

Supporting Information

Antifouling Potential of Functionalized Copper Nanoparticles

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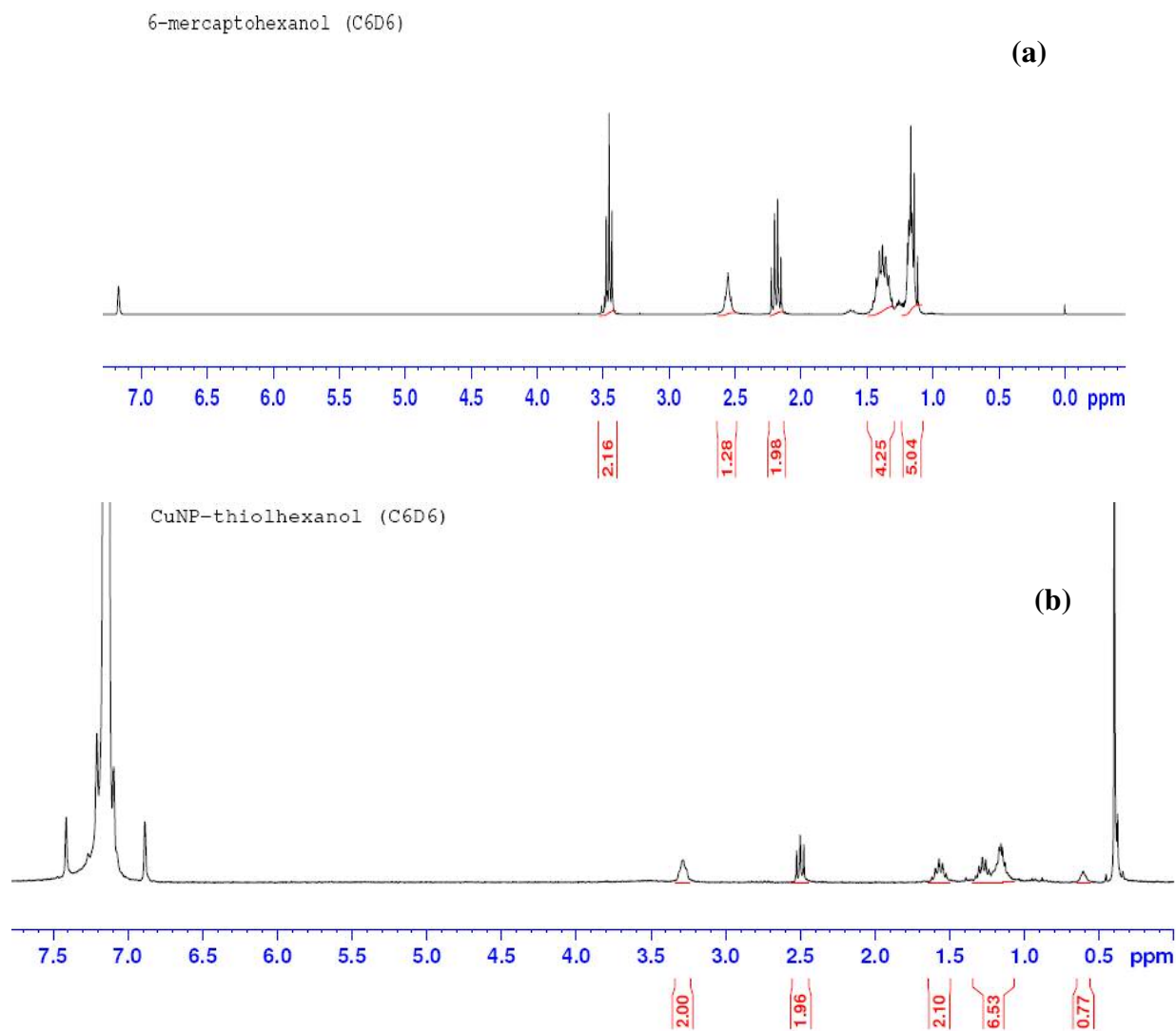


Figure S1. ^1H NMR of (a) 6-mercaptohexanol, and (b) mercaptohexanol-capped copper nanoparticles.

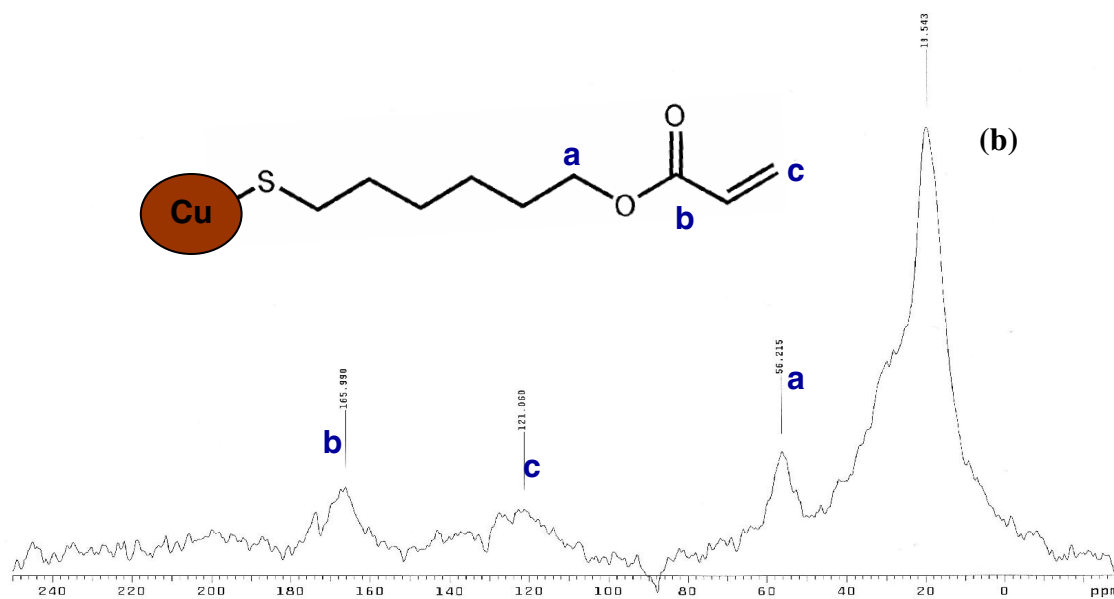
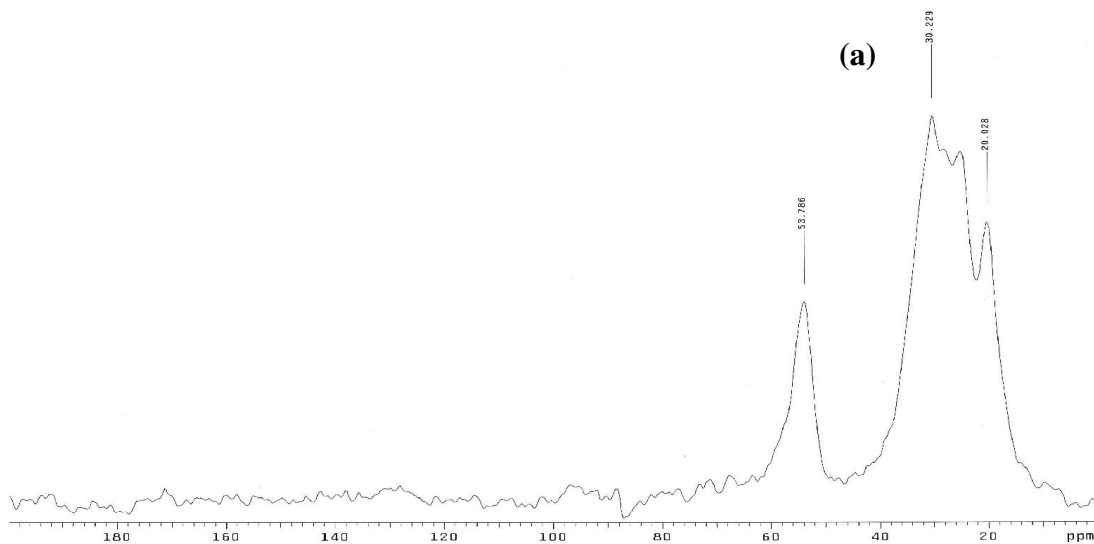


Figure S2. Solid-state ^{13}C NMR of (a) mercaptohexanol-capped, and (b) acrylated copper nanoparticles.

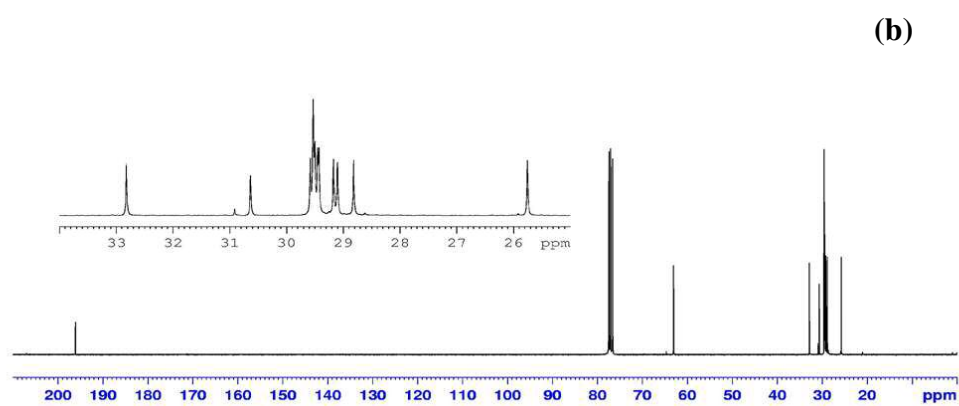
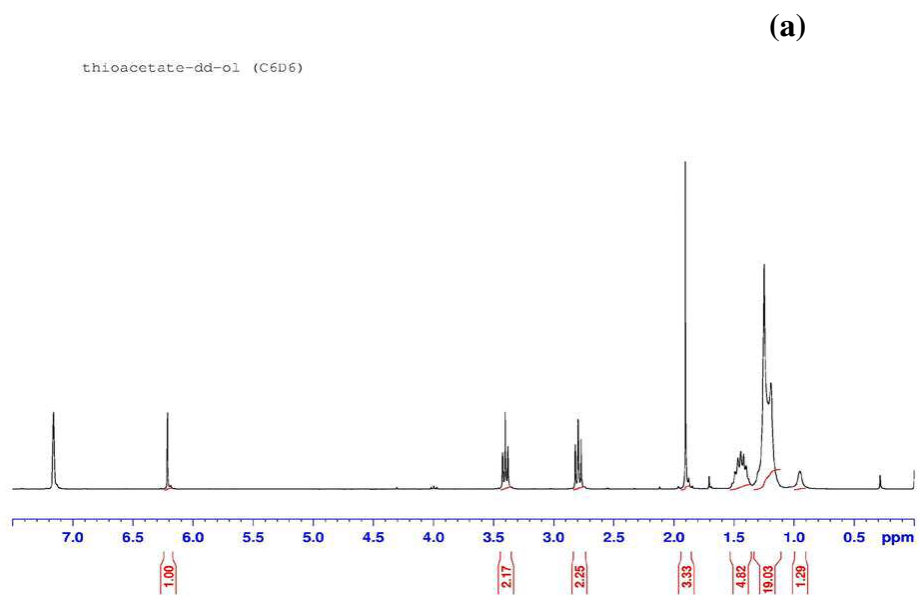


Figure S3. (a) ^1H NMR, and (b) ^{13}C NMR (CDCl_3) of 12-thioacetyldodecan-1-ol.

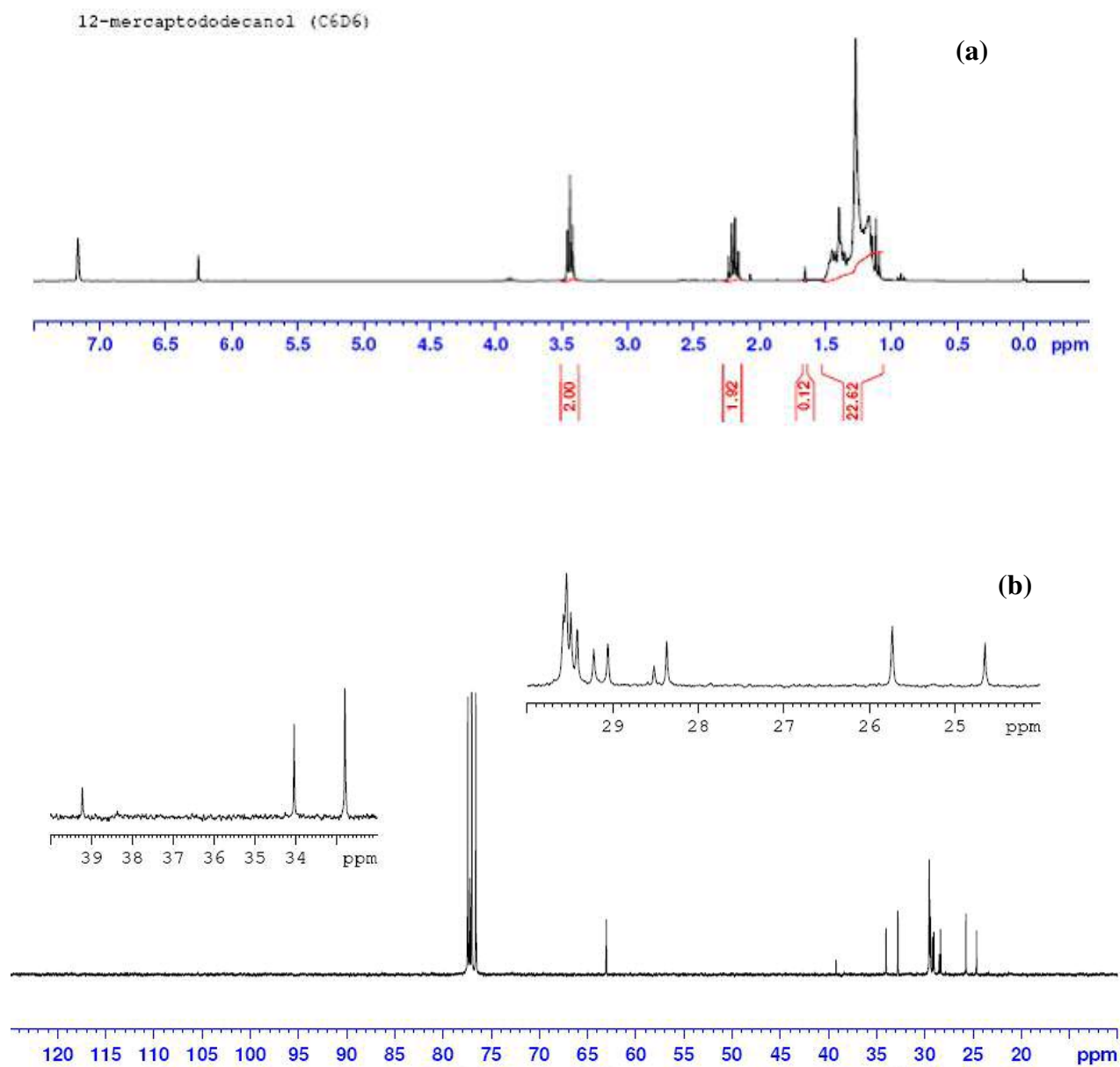


Figure S4. (a) ^1H NMR, and (b) ^{13}C NMR (CDCl_3) of 12-mercapto-1-dodecanol.

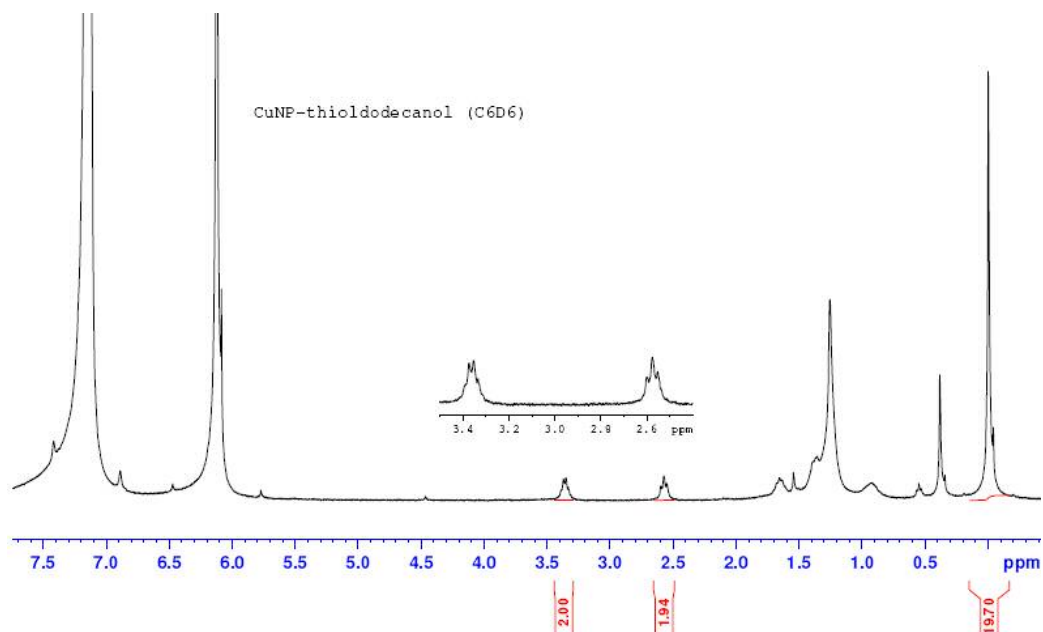


Figure S5. ^1H NMR of mercaptododecanol-capped copper nanoparticles.

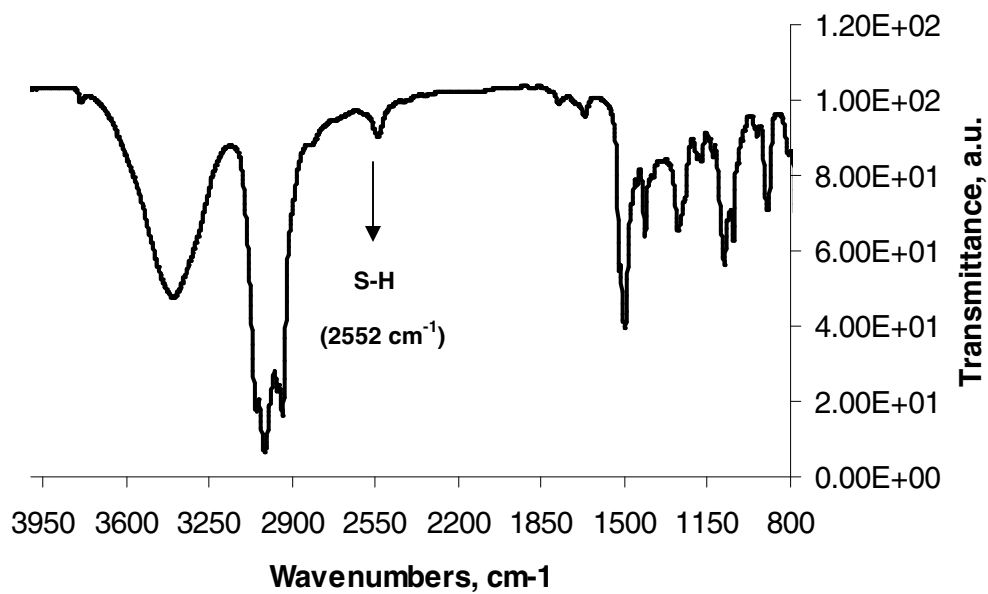


Figure S6. FTIR spectrum of 12-mercaptododecanol.

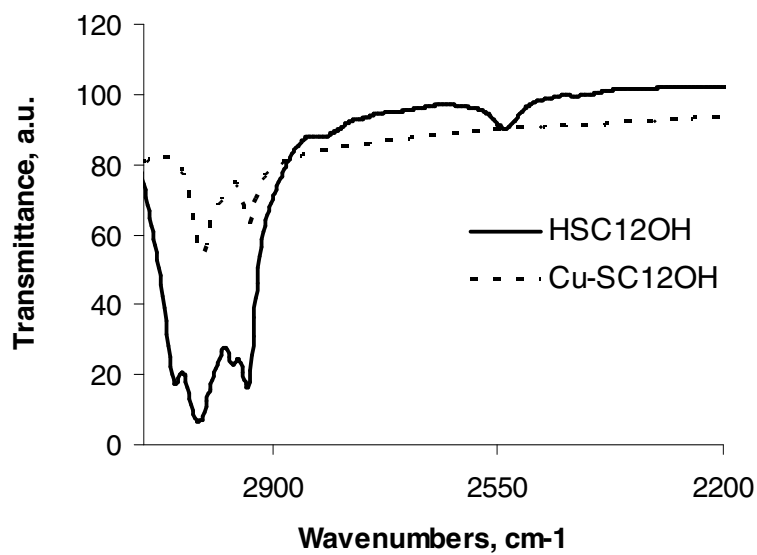


Figure S7. FTIR spectra of 12-mercaptododecanol and 12-mercaptododecanol-capped copper nanoparticles.

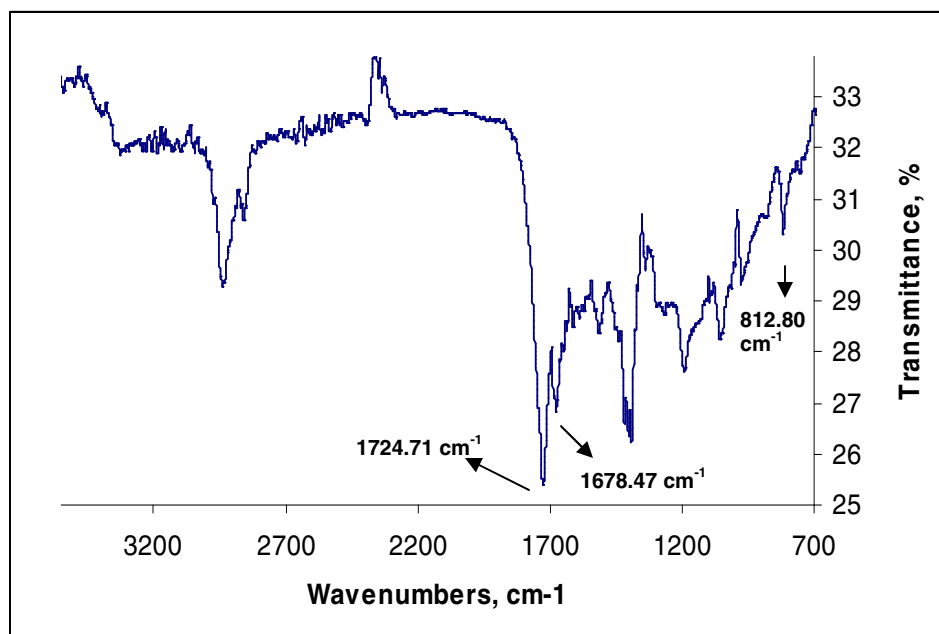
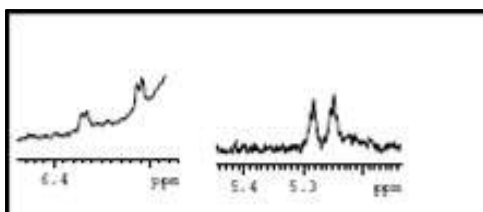
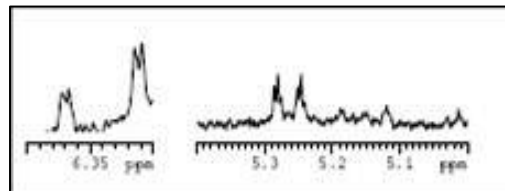


Figure S8. FTIR spectrum of CuC_{12}Ac .



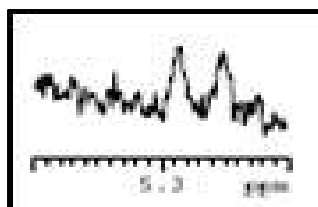
➤ NO PI

➤ NO Irradiation



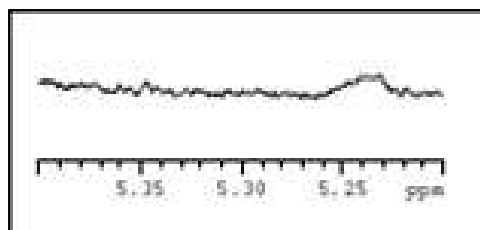
❖ NO PI

❖ Irradiation



✓ PI

✓ No Irradiation



▪ PI

▪ 15 min Irradiation

Figure S9. ^1H NMR probes (benzene- d_6) for polymerization of CuC_{12}Ac particles.

Irradiation was carried out with RMR-600 Rayonet photochemical reactor equipped with 7 lamps ($\lambda = 350\text{nm}$). P.I – photoinitiator.

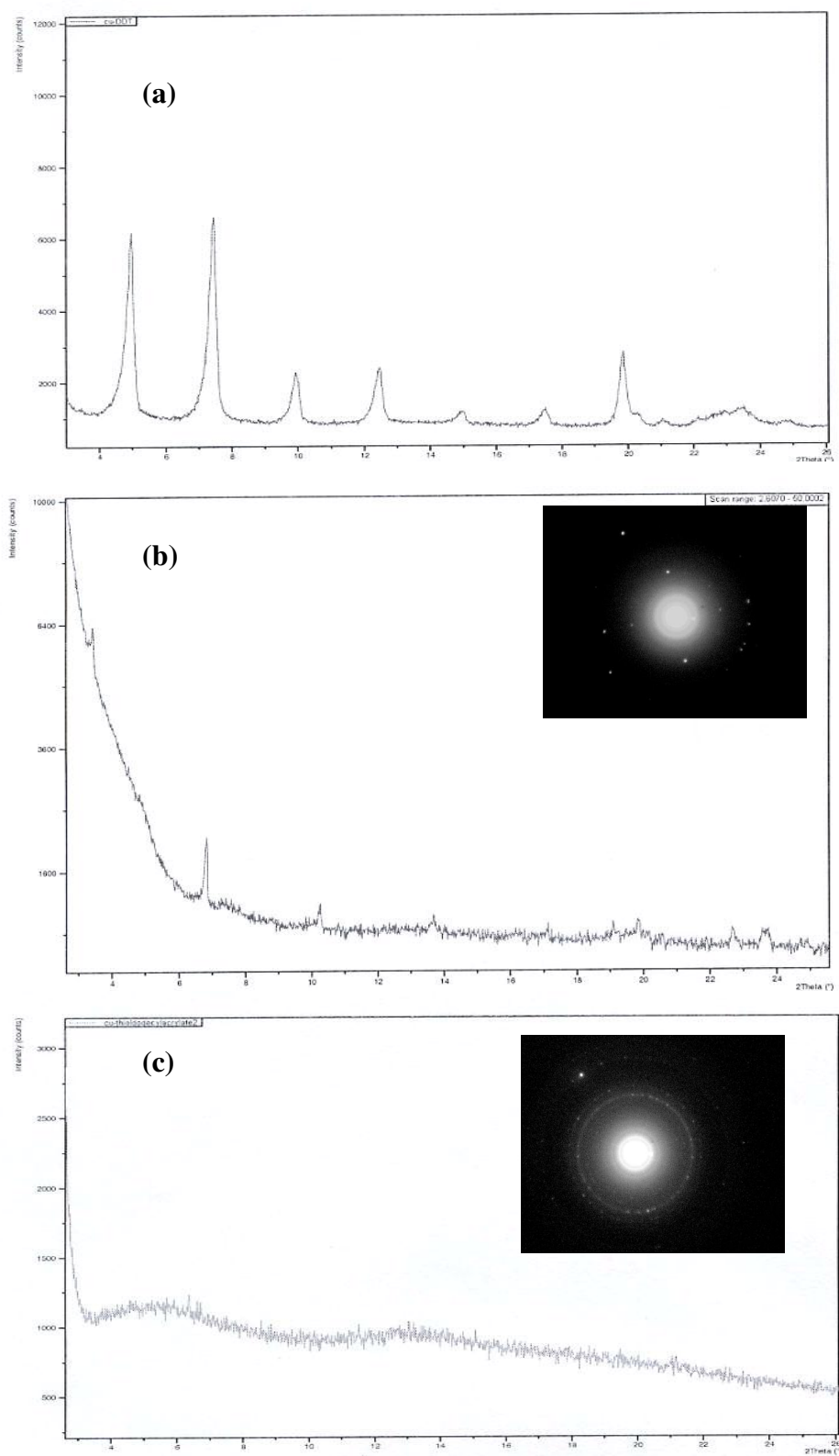


Figure S10. Powder X-ray diffractograms of (a) CuC_{12} , (b) CuC_{12}OH , and (c) CuC_{12}Ac .

Insets show SAED images.

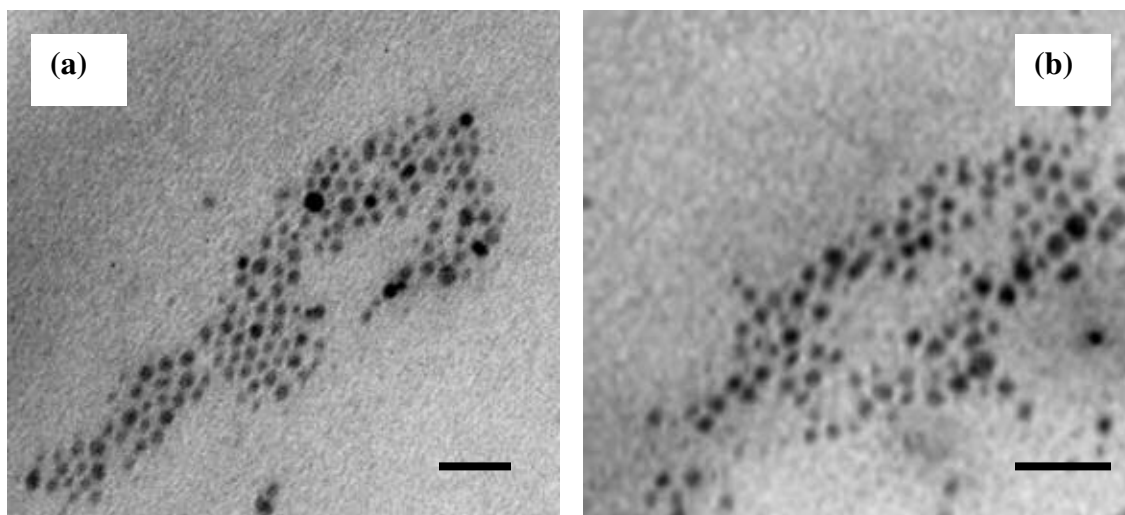


Figure S11. TEM images of CuC_6Pr (a) with photoinitiator; *no irradiation*, and (b) with photoinitiator; *30min irradiation*. Light source - RMR-600 Rayonet photochemical reactor equipped with 7 lamps ($\lambda = 350\text{nm}$). Scale bar represents 50nm.

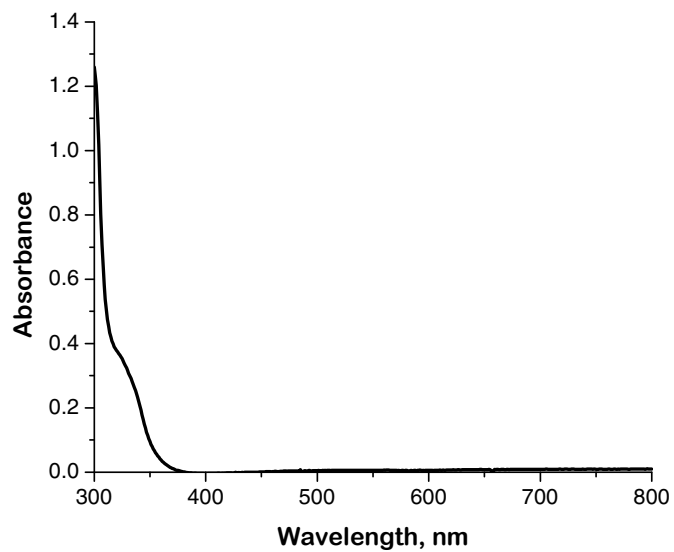


Figure S12. UV-Visible spectrum of n-hexyl acrylate monomer (Scientific Polymer Products, Inc; inhibited with HQ).

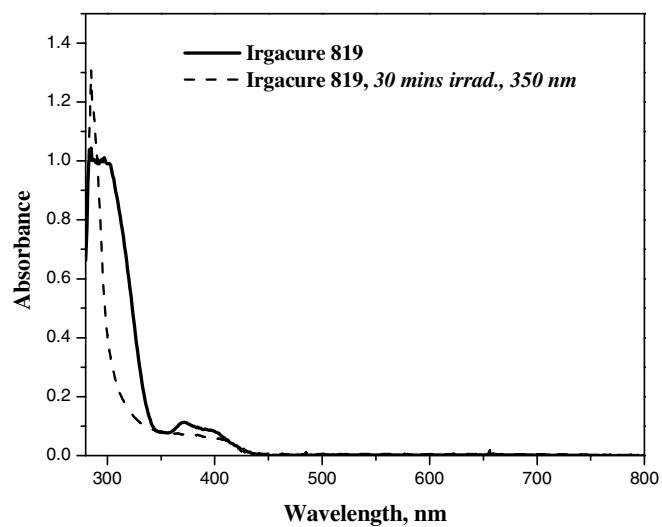


Figure S13. UV-Visible spectra of Irgacure 819 (0.01% in toluene) before (black line) and after (dash line) irradiation.

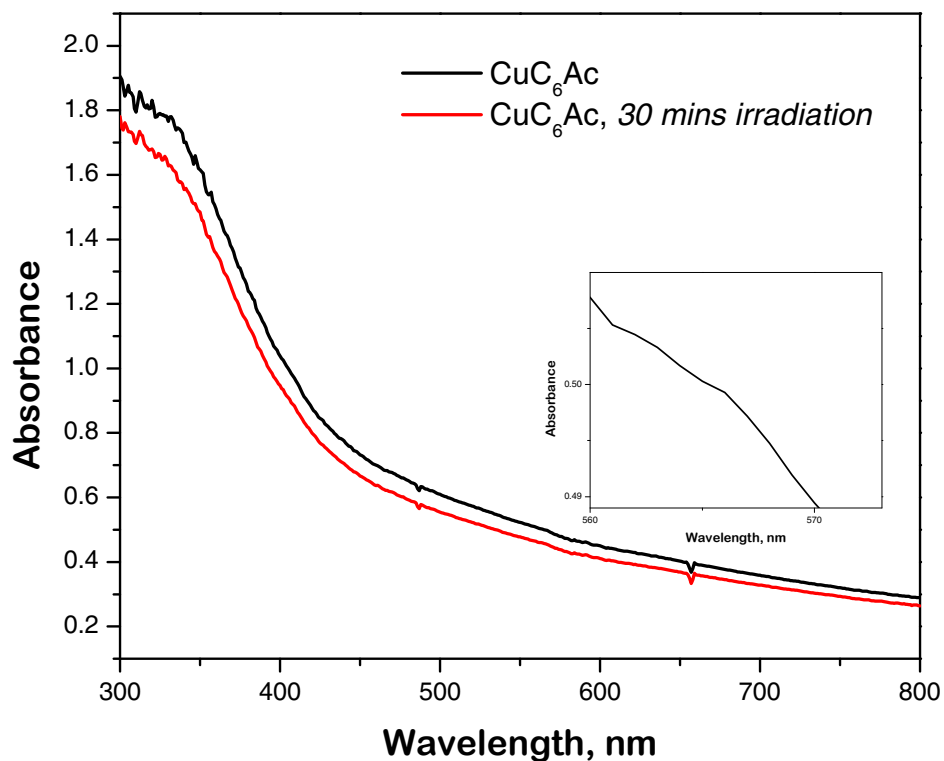


Figure S14. UV-Visible spectra of CuC_6Ac before (black line) and after (red line) irradiation.

The absence of a sharp plasmonic absorption band for the Cu NPs at $\sim 566\text{nm}$ (see also references 17 and 18) could be due to the relatively wide size distribution of the nanoparticles, as size-specific analysis was not a major target in this work.

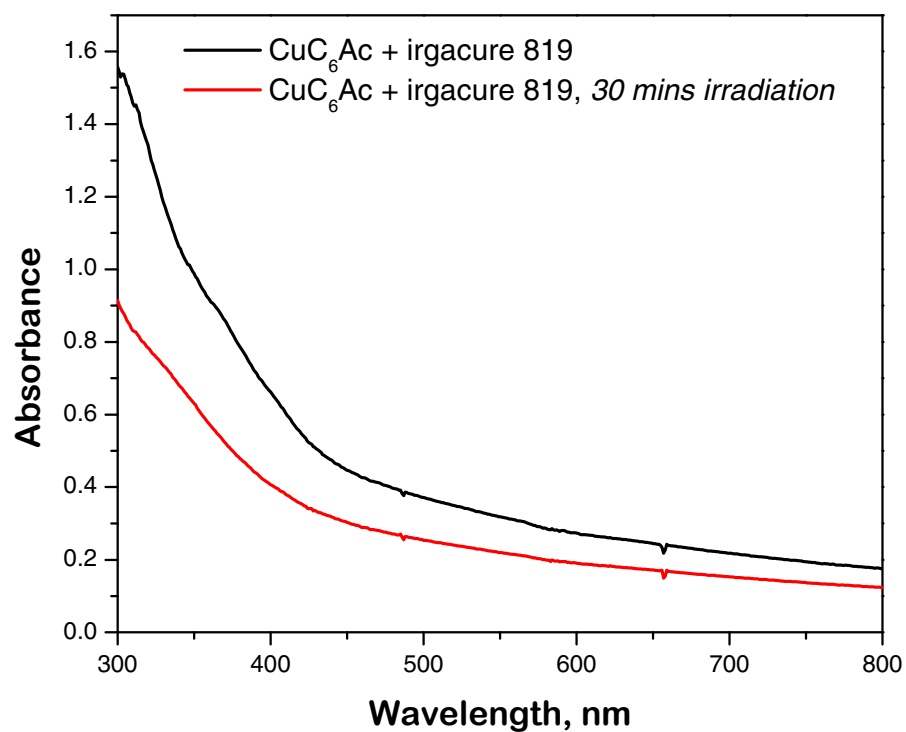


Figure S15. UV-Visible spectra of CuC_6Ac in the presence of Irgacure 819 before (black line) and after (red line) irradiation.

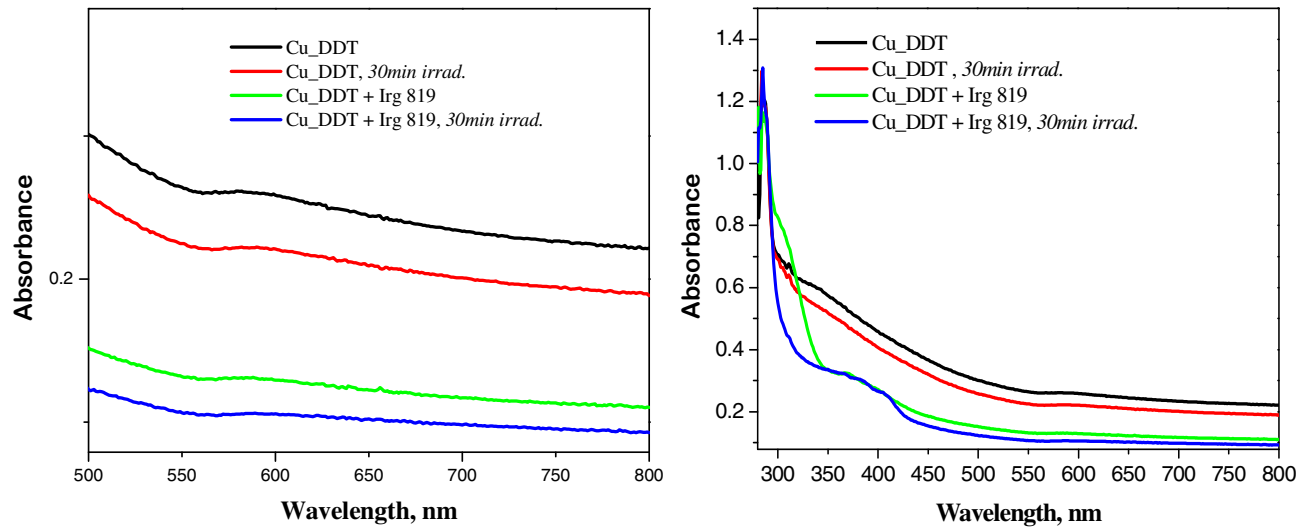


Figure S16. UV-Visible spectra of dodecanethiol-capped copper nanoparticles (~ 4nm) in the presence of Irgacure 819. No change in the plasmonic absorption region (~ 580nm) is observed after irradiation.

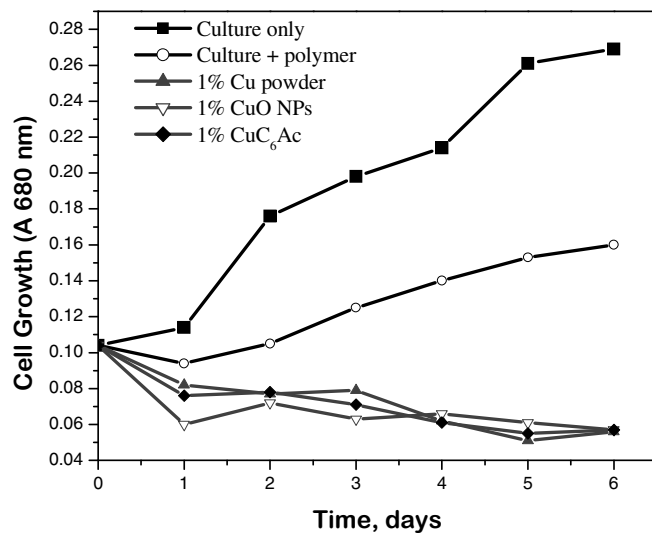


Figure S17. Biological activity of acrylated Cu NPs (compared to conventional Cu biocides) against *Chlamydomonas* sp. strain CD1 Red (green algae).

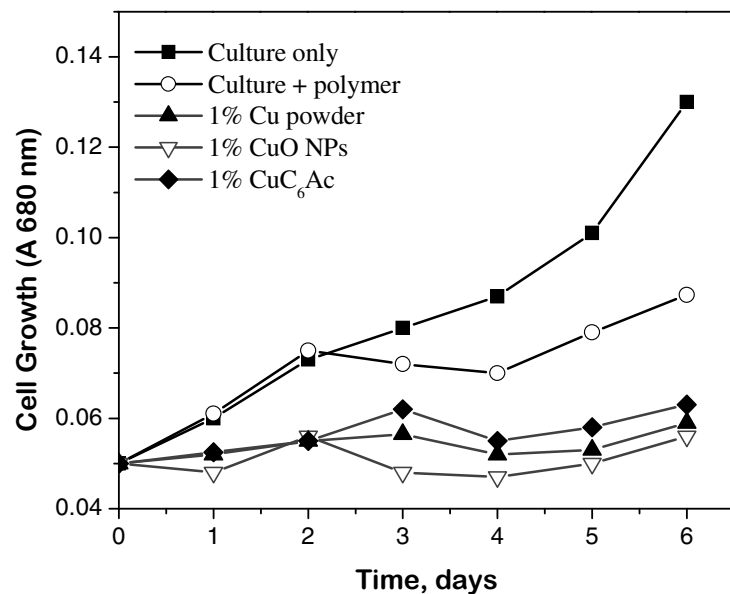


Figure S18. Biological activity of acrylated Cu NPs against *Synechococcus* sp. PCC 7002 (salt water cyanobacteria).

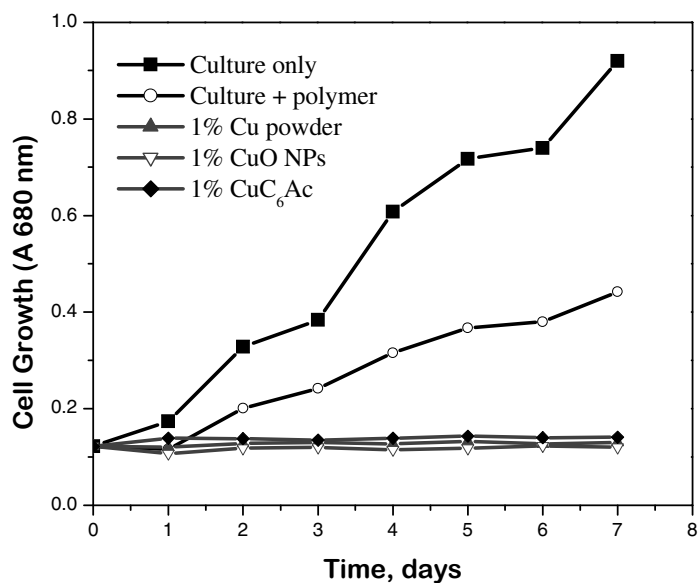


Figure S19. Biological activity of acrylated Cu NPs against *Synechocystis* sp. PCC 6803 (fresh water cyanobacteria).

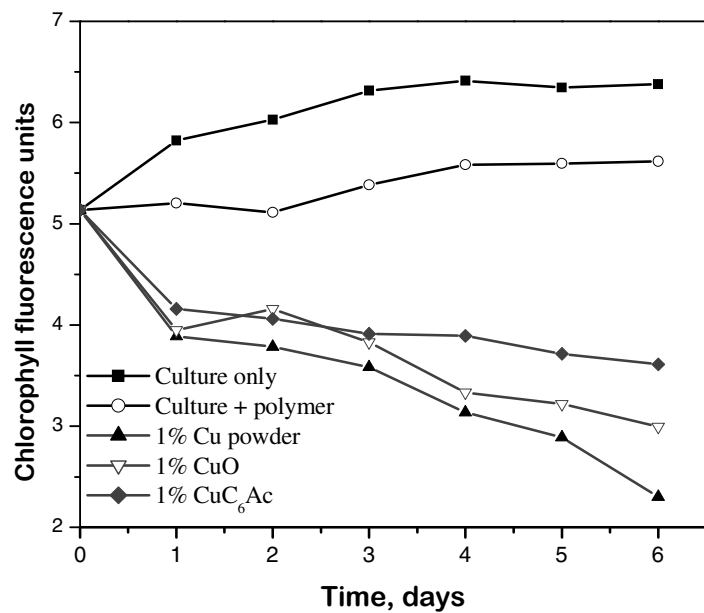


Figure S20. Biological activity of acrylated Cu NPs against *Phaeodactylum tricornutum* CCMP 1327 (Diatoms).

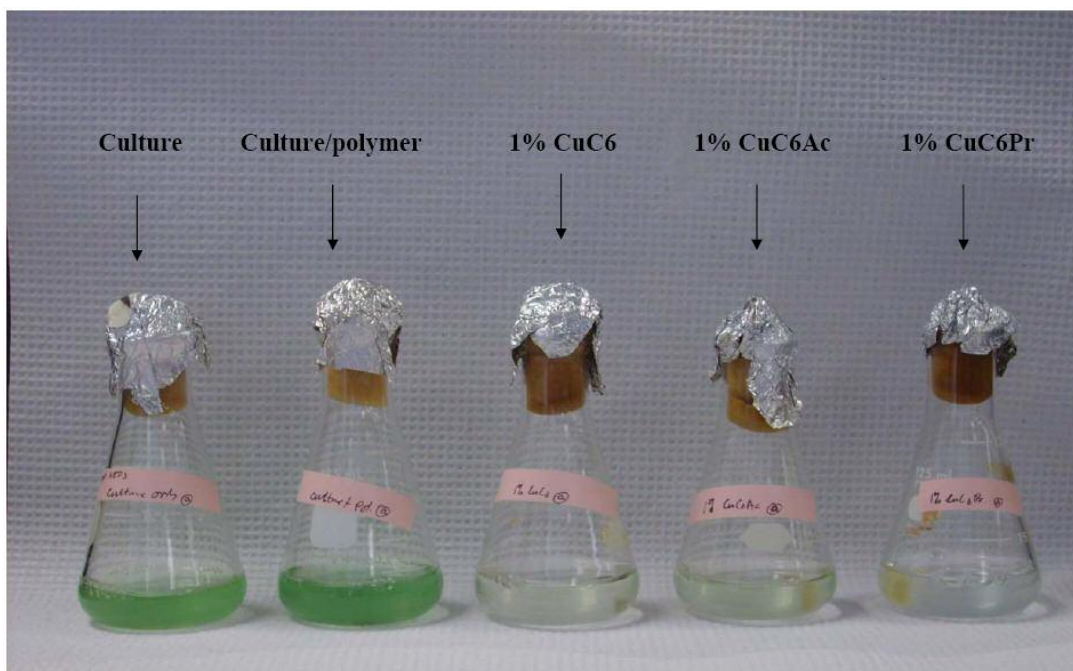


Figure S21. Biological activity of the stabilized Cu NPs against *Synechocystis* sp. PCC 6803 - Visual observation after 7 days.

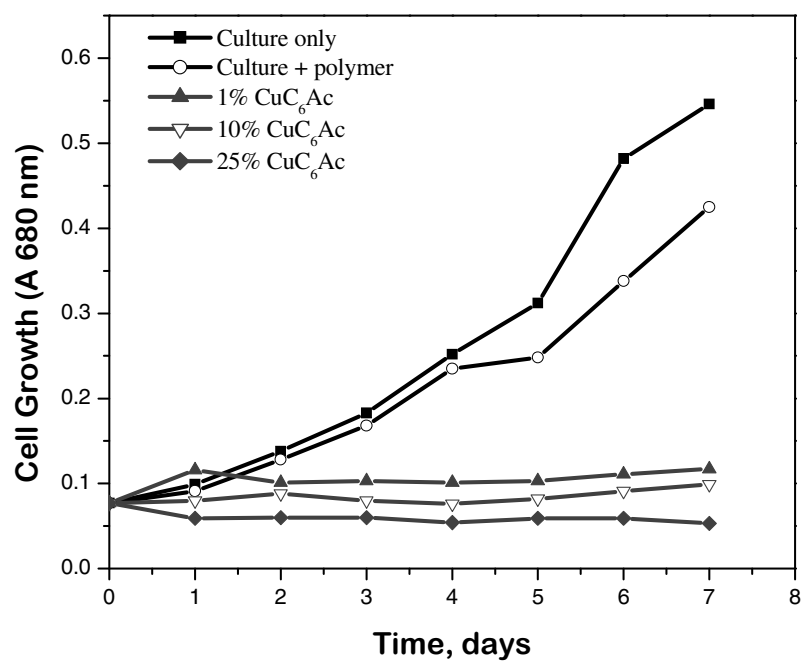


Figure S22. Biological activity of acrylated Cu NPs at different loads against *Synechosystis* sp. PCC 6803 (fresh water cyanobacteria).

from Bulky
1st

BG-11 medium (use carboy)

BG #1	NaNO_3	15g/100ml (1.765M)	#1- 10ml/L	17.6mM
BG #2	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	3.6g/100ml	#2- 1ml/L	
BG #3	$\text{FeNH}_4\text{Citrate}$	1.2g/100ml	#3- 1ml/L	
BG #4	$\text{EDTA} \cdot \text{Na}_2$	0.1g/100ml	#4- 1ml/L	
BG #5	K_2HPO_4	4.0g/100ml (0.23M)	#5- 1ml/L	230μM
BG #6	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	7.5g/100ml	#6- 1ml/L	
BG #7	Na_2CO_3	2.0g/100ml	#7- 1ml/L	
	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	3.6g/100ml		
BG #8	micronutrients (see separate card)		#8- 1ml/L	

(cover) →

BG #8 micronutrients

H_3BO_3	2.8g/L
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	1.91g/L
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.222g/L
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	0.39g/L
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	0.079g/L (0.051g if anhydrous)
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	0.012g/L

Figure S23. Composition of BG-11 culture medium.

Appendix II. Medium A composition modified

from Stevens *et al.* (1973).

Substance	g L ⁻¹	Final concentration (mmol L ⁻¹)
<i>salts solution 1^b</i>		
NaCl	25.00	427.8
MgSO ₄ · 7H ₂ O	3.50	14.1
KCl	0.50	6.7
MgCl ₂ · 6H ₂ O	2.00	9.8
<i>Nutrient & salt stocks</i>		
NaNO ₃ ^a	0.75	8.82
K ₂ HPO ₄ ^a	0.50	2.87
CaCl ₂ · 2H ₂ O ^a	0.50	3.4
Na ₂ CO ₃ ^a		0.19
Disodium EDTA ^c		0.1
Vitamin B ₁₂ ^a		1.5 × 10 ⁻⁵
<i>Trace Minerals</i>		
H ₃ BO ₃		4.6 × 10 ⁻³
MnCl ₂ · 4H ₂ O		9.1 × 10 ⁻⁴
ZnSO ₄ · 7H ₂ O		7.7 × 10 ⁻⁵
Na ₂ MoO ₄ · 2H ₂ O		1.6 × 10 ⁻⁴
CuSO ₄ · 5H ₂ O		3.2 × 10 ⁻⁵
CoCl ₂ · 6H ₂ O		1.7 × 10 ⁻⁷

a A 1000 x stock is made and added 1 mL for every 1 L. of medium A.

b A 10 x stock was made and added 100 mL for every 1 L. of medium A.

c A 10 mmol L⁻¹ stock was made

- Iron (FeCl₃) is added solely as a separate stock with 0.1 mmol L⁻¹ EDTA.
- pH of the medium is *ca.* 8.1
- Stocks were chelexed and filter sterilized when required.

Figure S24. Composition of Medium A.

f/2 Medium

(Guillard & Ryther 1962, Guillard 1975)

To 950 mL filtered seawater add:

Quantity	Compound	Stock Solution	Molar Concentration in Final Medium
1 mL	NaNO ₃	75 g/L dH ₂ O	8.83 × 10 ⁻⁴ M
1 mL	NaH ₂ PO ₄ · H ₂ O	5 g/L dH ₂ O	3.63 × 10 ⁻⁵ M
1 mL *	Na ₂ SiO ₃ · 9H ₂ O*	30 g/L dH ₂ O*	1.07 × 10 ⁻⁴ M*
1 mL	f/2 trace metal solution	(see recipe below)	-
0.5 mL	f/2 vitamin solution	(see recipe below)	-

Make final volume up to 1 L with filtered seawater and autoclave.

***Note:** Autoclaved f/2 medium produces extensive silica precipitate. We delete silicate when it is not required by the alga (see f/2-Si medium below).

Figure S25. Composition of f/2 medium.