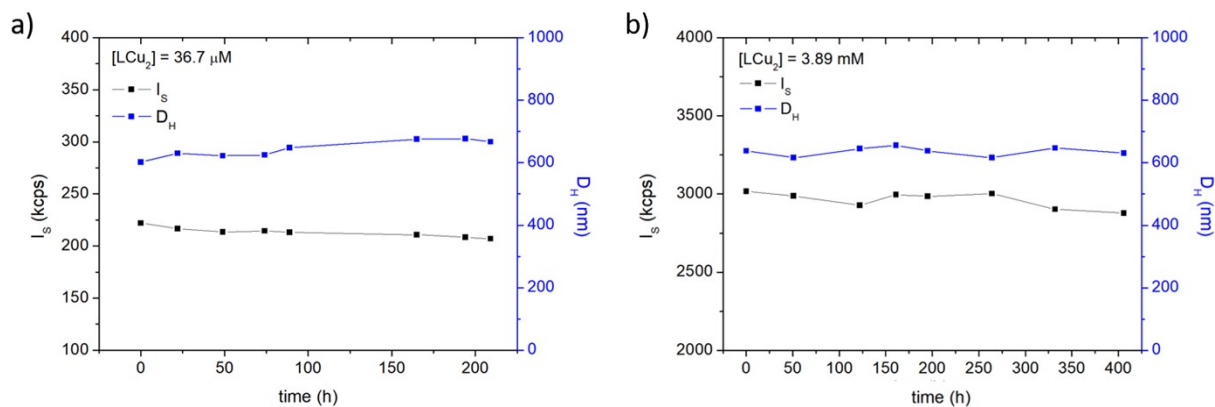## - 3. DLS and SLS analysis of $(LCu_2)_n$ particles

Fig. S3 DLS and SLS analysis of **$(LCu_2)_n$** particles after concentration by evaporation under vacuum. D_H and I_S *versus* time of **$(LCu_2)_n$** particles at (a) [**LCu_2**] = 36.7 µM, and (b) [**LCu_2**] = 3.89 mM. Particles were synthesized at [**LCu_2**] = 2 µM and then concentrated by evaporation under vacuum at 60 °C. t = 0 corresponds to the time when [**LCu_2**] was increased to respectively 36.7 µM and 3.89 mM.

$(LCu_2)_n$ particles at [**LCu_2**] = 2 µM were synthesized in V_{water}/V_{MeOH} = 90/10. 10 hours after the transfer of the MeOH **$(LCu_2)_n$** solution into water (D_H(**$(LCu_2)_n$** at t = 10 h) = 630 ± 25 nm), the solvent was evaporated at T = 60 °C under reduced pressure until concentration became respectively [**LCu_2**] = 36.7 µM and 3.89 mM. Fig. S3 displays D_H and Scattered Intensity (I_S) measurements as function of time of these dispersions at two concentrations. D_H before and after concentration process are similar, indicating that the particles did not aggregate. The colloidal stability of the dispersions is demonstrated by the constant values of both D_H and I_S over weeks.

- 4. Wide Angle X-ray Scattering (WAXS) of $(LCu_2)_n$ particles

$(LCu_2)_n$ particles at $[LCu_2]$ = 2 μM were synthesized in V_{water}/V_{MeOH} = 90/10. 10 hours after the the transfer of MeOH $(LCu_2)_n$ solution into water ($D_H((LCu_2)_n$ at t = 10 h) = 630 ± 25 nm), the solvent was evaporated at T = 60 °C under reduced pressure until concentration became respectively $[LCu_2]$ = 36.7 μM and 3.89 mM corresponding to $c_{(LCu_2)} = 0.36\ wt\%$. 51 h after having being concentrated, the particles were characterized by a D_H = 617 ± 25 nm and a polydispersity PDI = 0.286, and were analyzed by WAXS.
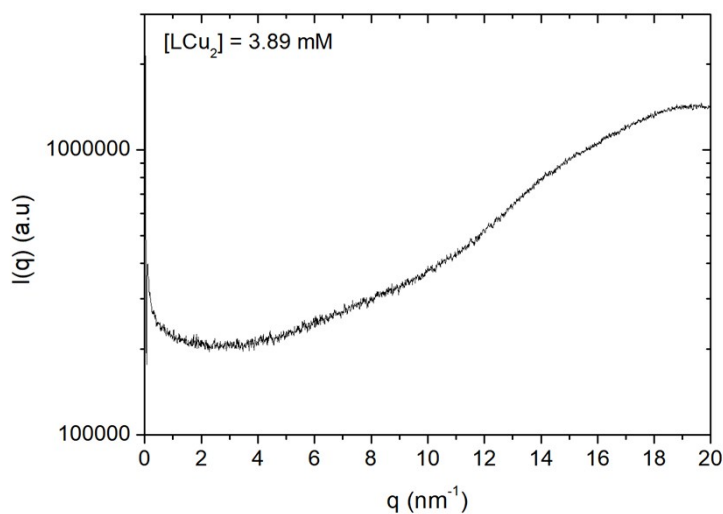
Fig. S4. WAXS pattern displaying I(q) *versus* q of $(LCu_2)_n$ nanoparticles at $[LCu_2]$ = 3.89 mM ($c_{(LCu_2)} = 0.36\ wt\%$).

Fig S4 displays the scattering pattern of an aqueous $(LCu_2)_n$ particle dispersion at $[LCu_2]$ = 3.89 mM. The overall shape of the curve is attributed to the scattering of the solvent whereas no peaks which would be related to $(LCu_2)_n$ particles themselves or to their microstructure are visible.

- 5. Electron Dispersive Spectroscopy (EDS) of (LCu$_2$)$_n$ particles

(LCu$_2$)$_n$ nanoparticles were synthesized at [LCu$_2$] = 2 μM and V_{water}/V_{MeOH} = 97.5/2.5. After 28 h of growth, the sample was dried on a Nickel grid and analyzed by EDS at 200 kV using magnification of 120520 x.
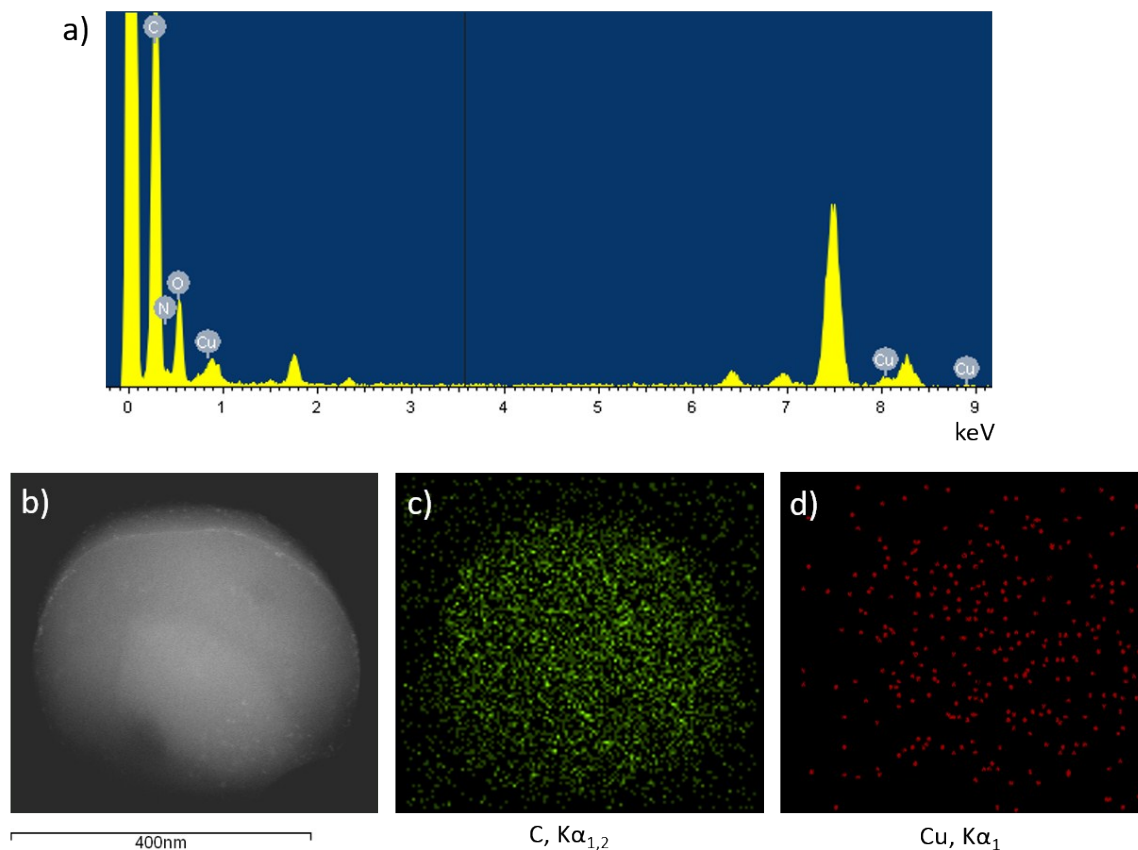

Fig. S5. **a)** EDS spectrum of the **(LCu$_2$)$_n$** particle pictured by TEM in "b". The spectrum reveals the presence of C, O, N and Cu. **b)** TEM image of the area on which is performed EDS. The grey object is a **(LCu$_2$)$_n$** particle. **c)** Image obtained using energies corresponding to the K$\alpha_{1,2}$ rays of Carbon. C element appears in green. **d)** Image obtained using energy corresponding to the Kα_1 ray of Copper. Cu element appears in red.

Fig. S5.b is a TEM image of a **(LCu$_2$)$_n$** particle. The EDS survey spectrum presented in Fig. S5.a corresponds to the scanning of the area of the grid shown in Fig. S5.b. The peaks of the spectrum are interpreted as corresponding to K$\alpha_{1,2}$ of C at 0.28 keV, K$\alpha_{1,2}$ of N at 0.39 keV, K$\alpha_{1,2}$ of O at 0.52 keV and L$_l$ of Cu at 0.81 keV, L$\alpha_{1,2}$ of Cu at 0.930 keV, K$\alpha_{1,2}$ of Cu at 8.04 ± 0.01 keV, and K$\beta_{1,3}$ of Cu at 8.90 keV. Fig. S5.c and d are images of the scanned area highlighting the presence of C and Cu through the detection of energies corresponding to the K$\alpha_{1,2}$ of C and to the Kα_1 of Cu, respectively.

- 6. Kinetic of depolymerization of (LCu₂)ₙ particles upon addition of HCl

(LCu₂)ₙ particles were synthesized in a 90/10 water/methanol mixture at [**LCu₂**] = 2 µM. After 46 h of growth, particles were concentrated to [**LCu₂**] = 36.7 µM by evaporation under reduced pressure at 60 °C. Once concentrated, pH of the dispersion was 7 and D_H of the particles was 675 ± 25 nm. 24 h after concentration, respectively 2.5, 100 and 1000 equivalents of HCl by **LCu₂** monomer unit were added to samples of **(LCu₂)ₙ** particles. Fig. S6.1 displays the Hydrodynamic diameters (D_H) measured by DLS in function of time for the three samples. Fig. S6.2 presents the absorbance spectra of samples with 100 (S6.2.a) and 1000 (S6.2.b) equivalents of HCl over time. t = 0 h corresponds to the time just before addition of HCl.
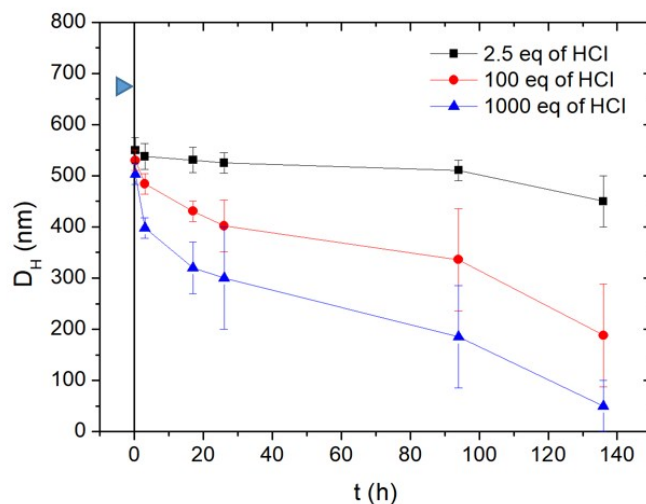

Fig. S6.1 Evolution of hydrodynamic diameters (D_H) measured by DLS as function of time for **(LCu₂)ₙ** particles at [**LCu₂**] = 36.7 µM upon addition of 2.5 (black), 100 (red) and 1000 (blue) equivalents of HCl by **LCu₂** monomer unit, respectively. t = 0 corresponds to the time when HCl was injected into particles dispersions. The blue triangle indicates the D_H of the particles before introduction of HCl.
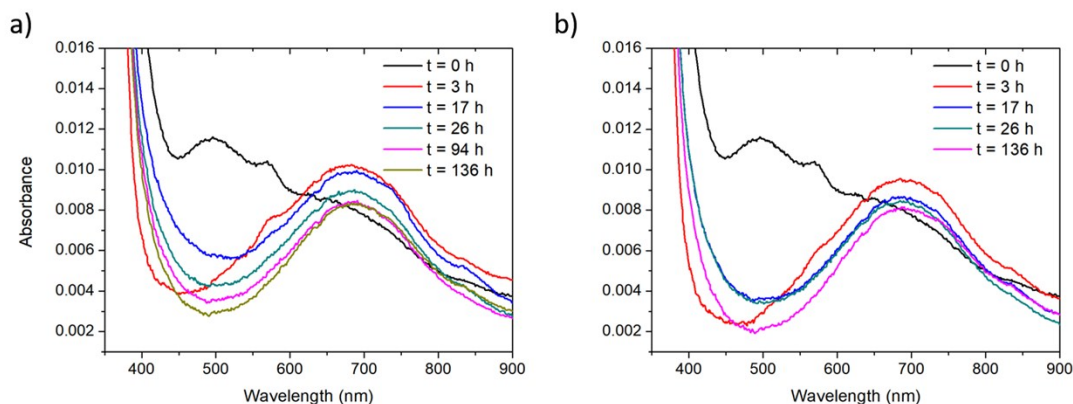

Fig. S6.2 Evolution of the UV-vis absorbance spectra of **(LCu₂)ₙ** particles at [**LCu₂**] = 36.7 µM upon addition of 100 (a) and 1000 (b) equivalents of HCl by LCu₂ monomer unit, as function of time. t = 0 h corresponds to the time just before addition of acid. Peaks at 500 nm and 690 nm are characteristic of **(LCu₂)ₙ** polymer and **LH₂Cu₂** monomer, respectively.

- 7. Protonation using *o*-nitrobenzaldehyde (NBA) as photo-acid generator (PAG)
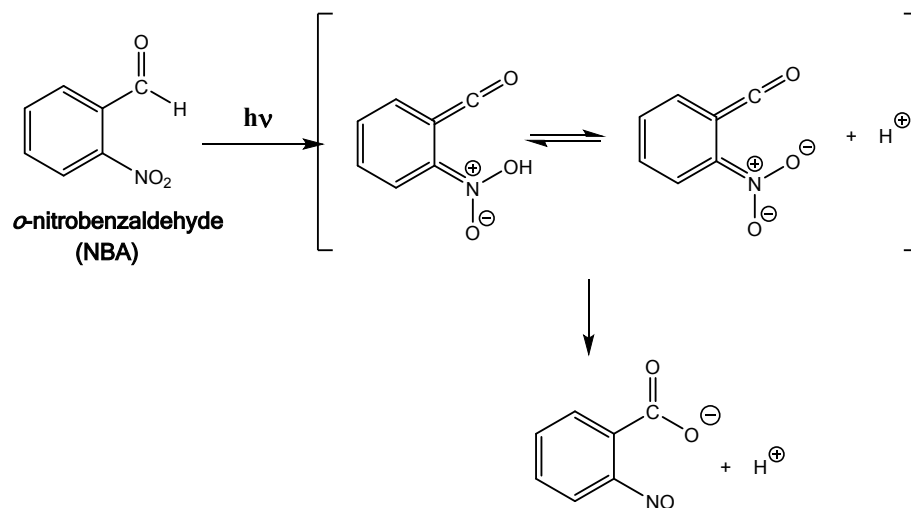

Fig. S7.1. Reactivity and H^{+} release during illumination of *o*-nitrobenzaldehyde.[2-4]
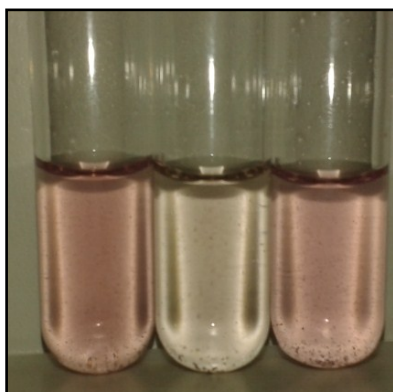

Fig. S7.2. Tests of photo-induced protons release in MeOH solutions of **(LCu₂)ₙ** polymer. Left: **(LCu₂)ₙ** alone upon illumination by UV light (365 nm). Center: after illumination (365 nm) in the presence of NBA. Right: in the presence of NBA without illumination. The fragmentation of the pink polymer to the dinuclear Cu²⁺ complex is observed only when the solution is irradiated in the presence of NBA.

- 8. Depolymerization of (LCu$_2$)$_n$ particles triggered by photo-induced liberation of protons

The preparation of the particles used in these experiments is described in part 3.3 of the article. The photo-acid generator, o-nitrobenzaldehyde (NBA), and its proton-release mechanism are presented in section 7 of this document.
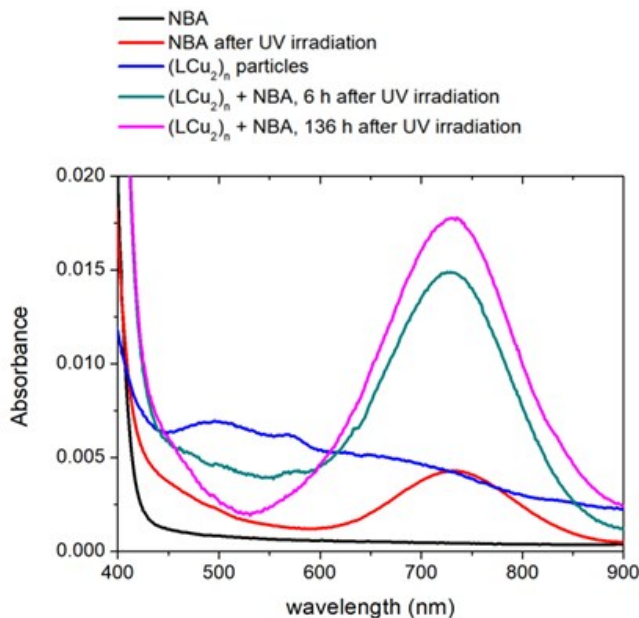

Fig. S8.1 Absorbance spectra of: NBA aqueous solution (protected from light before measurement) at [NBA] = 1.1 mM (black); NBA aqueous solution at [NBA] = 1.1 mM which has been irradiated by UV light (365 nm) for 2h (red); **(LCu$_2$)$_n$** particles at [**LCu$_2$**] = 22 μM (blue); mixture of **(LCu$_2$)$_n$** particles and NBA with [**LCu$_2$**] = 22 μM and [NBA] = 1.1 mM (50 equivalents of NBA by **LCu$_2$** monomer), irradiated by UV light for 2h, and measured 6 h (green) and 136 h (pink) after the end of irradiation.

Note: Once irradiated, NBA is transformed in new compounds having a strong and broad absorbance peak centered at 730 nm (Fig. S8.a, red curve). Therefore, supposedly released, the presence of **LH$_2$Cu$_2$** cannot be unambiguously evidenced by its characteristic absorbance peak centered at 690 nm.
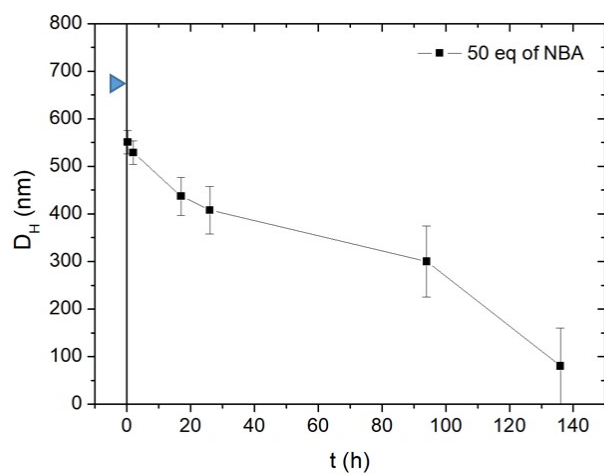
Fig. S8.2 Evolution of hydrodynamic diameters (D_H) measured by DLS as function of time for a mixture of **(LCu$_2$)$_n$** particles and NBA as **[LCu$_2$]** = 22 µM and [NBA] = 1.1 mM (50 equivalents of NBA by **LCu$_2$** monomer) which has been irradiated by UV light (365 nm) for 2h. t = 0 corresponds to the end of the 2 h of UV illumination. The blue triangle indicates the D_H of the particles before introduction of HCl.

- 9. Depolymerization of (LCu$_2$)$_n$ particles triggered by addition of a competing chelator

Fig. S9.1.a shows that aqueous solution of EDTA at 3 mM and with pH adjusted to 7.2 does not absorb in the visible range (black curve) whereas CuCl$_2$ solution at 2.31 mM strongly absorbs around $\lambda_{max}(CuCl_2)$ = 807 nm. Absorbance spectrum of Cu^{2+}-EDTA complexes, prepared by mixing CuCl$_2$ and EDTA as $n_{EDTA}/n_{CuCl_2} = 1.3$ and [EDTA] = 3 mM and [CuCl$_2$] = 2.31 mM, exhibits a peak at $\lambda_{max}(Cu^{2+} - EDTA)$ = 732 nm.
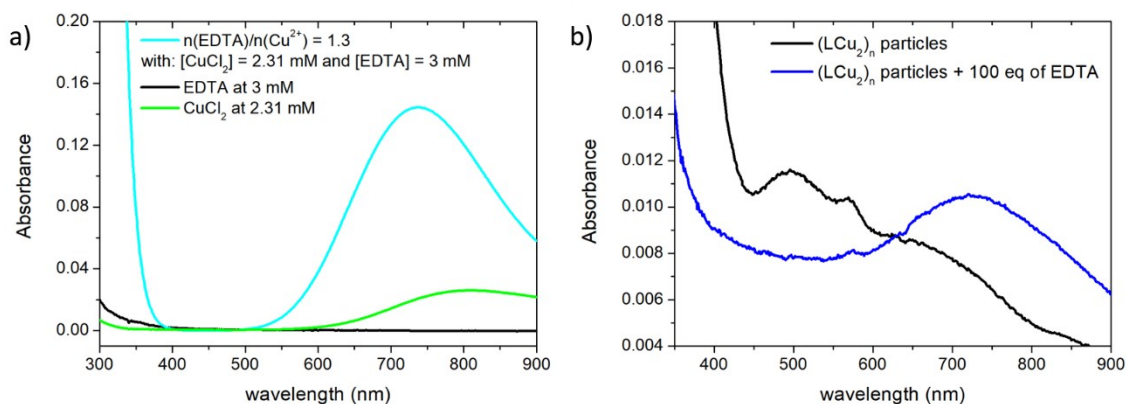

Fig. S9.1 a) UV-visible analysis of Cu^{2+}-EDTA complex. Absorbance spectra of an EDTA solution at [EDTA] = 3 mM (black curve), a CuCl$_2$ solution at [CuCl$_2$] = 2.31 mM (green curve) with a maximum of absorbance at $\lambda_{max}(CuCl_2)$ = 807 nm, and a mixture of EDTA and CuCl$_2$ with $n_{EDTA}/n_{CuCl_2} = 1.3$, [EDTA] = 3 mM and [CuCl$_2$] = 2.31 mM (blue-green curve) with a maximum of absorbance at $\lambda_{max}(Cu^{2+} - EDTA)$ = 732 nm. Spectra were measured 24 h after preparation of the samples. **b)** Effect of addition of EDTA on **(LCu$_2$)$_n$** particles. UV-vis absorbance spectra of **(LCu$_2$)$_n$** particles at [**LCu$_2$**] = 36.7 µM (see part 3.3) (black curve), and of the same particles 260 h after addition of 100 equivalents of EDTA by **LCu$_2$** monomer units (blue curve). The spectrum corresponding to **(LCu$_2$)$_n$** particles and EDTA mixture (blue curve) exhibits an absorption band at 732 nm.

Fig. S9.2 shows pictures of concentrated **(LCu₂)ₙ** particles 48 h (Fig. S9.2.a) and 96 h (Fig. S9.2.b) after injection of 100 equivalents of EDTA by **LCu₂** monomer unit. 2.846 mL of EDTA solution at 0.27 M were added to 2 mL of (LCu₂)ₙ particles at [**LCu₂**] = 3.89 mM (prepared as described in part 2.3), resulting in a pH = 7.2 mixture at [**LCu₂**] = 1.57 mM and [EDTA] = 157.2 mM (100 equivalents of EDTA by **LCu₂** monomer). The sample was incubated at 22°C.
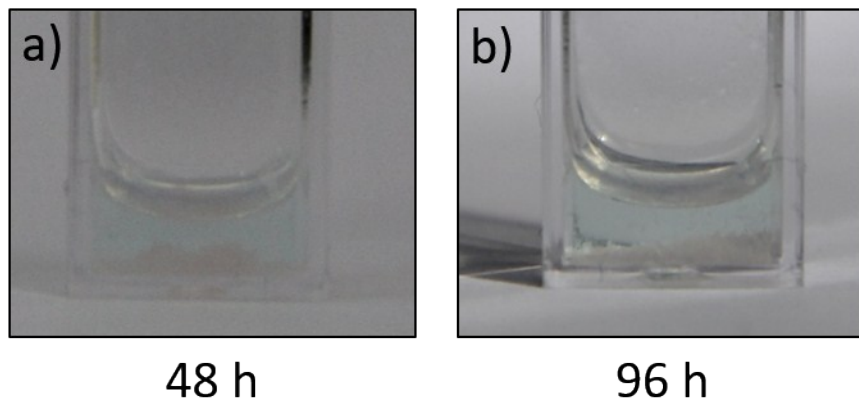

Fig. S9.2 Pictures of **(LCu₂)ₙ** particles at [**LCu₂**] = 3.51 mM mixed with 100 equivalents of EDTA by LCu₂ monomer unit after 48 h (**a**) and 96 h (**b**) of incubation. Blue-green solutes reveal the presence of Cu²⁺-EDTA complex. The slightly pink precipitate visible at t = 48 h suggests the presence of **LCu** units, whereas the white one visible at t = 96 h suggests that this solid matter is copper-free **L** ligand.

- 10. References

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