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Self-Assembly of Copper Nanoclusters: Isomeric Ligand Effect on Morphological Evolution

Sarita Kolay[a], Subarna Maity[a], Dipankar Bain[a], Sikta Chakraborty[a], and Amitava Patra[a,b]*

[a]School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India

[b]Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Email address of the correspondence; E-mail: msap@iacs.res.in Phone: (91)-33-2473-4971, Fax: (91)-33-2473-2805

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Experimental Section

Materials: Copper nitrate trihydrate [$Cu(NO_3)_2.3H_2O$] was purchased from Loba Chemie. 2,4-Dimethylbenzenethiol (2,4-DMBT), 2,5-dimethylbenzenethiol (2,5-DMBT), 2,6-dimethylbenzenethiol (2,6-DMBT), tetraphenylphosphonium bromide (PPh4Br) and trans-2-3-[3-(4-tert- Butylphenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB) were purchased from Sigma Aldrich. Sodium borohydride ($NaBH_4$), methanol (MeOH), and dichloromethane (DCM) were purchased from Merck. Milli-Q water (18.2 MΩ) was used to prepare the solutions.

Preparation of self-assembled CuNCs capped with 2,4-DMBT

26.58 mg of $Cu(NO_3)_2.3H_2O$ (0.11 mmol) was dissolved in 0.5 mL methanol in a round bottom flask. Next, 9 mL DCM was added to the flask and the solution was allowed to cool with stirring under an ice bath for 20 min. Then, 45 µL 2,4-DMBT (0.33 mmol) was added which produced a thick brown color solution indicating the formation of Cu-thiolate complexes. A freshly prepared PPh$_4$Br (3 mg, 0.007 mmol) in 0.25 mL MeOH was added to this yellow solution. Next, 1 mL freshly prepared, ice-cold aqueous $NaBH_4$ (30 mg in 1 mL) was added dropwise. The color of the reaction mixture changed from light brown to bright yellow. This mixture was allowed to stir for 5 hours under the ice bath and then centrifuged at 5000 rpm for 5 minutes. Dark greenish-yellow color self-assembled Cu NCs were formed with red emission.

Preparation of self-assembled CuNCs capped with 2,5-DMBT

45 µL 2,5-DMBT was used instead of 2,4 isomer used in the above synthesis. All the other conditions were kept unchanged during the synthesis. Yellowish-brown color self-assembled Cu NCs were formed with red emission.

Preparation of self-assembled CuNCs capped with 2,6-DMBT

45 µL 2,6-DMBT was used instead of 2,4 isomer used in the above synthesis. All the other conditions were kept unchanged during the synthesis. Muddy color self-assembled Cu NCs were formed with red emission.

Purification

The obtained precipitates were washed with MeOH and centrifuged at 5000 rpm for 5 minutes. The precipitates were collected, air-dried, and dispersed in DCM for further characterization.

Instrumentation

The transmission electron microscopy (TEM) images were obtained by using a JEOL-JEM-2100F transmission electron microscope. The field emission scanning electron microscopy (FE-SEM) images were recorded using JEOL, JSM-6700F microscope and atomic force microscopy (AFM) images was obtained using VEECO, dicp – II instrument for morphological characterization of the assembled structure. The mass of the Cu NCs was measured by MALDI-TOF mass spectrometry on a Bruker Daltonics Autoflex II TOF/TOF system. A pulse laser of 337 nm was used and a saturated [3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) solution was selected as the matrix for the MALDI-TOF measurements. Powder X-ray diffraction (PXRD) was performed by using a Bruker D8 ADVANCE powder diffractometer having Cu Kα radiation (1.546°). Fourier-transform infrared (FTIR) spectroscopy measurements were performed on a SHIMADZU-made FTIR-8300 Spectrometer using KBr pellets. The XPS measurements were procured using an Omicron Nanotechnology instrument. ^{1}H NMR spectra were recorded on Bruker AVANCE III 400 MHz spectrometers in deuterated solvents. Proton chemical shifts are reported in ppm (δ) with the solvent CDCl$_3$ (δ 7.26 ppm). Room temperature absorption spectra were recorded with a Shimadzu-made UV-Vis spectrophotometer using a cuvette with a path length of 1 cm. The emission spectra of all of the samples were taken with a FluoroMax-P (HORIBA Jobin Yvon) luminescence spectrophotometer. All the photophysical experiments were done by dispersing the samples in toluene and recorded at room temperature (UV, PL and TCSPC). The quantum yield (QY) of Cu NCs was measured using quinine sulfate as reference dye using the following equation.

$$QY_s = (F_s \times A_r \times \eta_s^2 \times QY_r) / (F_r \times A_s \times \eta_r^2) \tag{1}$$

where, F_s and F_r are the integrated fluorescence emission of the sample and the reference respectively. A_s and A_r are the absorbance of the sample and the reference respectively at the excitation wavelength. QY_s and QY_r are the quantum yields of the sample and the reference ($QY_r = 0.53$). The refractive indices of the solvents used for the preparation of the sample and reference are given by η_s (1.4969) and η_r (1.33) respectively (here the solvent used for sample preparation was toluene and water was used for the reference). For time-correlated single-photon counting (TCSPC) measurement, the samples were excited at 370 nm by Spectra-LED-370. The fluorescence decays were collected on a Hamamatsu MCP photomultiplier. The following expression was used to analyze the experimental time-resolved fluorescence decays, P(t):

$$P(t) = b + \sum_{i}^{n} \alpha_i \exp(-t/\tau_i) \tag{2}$$

Here, n is the number of emissive species, b is the baseline correction, and α_i τ_i are the pre-exponential factor and the excited-state fluorescence decay time associated with the ith component. The average decay time $\langle \tau \rangle$ was calculated from the following equation.

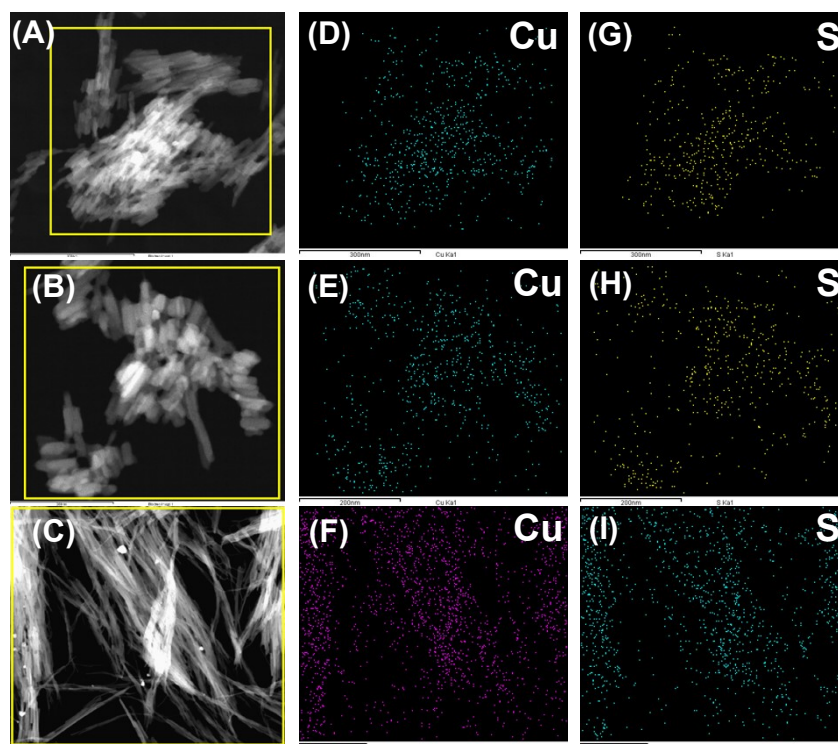$$\langle \tau \rangle = \sum_{i=1}^{n} \beta_i \tau_i \tag{3}$$

Where $\beta_i = \alpha_i / \sum \alpha_i$ and is the contribution of the decay component.[1]
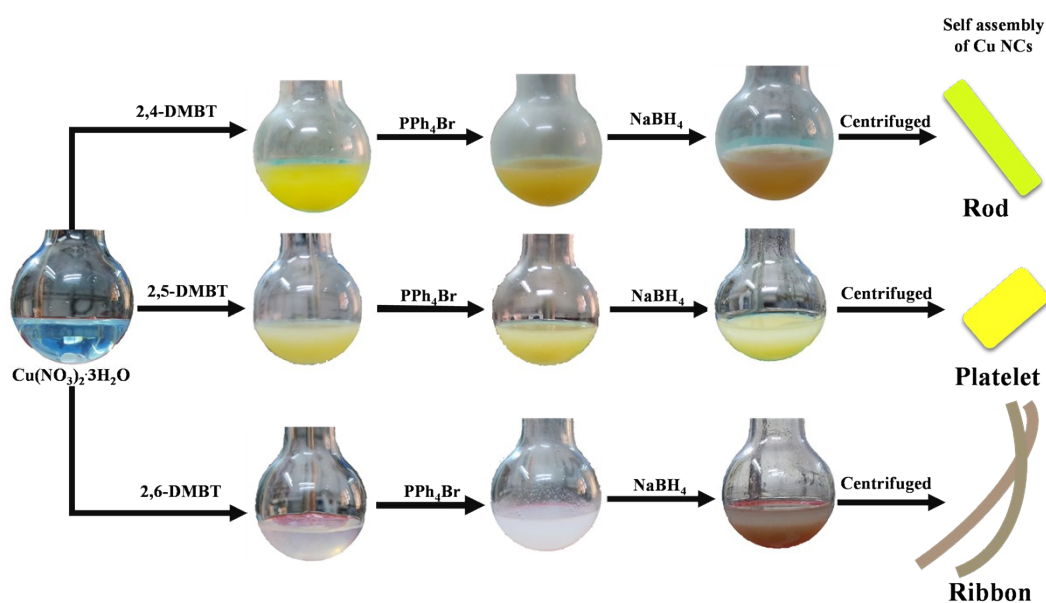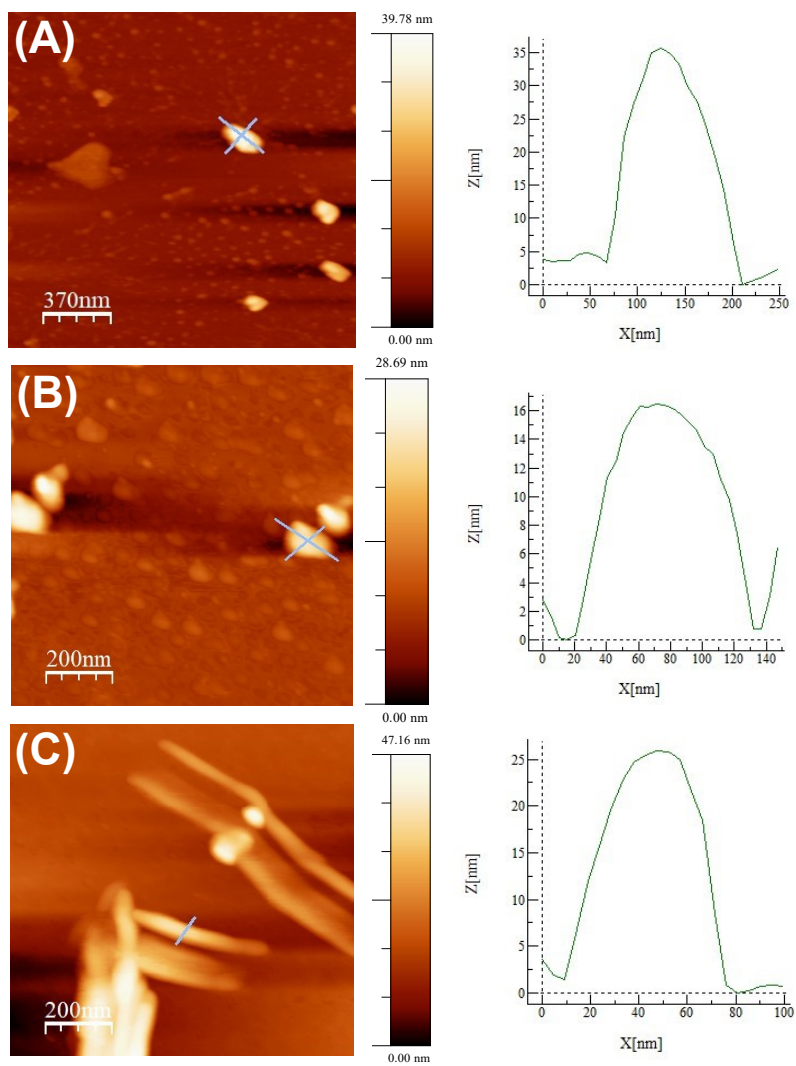

Fig. S1: Schematic representation of the synthetic procedure of the self-assembled Cu NCs
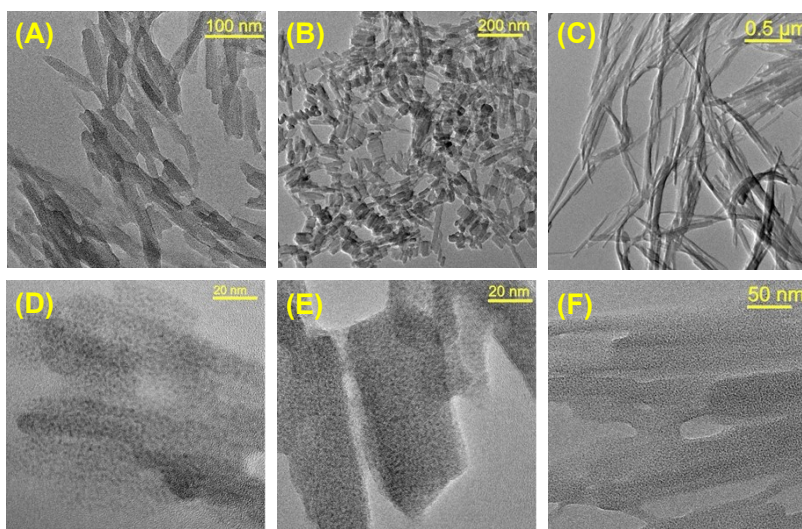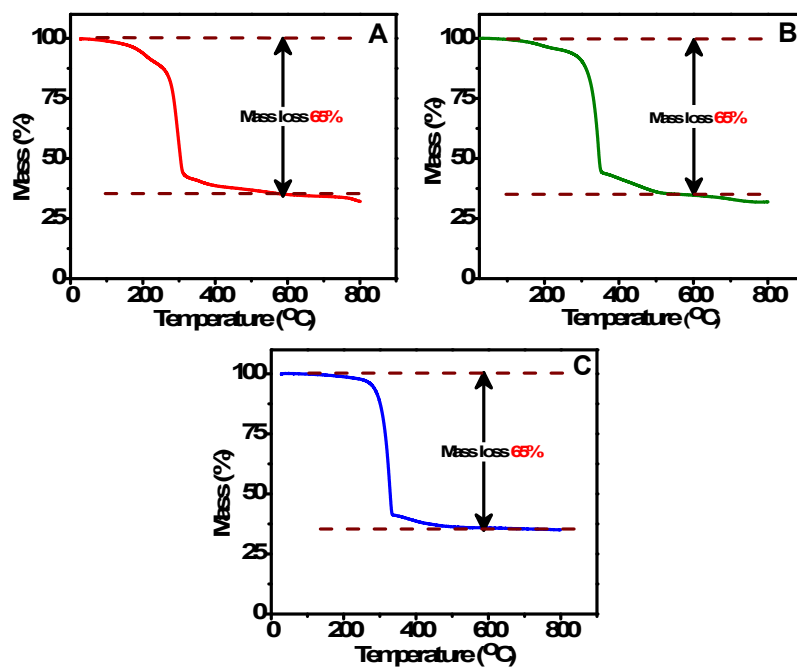
Fig. S2: TEM images of self-assembled Cu NCs protected with (A) 2,4-, (B) 2,5- and (C) 2,6-DMBT
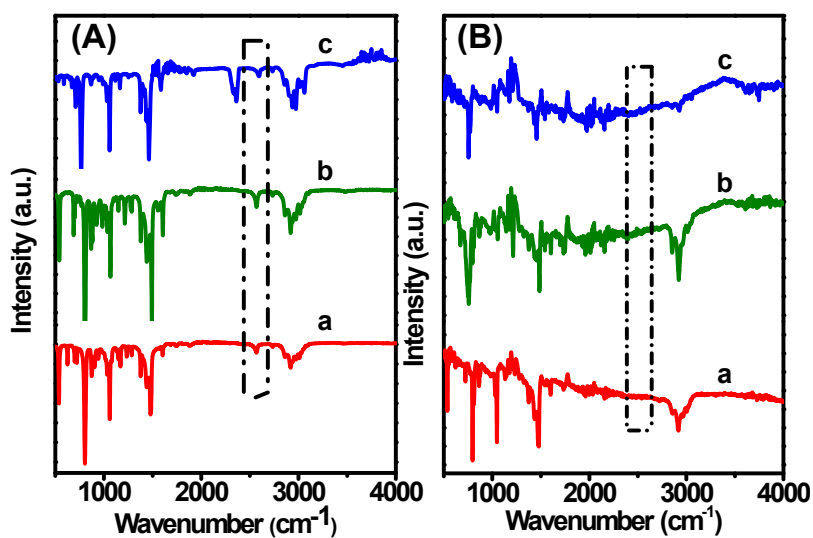

Fig. S3: HAADF STEM image (A-C) and elemental mapping for Cu (D-E) and S (F-I) for rod, platelet and ribbon-like self-assembled Cu NCs respectively.

Fig. S4: AFM images of self-assembled Cu NCs protected with (A) 2,4- (B) 2,5- and (C) 2,6-DMBT ligand.
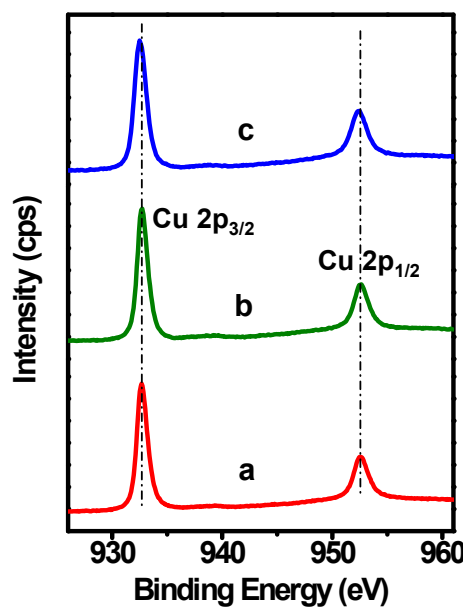
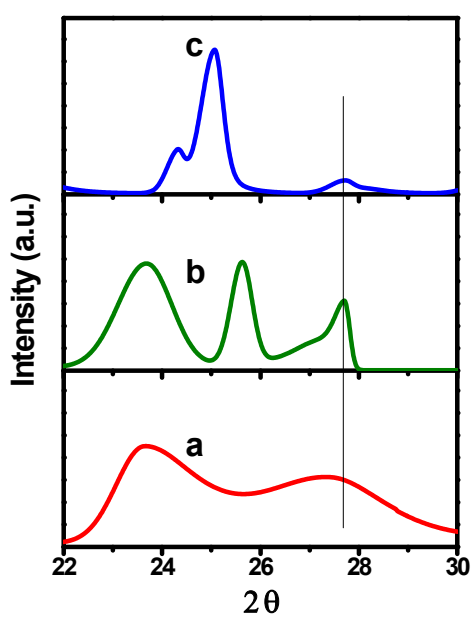**Fig. S5:** TGA curves of the self-assembled Cu NCs capped with (A) 2,4-, (B) 2,5-, and (C) 2,6-DMBT.

Fig. S6: FTIR spectra of (A) DMBT and (B) DMBT capped self-assembled Cu NCs with 2,4-, 2,5-, and 2,6-DMBT (a-c) respectively.
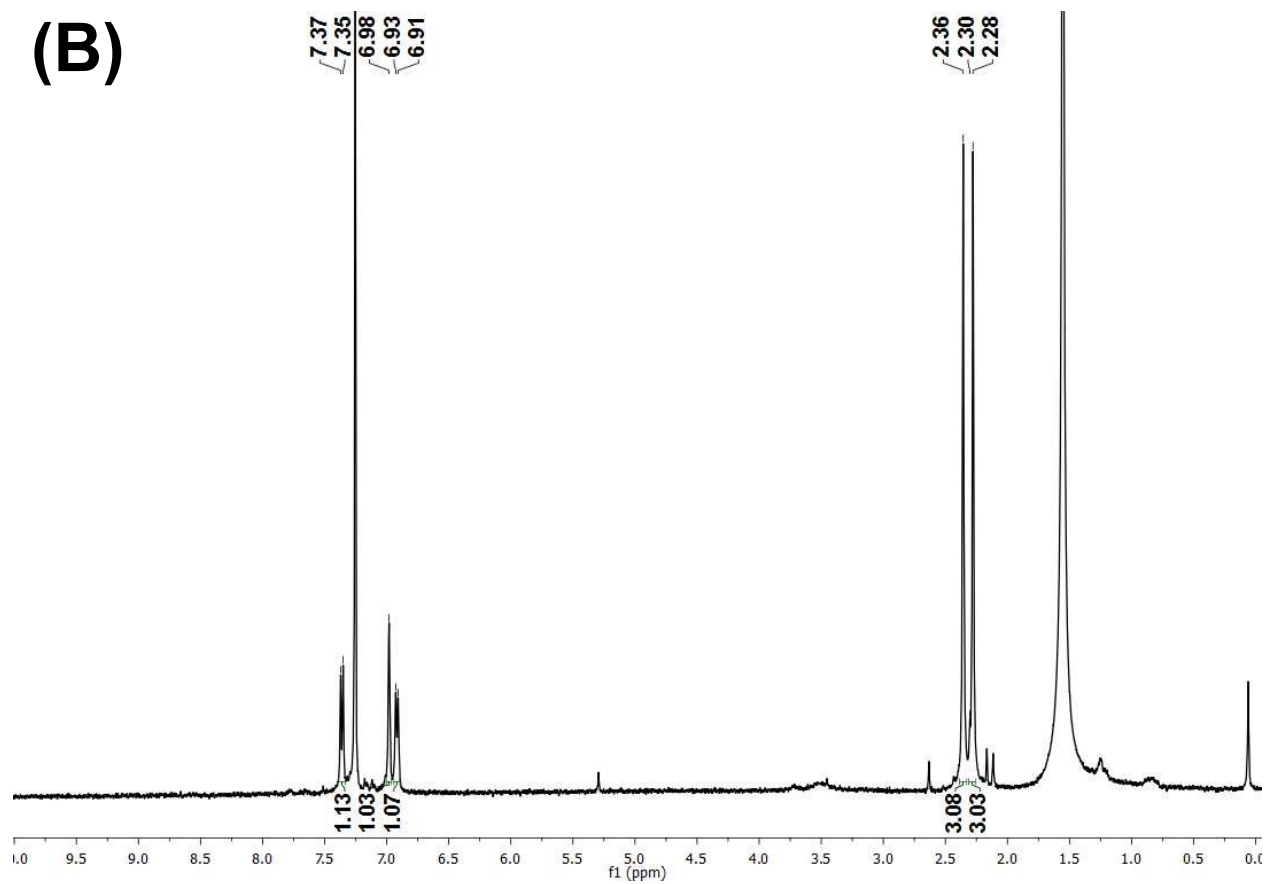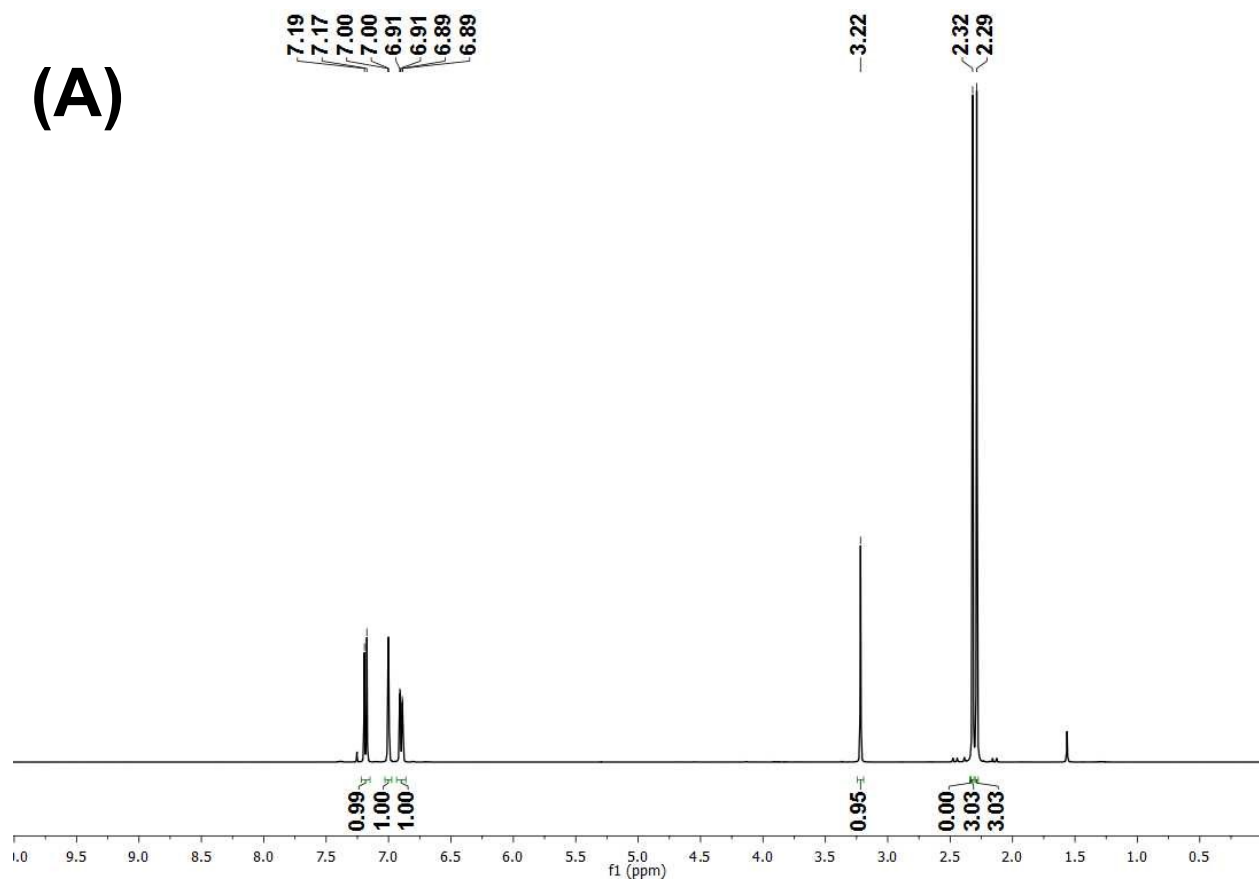
Fig. S7: XPS spectra for Cu 2p of self-assembled Cu NCs protected with 2,4-, 2,5-, and 2,6-DMBT (a-c) respectively.

Fig. S8: Powder X-ray diffraction patterns of self-assembled Cu NCs protected with 2,4-, 2,5-, and 2,6-DMBT (a-c) respectively.

(A)

7.19
7.17
7.00
7.00
6.91
6.91
6.89
6.89

3.22

2.32
2.29

0.99
1.00
1.00

0.95

0.00
3.03
3.03

f1 (ppm)

(B)

7.37
7.35
6.98
6.93
6.91

2.36
2.30
2.28

1.13
1.03
1.07

3.08
3.03

f1 (ppm)

Fig. S9: ^{1}H NMR of (A) 2,4-DMBT ligand (B) rod-like assembly

(A)

7.26 7.22 7.21 7.20 7.19 7.15 7.07 7.07 7.06 7.05 7.04   3.42 3.41   2.47 2.44

0.97 0.98 0.97   0.93   6.16

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

(B)

7.33 7.18 7.16   2.37 2.36 2.25

1.00 0.70 0.84   5.15

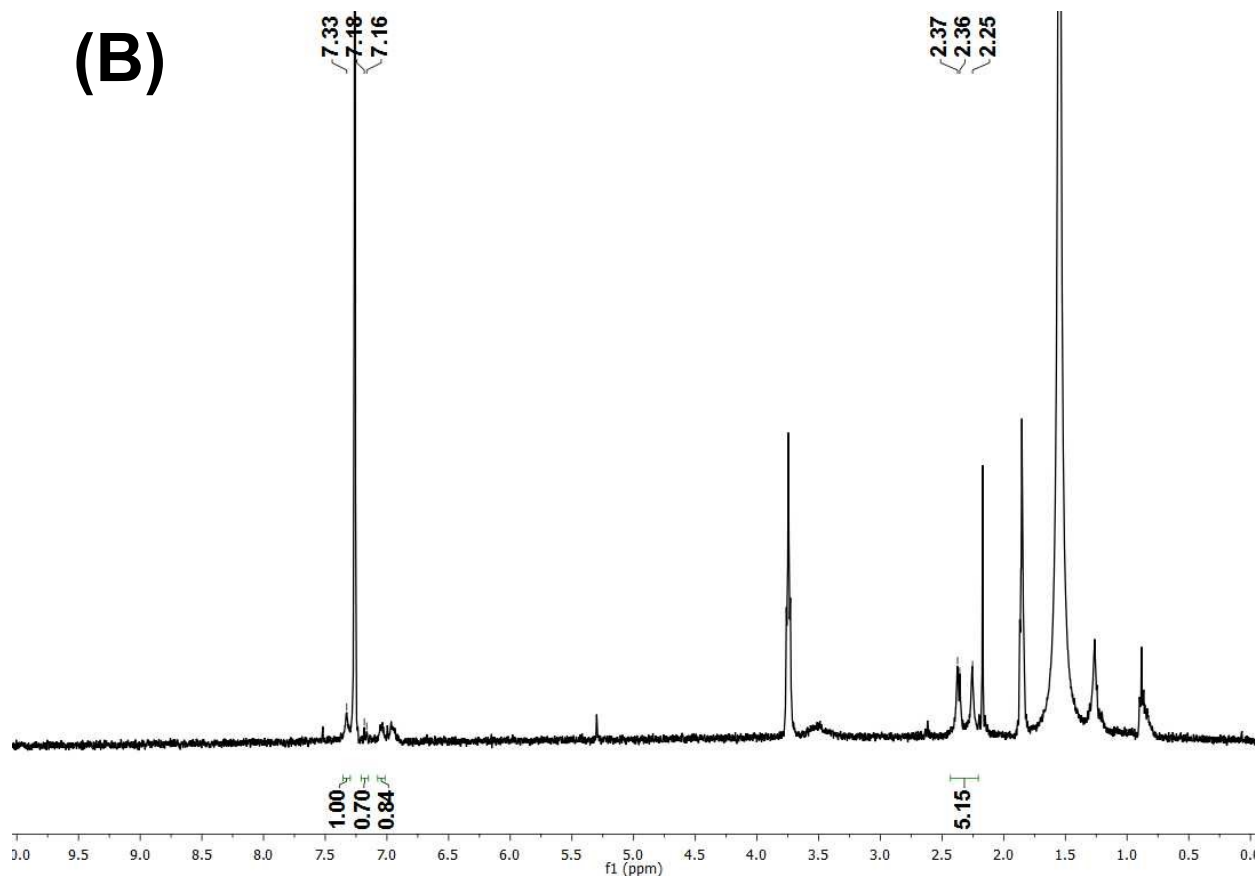10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
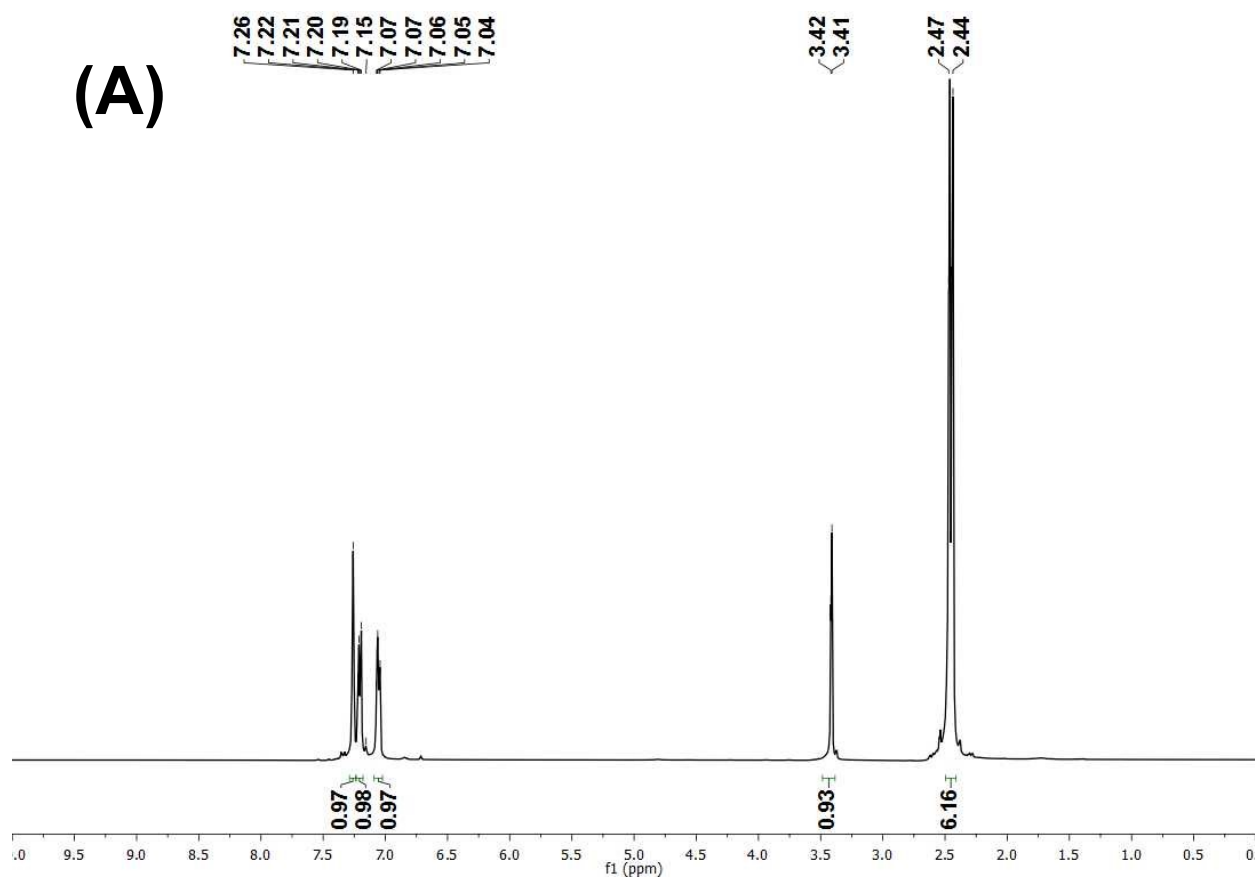
Fig. S10: ^{1}H NMR of (A) 2,5-DMBT ligand (B) platelet-like assembly

(A)

7.07
7.07
7.05
7.02
7.00
6.99
6.98

3.25

2.38

2.99

0.94

6.13

(B)

7.24
7.18
7.16

2.36
2.23
2.17

0.98
2.01

3.00
3.28
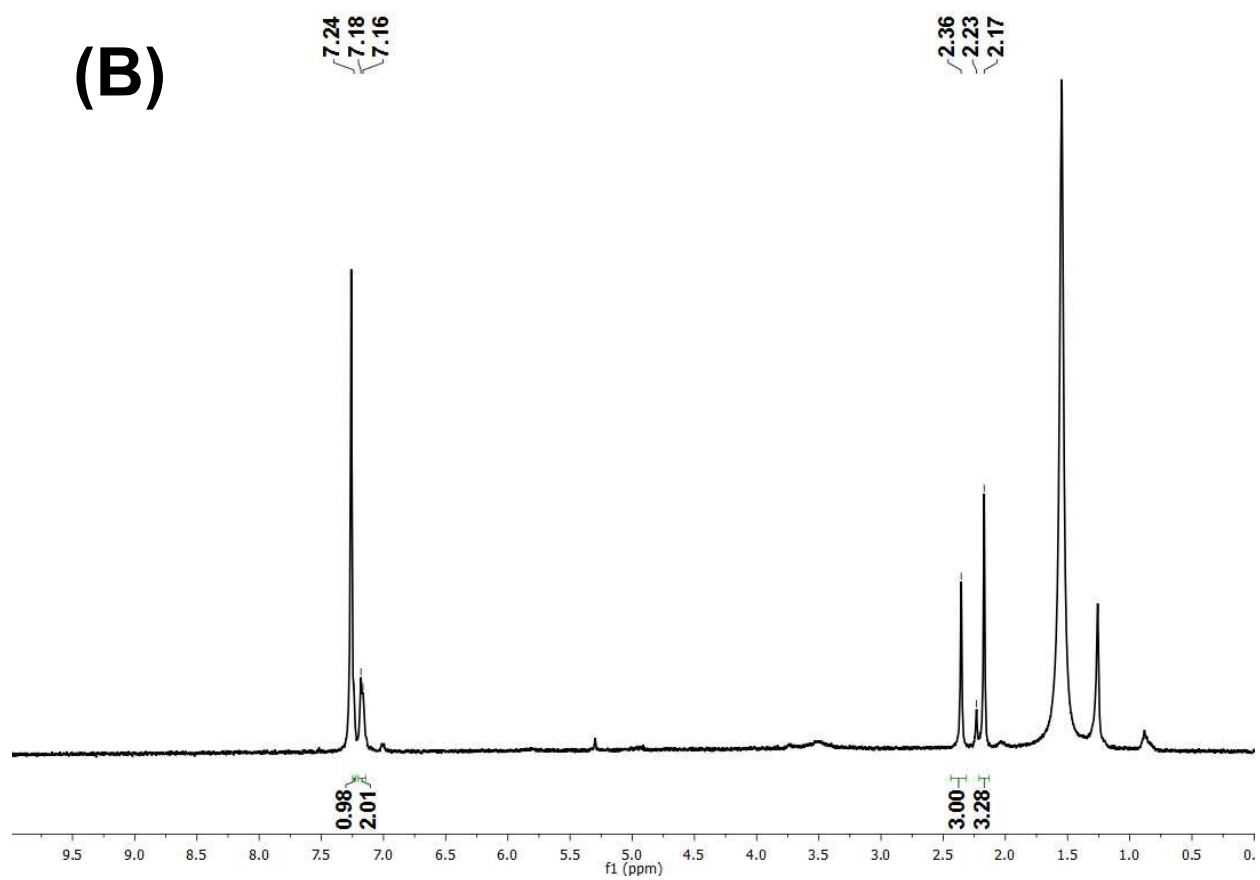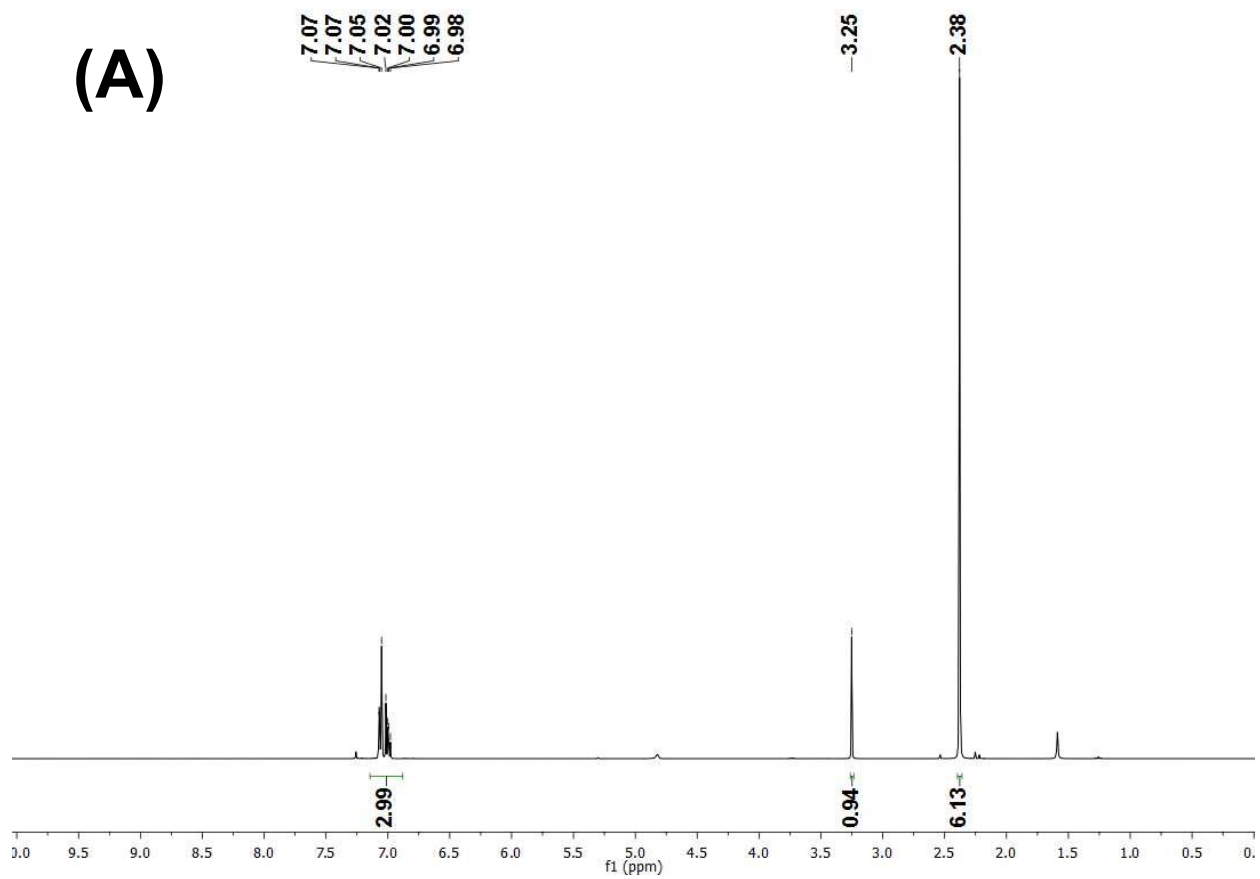
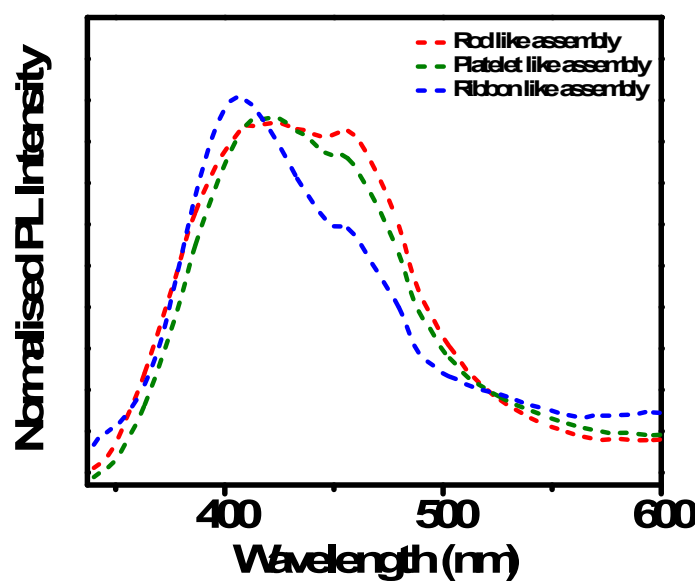**Fig. S11:** ^{1}H NMR of (A) 2,6-DMBT ligand (B) ribbon-like assembly

Fig. S12: PL excitation spectra of the self-assembled Cu NCs

Table S1: TCSPC fitting parameters

Self-assembly	Excitation (nm)	Emission (nm)	PL Lifetime			
			$\tau_1 \, (\mu s)$	$\tau_2 \, (\mu s)$	$\tau_3 \, (\mu s)$	$\tau_{avg} \, (\mu s)$
Rod	370	650	0.91 (0.56)	0.50 (0.36)	1.74 (0.07)	0.35
Platelet	370	655	0.34 (0.74)	1.17 (0.22)	3.38 (0.04)	0.65
Ribbon	370	640	0.24 (0.48)	2.01 (0.40)	6.03 (0.13)	1.69

References

1. Lakowicz, J. R. Principles of Fluorescence Spectroscopy, 3rd ed.; Springer, 2006