Design of experiments a powerful tool to improve the selectivity of copper antimony sulfide nanoparticles synthesis

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Supplementary Information

The main effects and the interaction effects of the synthesis parameters in the nanoparticle size are calculated through the following equations:

$$t = \frac{(50 + 15.5 + 10.6 + 16.9) - (8.7 - 12.7 - 19.3 - 10.9)}{8} = 5.18$$

$$T = \frac{(50 + 12.7 + 19.3 + 16.9) - (8.7 + 15.5 + 10.6 + 10.9)}{8} = 6.65$$

$$S = \frac{(12.7 + 15.5 + 10.9 + 16.9) - (8.7 + 50 + 19.3 + 10.6)}{8} = -4.08$$

$$M = \frac{(19.3 + 10.6 + 10.9 + 16.9) - (8.7 + 50 + 12.7 + 15.5)}{8} = -3.65$$

$$t{:}T = \frac{(8.7 + 50 + 10.9 + 16.9) - (12.7 + 15.5 + 19.3 + 10.6)}{8} = 3.55$$

$$t{:}S = \frac{(8.7 + 15.5 + 19.3 + 16.9) - (50 + 12.7 + 10.6 + 10.9)}{8} = -2.98$$

$$t{:}M = \frac{(8.7 + 12.7 + 10.6 + 16.9) - (50 + 15.5 + 19.3 + 10.9)}{8} = -5.85$$

Table S1: Performed synthesis with design of experiments.

Synthesis	T	t	S	M	Experimental Order
1	-	-	-	-	2
2	+	-	-	-	11
3	-	+	-	-	3
4	+	+	-	-	12
5	-	-	+	-	15
6	+	-	+	-	5
7	-	+	+	-	16
8	+	+	+	-	6
9	-	-	-	+	4
10	+	-	-	+	9
11	-	+	-	+	1
12	+	+	-	+	10
13	-	-	+	+	7
14	+	-	+	+	13
15	-	+	+	+	8
16	+	+	+	+	14

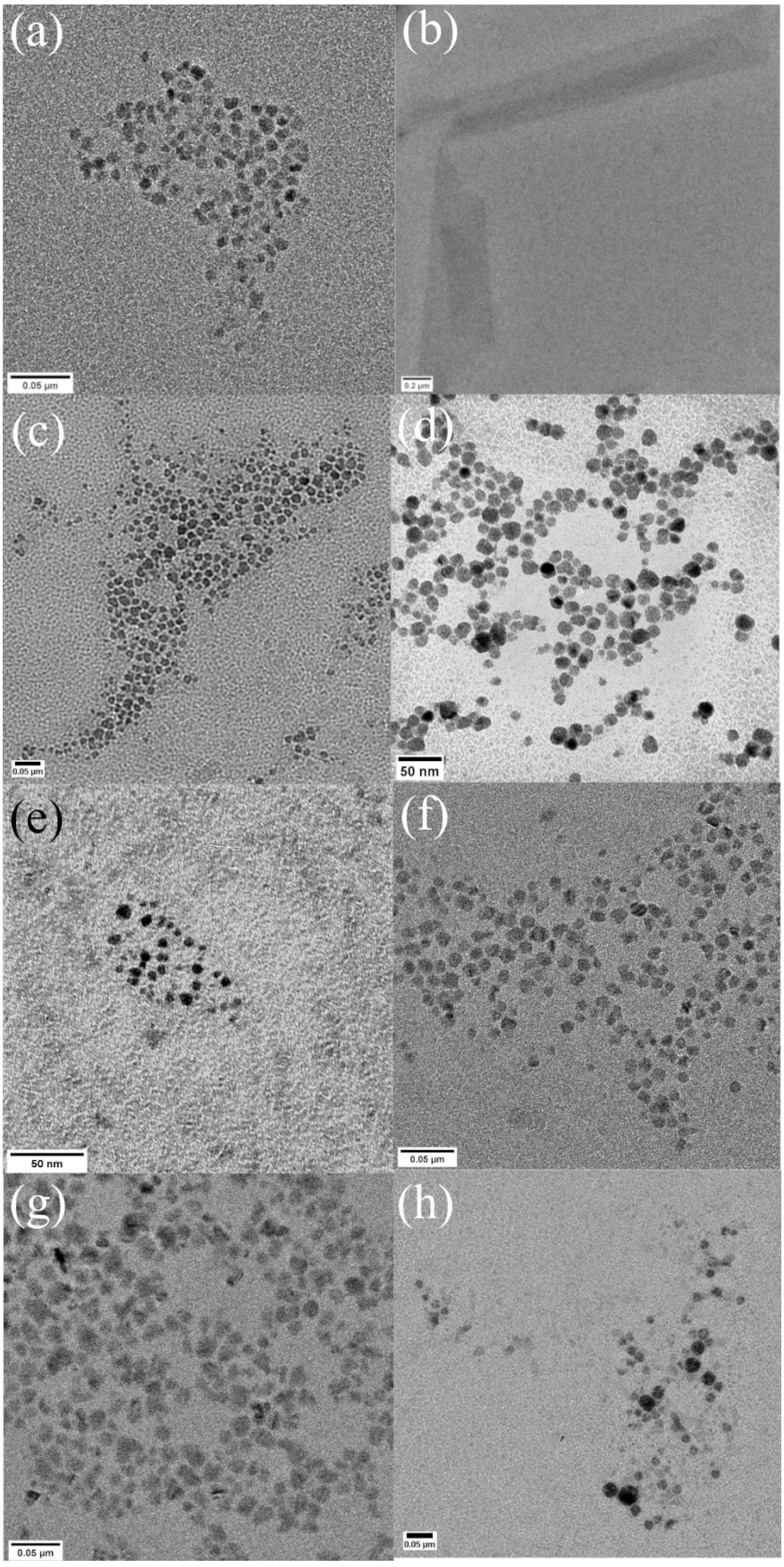

Figure S1: Figure S1: TEM images of the samples 01 (a), 04 (b), 06 (c), 07 (d), 10 (e), 11 (f), 13 (g), 16 (h).

The effect graphics are presented as Pareto Plots. A positive effect means that the observed

parameter has an increased response for the effect, and the contrary is true. For example, if a temperature column (parameter) shows a positive response on particle size, it means that increasing temperature (in this case from 200ºC to 250ºC) will generate larger particle sizes; and decreasing temperature (here from 250ºC to 200ºC) will result in smaller particles. The interaction among the parameters should also be observed (either positive or negative). In a positive interaction, keeping both variables at the same level (up or down) leads to an increase in nanoparticle size, while setting those variables in different levels (one up, other down) leads to a decrease in size. On the other hand, if the interaction is negative, setting both variables on the same level will result in a decrease of the nanoparticle size, while keeping the variables on different levels leads to a larger size.

In Figure 1, The magnitude of effect represents the size of that effect. Considering as an example a 2^4 factorial design used in this work.

It's calculated with the Equation (1), for 2-level factorial design, with T, t, S and M parameters (2^3 factorial design):

$$T = \bar{y}_{A+} - \bar{y}_{A-} \quad (1)$$

Where T is the analyzed parameter, $\bar{y}_{A+}$ represents the of the 8 experiments where T is at the high level (+) minus the average of the 8 experiments where T is at the low level (-)

Considering the interactions of effects, Equation 1 becomes Equation 2:

$$T = \frac{1}{n}[(y2 + y4 + y6 + y8 + y10 + y12 + y14 + y16) - (y1 + y3 + y5 -$$
$$]$$

(2)

Where the (k-1) from $2^{(k-1)}$ is the number n, here n = 8.

Equation 2 is done for every effect: T, t, S and M and also for every desired information: size, phase, fluorescence and go on. The interaction of the effects can be calculated with Equation 3, considering the interaction between effects T and t:

$$Tt = \frac{1}{n}[(y1 - y4 + y5 + y8 + y9 + y12 + y13 + y16) - (y2 + y3 + y6 +$$

(3)

Where the (k-1) from $2^{(k-1)}$ is the number n, here n = 8.

Like Equation (2), Equation (3) is the difference between two averages: the 8 experiments with equal signs for Tt interaction and the 8 experiments with different signs for Tt interaction.

These Equation can be found on the book Statistics for Experimenter, Design, Innovation, and Discovery, 2nd Ed., 2005, Wiley, by G. E. P. Box, J. S. Hunter, W. G. Hunter. With these equations, a matrix could be developed and that is what the code applied to this article uses.

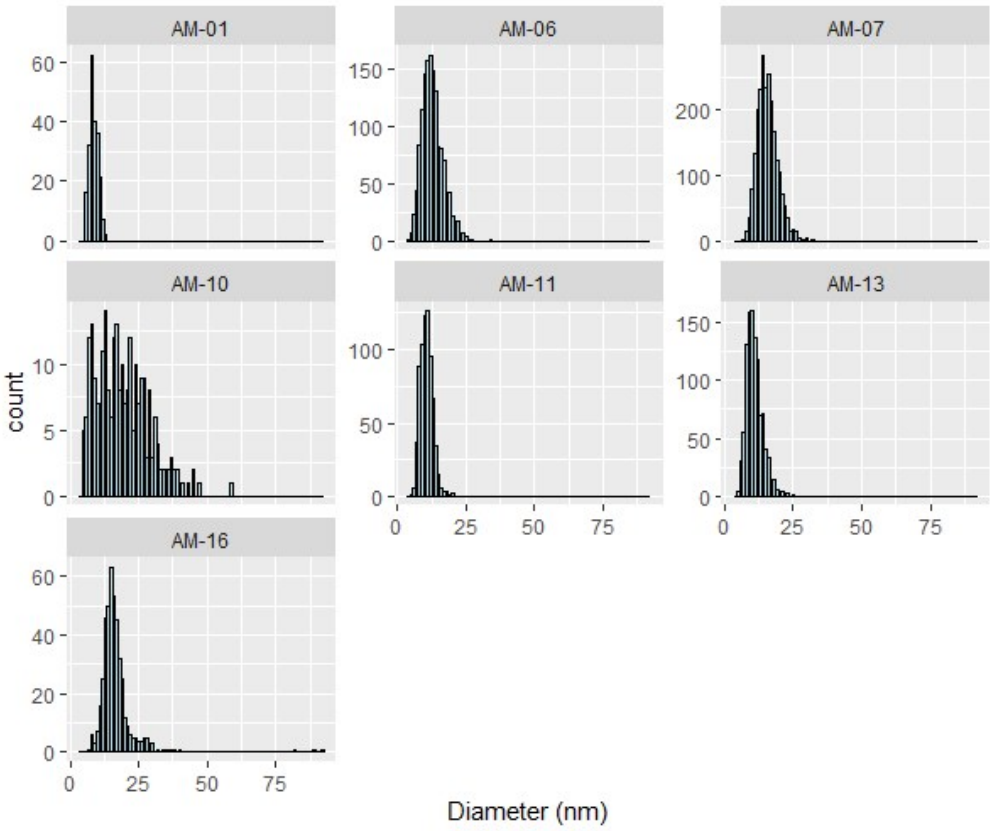

Figure S2: Histograms of TEM images of the nanoparticles synthesized on conditions 1, 6, 7, 10, 11, 13 and 16.

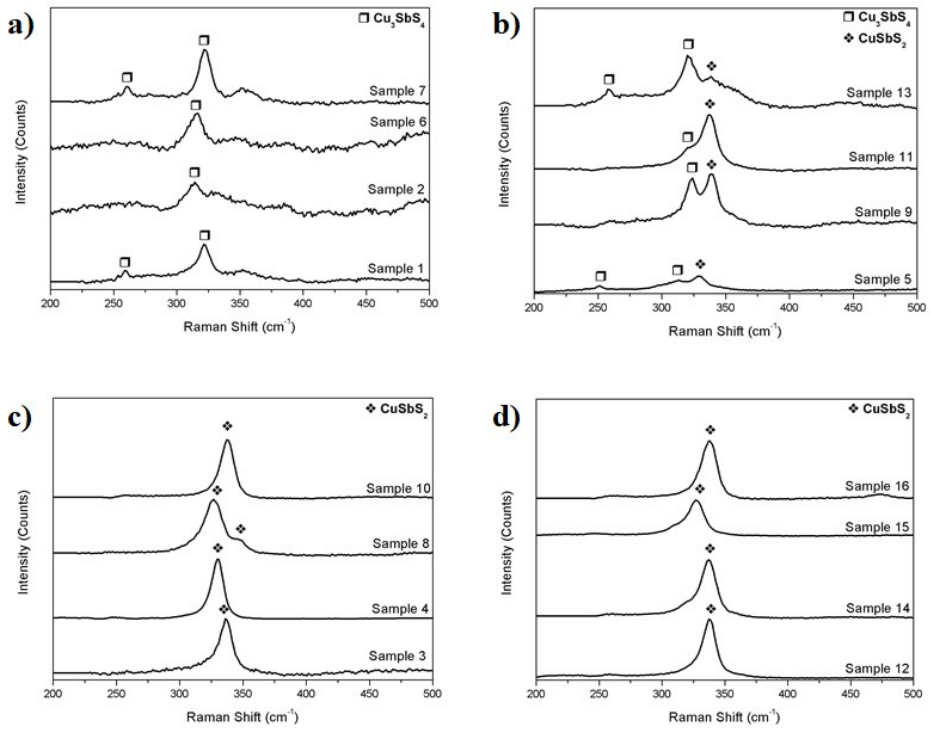

Figure S3: Raman spectra for 16 samples, where a) Cu_3SbS_4, b) both phases, c) and d) $CuSbS_2$.

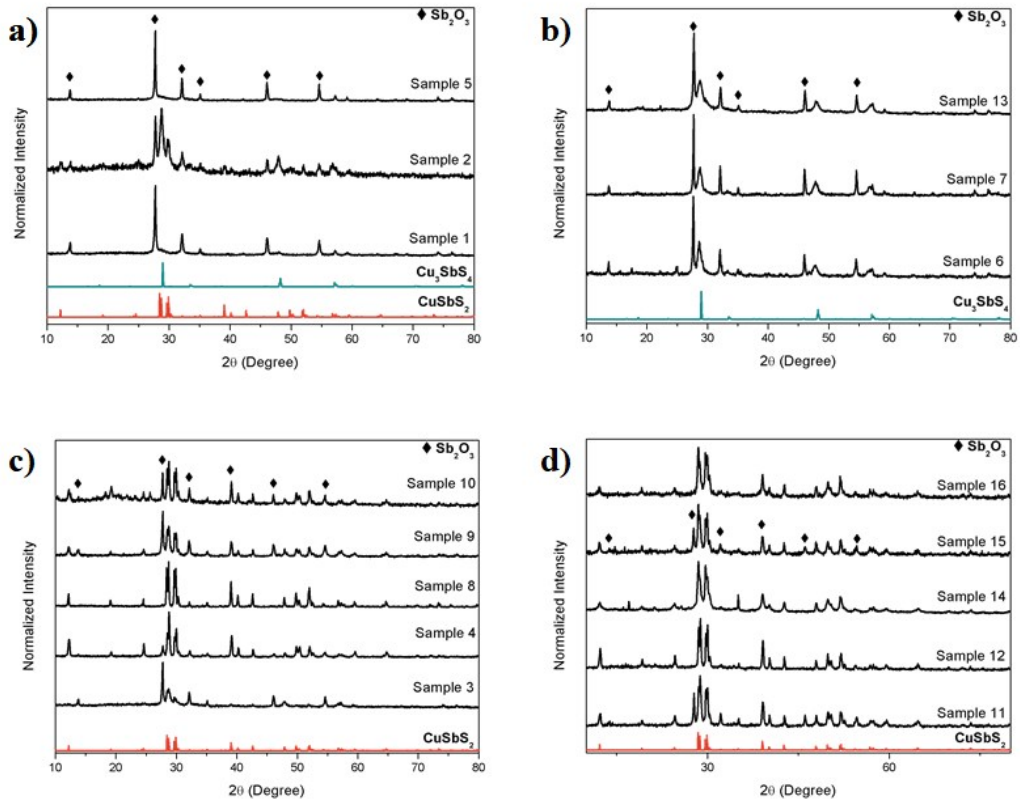

Figure S4: XRD diffration pattern for 16 samples, where a) and b) are for Cu3SbS4 (or a mixture of both phases); c) and d) CuSbS2.

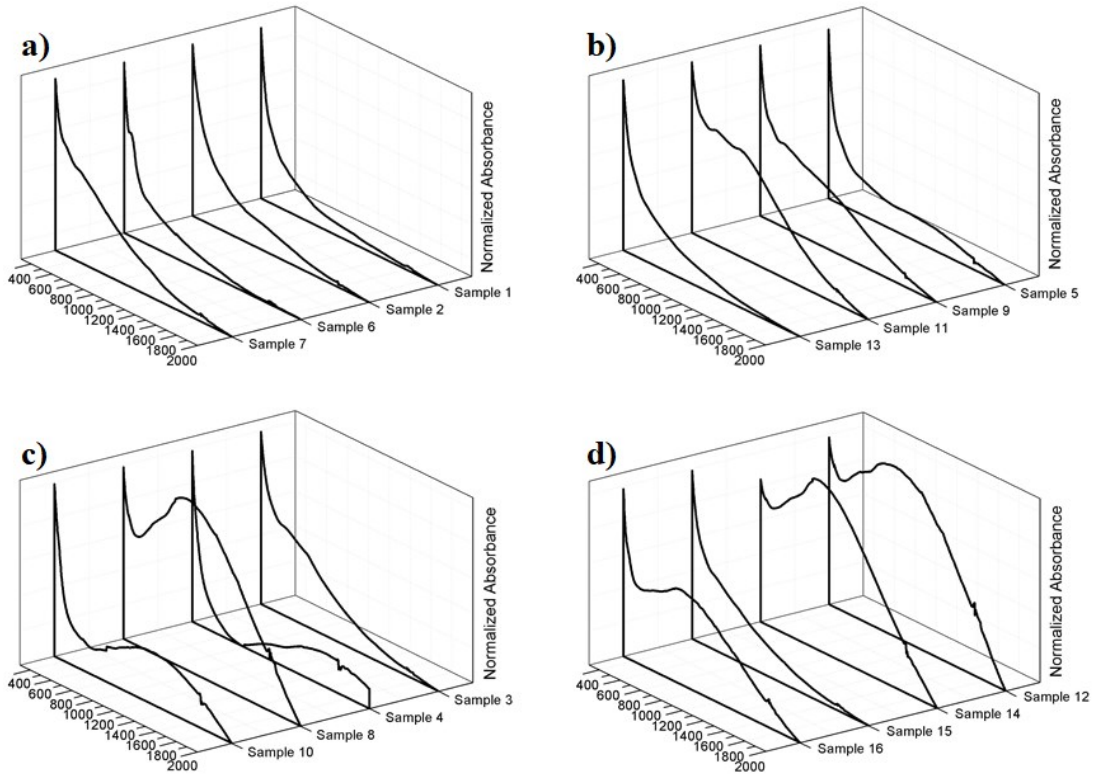

Figure S5: absorbance spectra for 16 samples, where a) and b) are for Cu_3SbS_4 (or a mixture of both phases); c) and d) $CuSbS_2$.

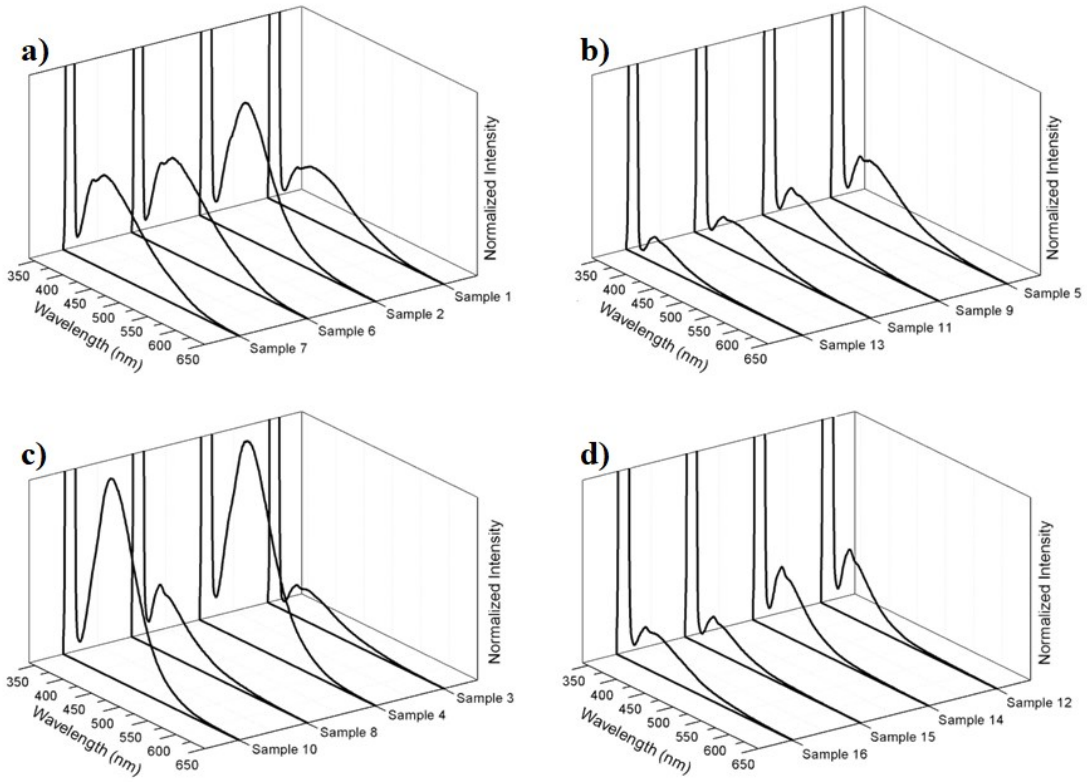

Figure S6: Fluorescence spectra for the 16 samples.

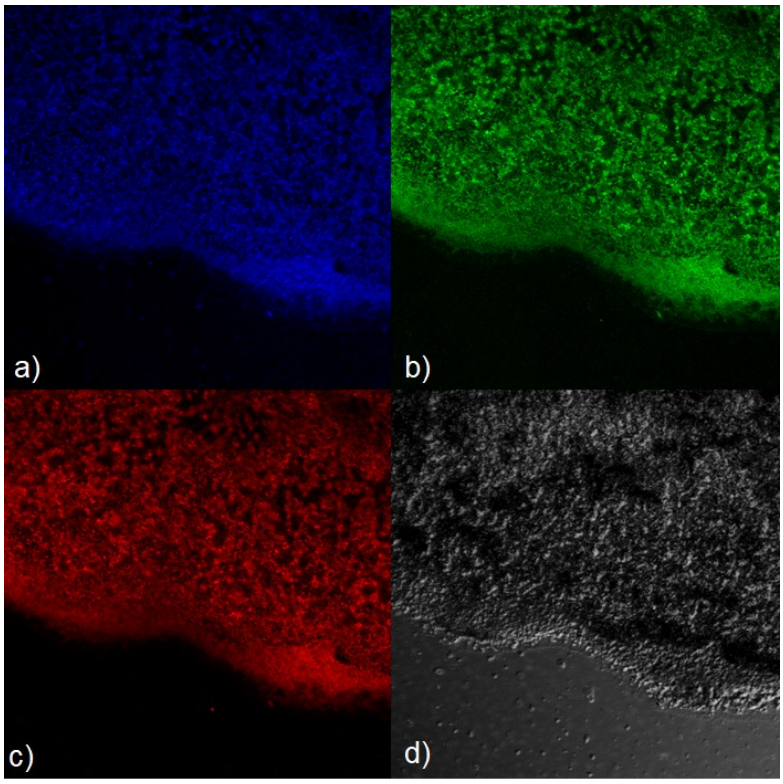

Figure S7: Confocal microscopy images of Cu_3SbS_4 with excitations wavelengths at a) 405 nm, b) 473 nm, c)559 nm and d) no excitation.

Code 1 – referred here for fluorescence analysis

```
T <- c(-1,+1,-1,+1,-1,+1,-1,+1,-1,+1,-1,+1,-1,+1,-1,+1)

t <- c(-1,-1,+1,+1,-1,-1,+1,+1,-1,-1,+1,+1,-1,-1,+1,+1)

S <- c(-1,-1,-1,-1,+1,+1,+1,+1,-1,-1,-1,-1,+1,+1,+1,+1)

M <- c(-1,-1,-1,-1,-1,-1,-1,-1,+1,+1,+1,+1,+1,+1,+1,+1)

y1 <- c(70.9, 152.4, 34.8, 220, 59.9, 105, 102.2, 52.35, 33.3, 220.4, 32.1, 48.6,
19.4, 50.4, 24.6, 42.4)

#install.packages("pid")  # Only required once, if you've not installed "pid" already

library(pid)

# fluorescence

model.y1 <- lm(y1 ~ T*t*S*M)    # fluorescence

summary(model.y1)

paretoPlot(model.y1)

model.y1$coefficients[1]

graf <- model.y1$coefficients[-1]

graf <- as.data.frame(graf)

graf$Effect <- rownames(graf)

rownames(graf) <- NULL

names(graf) <- c("Magnitude of Effect","Effect Name")

graf$`Effect Name` <- factor(graf$`Effect Name`, levels = graf$`Effect
Name`[order(abs(graf$`Magnitude of Effect`), decreasing = FALSE)])

custom.col <- c("#C3D7A4", "#52854C")

library(ggplot2)

library(ggthemes)

ggplot(graf, aes(`Effect Name`,abs(`Magnitude of Effect`),

                 fill = `Magnitude of Effect` > 0)) +

  geom_col()  + coord_flip()+ ylab("Magnitude of Effect") +

  guides(fill = FALSE) + scale_fill_manual(values=custom.col) + theme_base()
```