Supporting Information for

One-pot synthesis and characterization of subnanometer-size benzotriazolate protected copper clusters

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Additional UV-Vis, Raman, mass and TEM data

The benzotriazolate-copper(II) complex formation was studied in methanol by UV-Vis spectroscopy (Figure S1). To a yellow solution of $CuBr_2$ (4.4 mM) in methanol was added an equal amount of colorless solution of benzotriazole (8.9 mM) in methanol which resulted in a lime green solution of the BTA-Cu(II) complex (2:1). The samples were diluted with methanol and UV-Vis spectra were recorded at 250 – 900 nm (Figure S1).

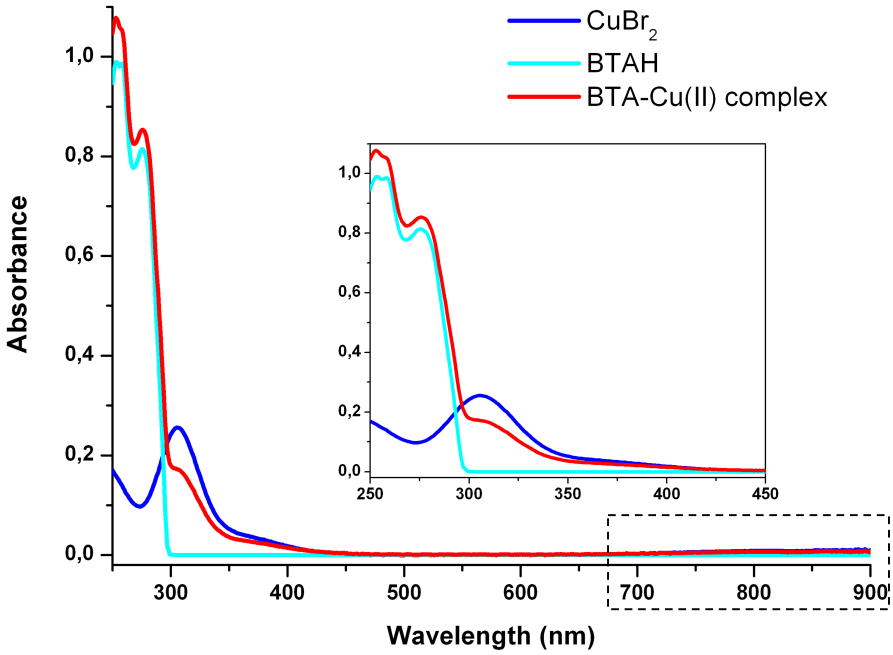

Figure S1. UV-Vis spectra of $CuBr_2$ (blue), BTAH (cyan) and BTA-Cu(II) complex (red) in methanol. The area at 750-850 nm, in which the weak absorption resulting from the d-d transitions is highlighted with dashed lines.

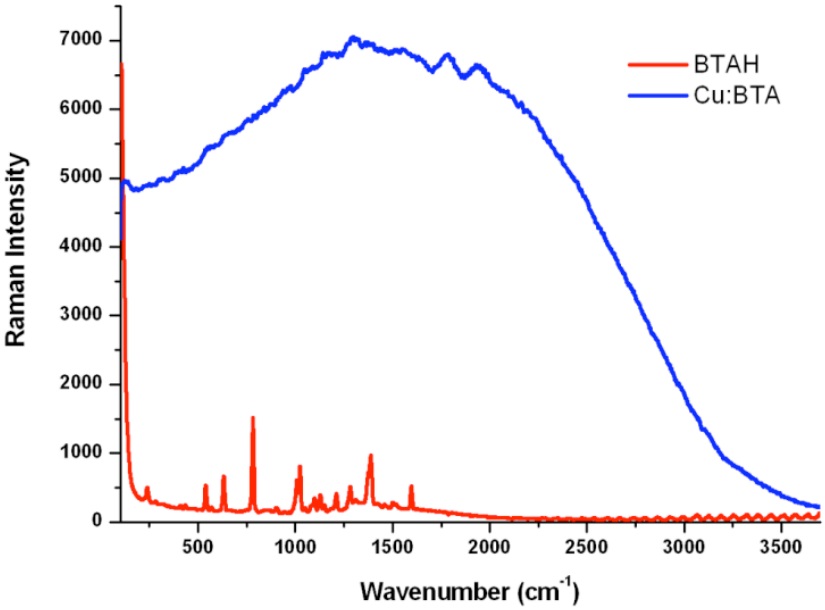

Figure S2. Raman spectra of the Cu:BTA clusters (blue) and BTAH (red). The Raman spectra were measured from the solid Cu:BTA sample with a Bruker Senterra dispersive Raman spectrometer at a resolution of 3-5 cm^{-1}.

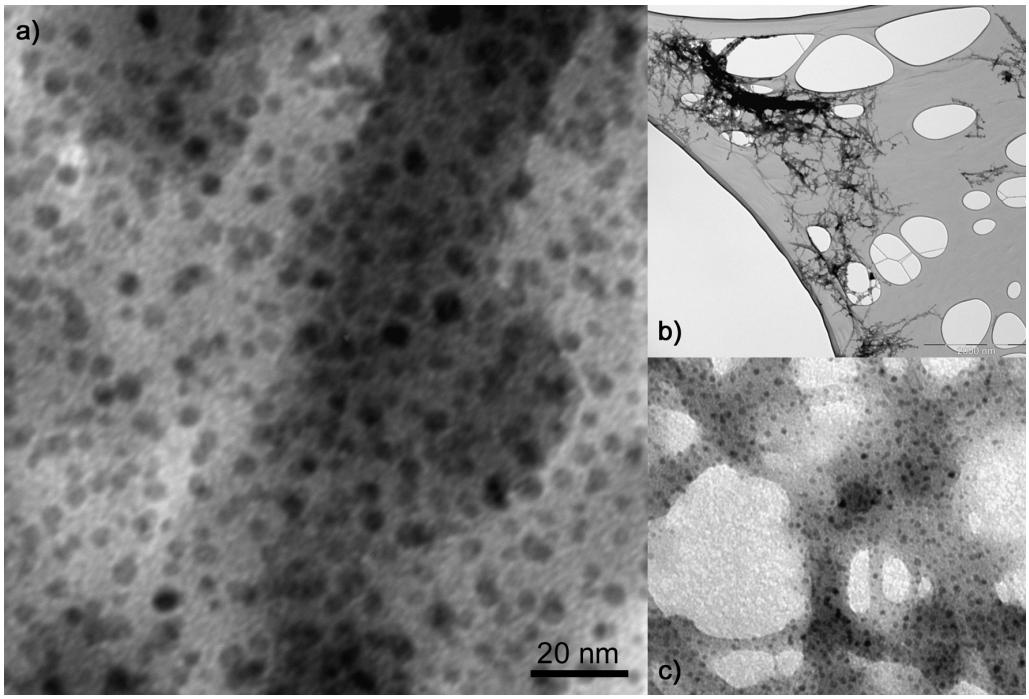

Figure S3. TEM images of the Cu:BTA nanoclusters at different magnification a-c (scale bar shown in the figure). The TEM samples were prepared from Cu:BTA dispersions in DMF on a HC200-Cu grid from Electron Microscopy Sciences.

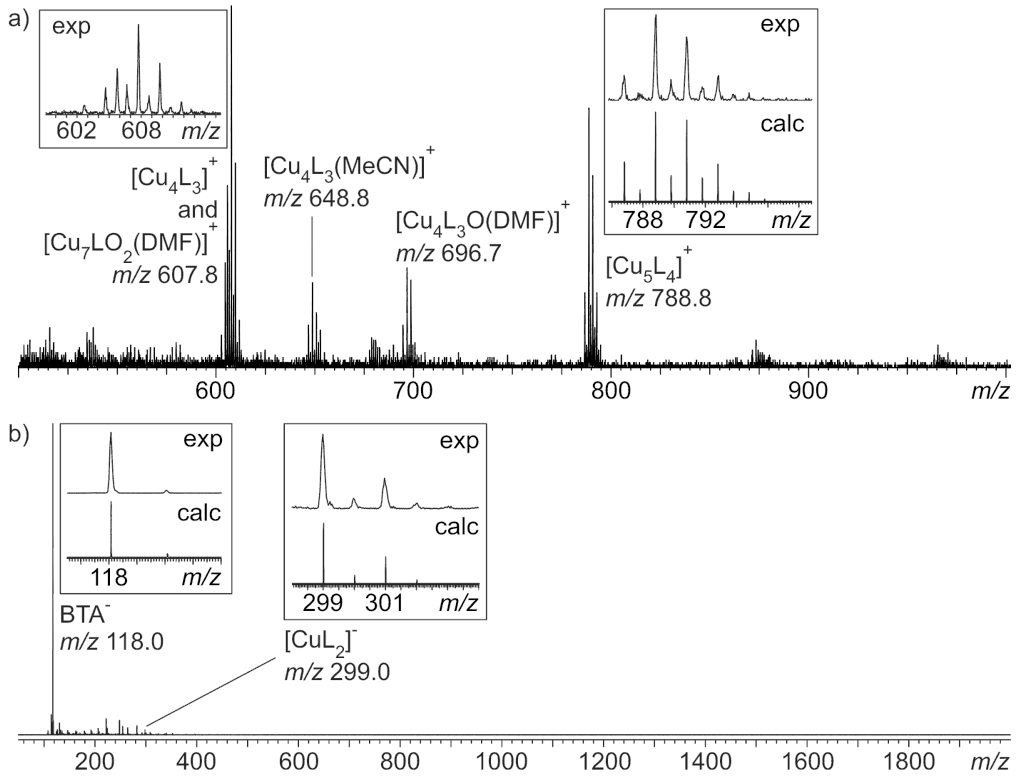

Figure S4. Figure 3 from the article at a larger scale.

Experimental procedure and analytical data for the modified two-phase Brust-Schiffrin method

The modified two-phase Brust-Schiffrin method[1] involves three steps and the reaction is carried out as a one pot reaction in ethanol. The first step involves the formation of $[TOA]_2[CuBr_4]$ salt, which is then reacted with benzotriazole to afford the benzotriazolate-Cu(II) complex. The formed Cu(II) complex is then reduced by the addition of $NaBH_4$, which after overnight stirring affords the Cu:BTA clusters.

A solution of $CuBr_2$ (0.051 g, 0.23 mmol) and tetraoctylammonium bromide (0.25 g, 0.45 mmol) in absolute ethanol (50 mL) was stirred at 90°C for 30 minutes. The dark green solution was allowed to cool to room temperature and solid benzotriazole (0.13 g, 1.08 mmol) was added to the reaction mixture. The resulting greenish-brown mixture was stirred under argon flow for five hours, after which freshly prepared $NaBH_4$ (0.12 g, 3.09 mmol) in ethanol (5 mL) was added in one portion. The reaction mixture immediately changed to black and the stirring was continued overnight, upon which the reaction mixture had changed to light yellow. The light yellow precipate was collected by centrifugation and washed two times with ethanol. The pale greenish precipate was dried in vacuum and redispersed in toluene for UV-Vis, MS (diluted with methanol or acetonitrile) and TEM analyses.

[1] P. J. G. Goulet and R. B. Lennox, *J. Am. Chem. Soc.,* 2010, **132**, 9582-9584; Y. Li, O. Zaluzhna and Y. J. Tong, *Chem. Commun.,* 2011, **47**, 6033-6035; W. Wei, Y. Lu, W. Chen and S. Chen, *J. Am. Chem. Soc.,* 2011, **133**, 2060-2063.

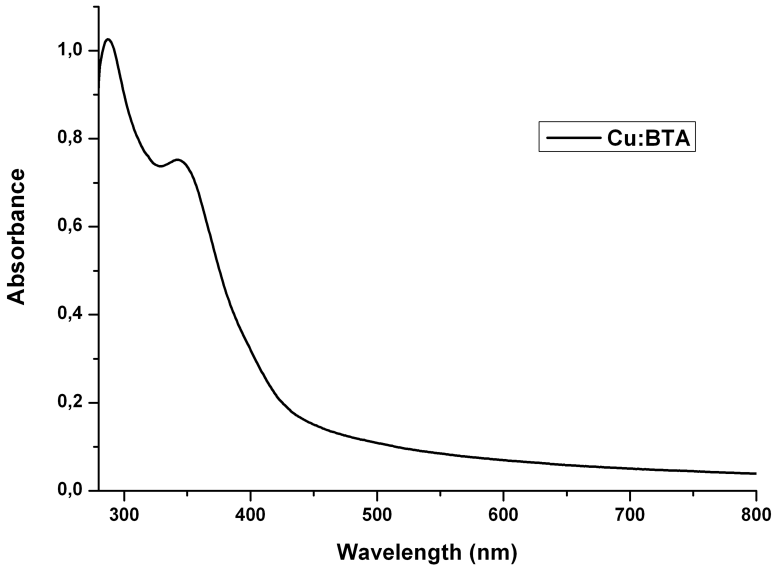

Figure S5. UV-Vis spectrum of Cu:BTA clusters in toluene by the modified two-phase Brust-Schiffrin method.

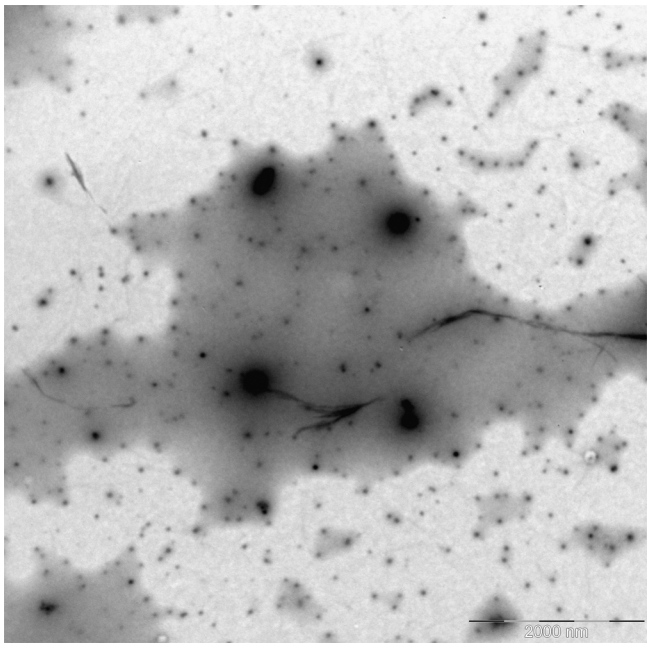

Figure S6. TEM image of the Cu:BTA dispersion in toluene by the modified two-phase Brust-Schiffrin method.

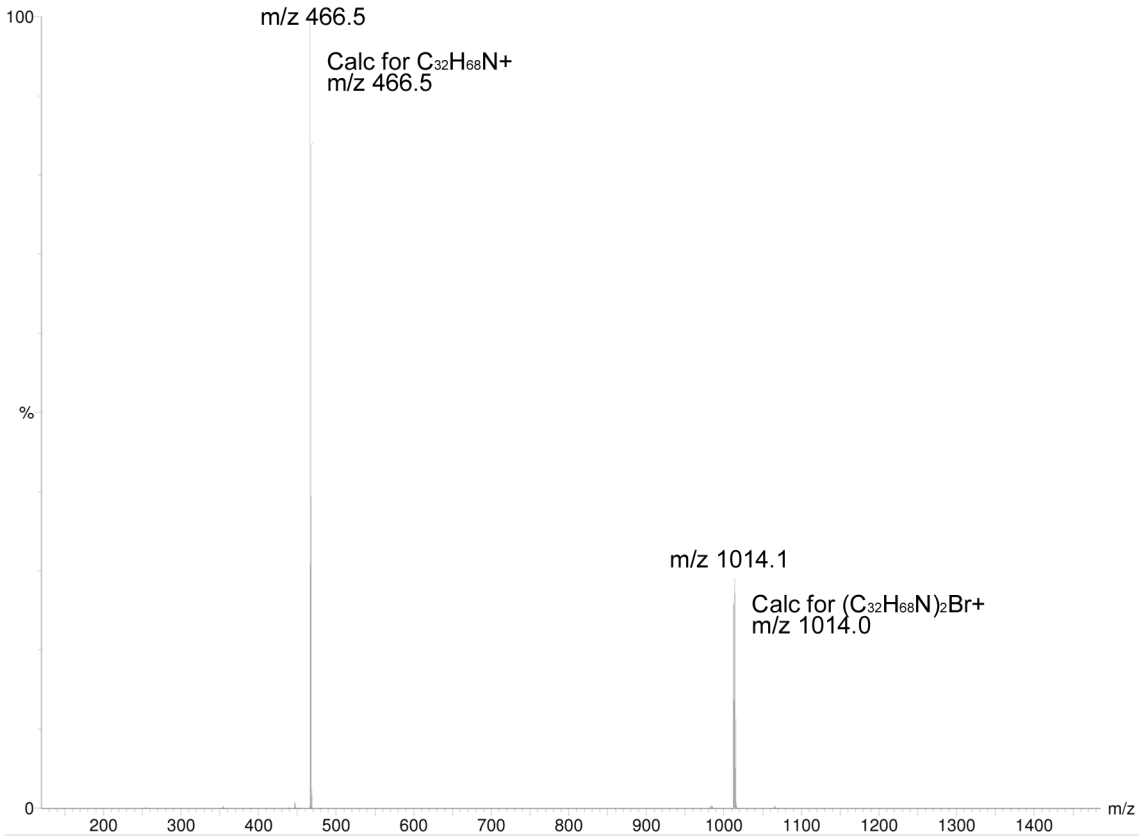

Figure S7. ESI-TOF MS spectrum of the Cu:BTA clusters, in which the TOA ($C_{32}H_{68}N$) cation was the major observed peak.

Coordinates of the Cu_6BTA_4 cluster

C	-4.105339033737654	-3.488950000368489	4.242176896436417
C	-4.211815865535951	-3.423173341518828	5.620377663378049
C	-3.361282496973741	-2.589062422601275	6.394256073990524
C	-2.382746528678364	-1.798057355012945	5.815037205401248
C	-2.265491061182637	-1.859545230860572	4.414592626029185
C	-3.115278185577820	-2.691372189837772	3.636061350834018
H	-4.754351792690956	-4.124296217176146	3.639941127049338
H	-4.963792361870055	-4.024219100347280	6.133049599869635
H	-3.485840112391461	-2.573371762094403	7.477815548660582
H	-1.735744537878157	-1.158472489372850	6.416083642370671
N	-2.782504056138507	-2.548238392726143	2.318408926749326
N	-1.793071536518118	-1.685803207483453	2.291581105947920
N	-1.435301801427226	-1.232791249493618	3.532669842126522
Cu	-0.042992944927828	0.011481007824196	3.582230850903857
C	2.244959642914941	1.811845601374458	5.849021712784351
C	3.224092497890105	2.583963619024365	6.451622563579447
C	4.103700549502143	3.407099224477269	5.698177948917506
C	4.030040849965619	3.477371417941905	4.318016784033942
C	3.041322778378422	2.696988647380792	3.687277273450180
C	2.161565104933738	1.878260398629052	4.446436208898758
H	1.575628127331891	1.178750519459150	6.432815501032392
H	3.327809510158339	2.562177138579672	7.537376146828469
H	4.855687117033890	3.993080713056944	6.228155316117663
H	4.705006135106094	4.103459005570153	3.734334793224081
N	1.345197091618207	1.260636741560740	3.545924795817038
N	1.741287759124008	1.701597878294375	2.312773068716274
N	2.741597312851049	2.550574821856916	2.361773940956686
Cu	-0.830606654223539	-0.840087555306042	0.874655325782646
Cu	0.827311143548453	0.856143960063822	0.864098492080776
C	3.452157971342194	-4.130132134958299	-4.234226195591123
C	3.377997291263569	-4.241658877875934	-5.611261198751079
C	2.563167724871850	-3.373234230961012	-6.386169277403543

C	1.801977738251027	-2.370764993368814	-5.808282788355990
C	1.867488364551026	-2.253184651964443	-4.408365672400095
C	2.679277216832716	-3.120956291581807	-3.628735376308414
H	4.074566907011189	-4.792534193599663	-3.632395872460023
H	3.955308913897756	-5.013548008741652	-6.121633857248144
H	2.538806142619228	-3.504062976266892	-7.468698494509260
H	1.177162590680162	-1.709545113260591	-6.409238838429436
N	2.535972060991911	-2.789261191128853	-2.310953139094350
N	1.692813941842843	-1.783811175169197	-2.285223025719597
N	1.254715140355675	-1.412579514613924	-3.527612584971449
Cu	0.014731747533462	-0.017248401453465	-3.594159060202175
C	-1.774785850890909	2.296799730544519	-5.854546526176656
C	-2.566253911747708	3.263739609553246	-6.452308690166956
C	-3.432890420729904	4.099957029821937	-5.698920036872249
C	-3.531150526004434	3.989991200366598	-4.322801177550707
C	-2.731130332048542	3.014548356244893	-3.696288067795194
C	-1.866010748666701	2.181069185241988	-4.455792732190620
H	-1.109596478224296	1.660197952749188	-6.439017867250233
H	-2.525109249926665	3.391511442831666	-7.534656868036813
H	-4.030616761818761	4.845886623889903	-6.224317785217854
H	-4.192443361980886	4.628930845387847	-3.737752066953655
N	-1.237092150032497	1.369394848042283	-3.558430632639846
N	-1.715939477232439	1.724749802517382	-2.326686780966639
N	-2.602995454563290	2.691819410147611	-2.373824579725904
Cu	0.854306099573087	-0.834059343192607	-0.856514410152881
Cu	-0.850936107329048	0.817910473528672	-0.882179308086045