Electronic Supplementary Material (ESI) for RSC Advances
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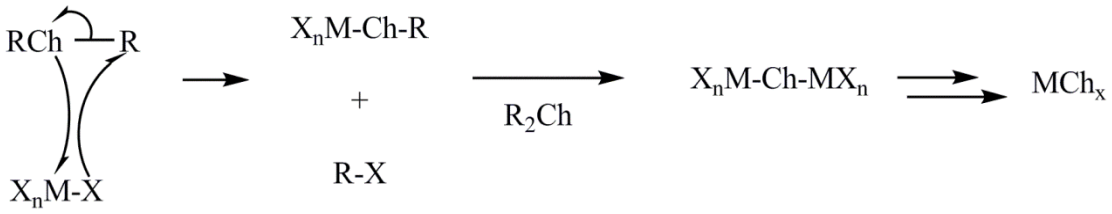
Supplementary Materials

Non-hydrolytic sol-gel reaction scheme:



Reaction equations for reactions of copper chloride (not that continued reaction results in formation of metal sulfides):

(i) $CuCl + (CH_3)_3Si\text{-}S\text{-}Si\text{-}(CH_3)_3 \rightarrow Cu\text{-}S\text{-}Si(CH_3)_3 + (CH_3)_3SiCl$
$Cu\text{-}S\text{-}Si(CH_3)_3 + CuCl \rightarrow Cu\text{-}S\text{-}Cu + (CH_3)_3SiCl$
overall: $x\ CuCl + x/2\ (CH_3)_3Si\text{-}S\text{-}Si\text{-}(CH_3)_3 \rightarrow (Cu_2S)_x + x\ (CH_3)_3SiCl$

(ii) $CuCl_2 + (CH_3)_3Si\text{-}S\text{-}Si\text{-}(CH_3)_3 \rightarrow Cl\text{-}Cu\text{-}S\text{-}Si(CH_3)_3 + (CH_3)_3SiCl$
$Cl\text{-}Cu\text{-}S\text{-}Si(CH_3)_3 + CuCl_2 \rightarrow Cl\text{-}Cu\text{-}S\text{-}Cu\text{-}Cl + (CH_3)_3SiCl$
$x\ (Cl\text{-}Cu\text{-}S\text{-}Cu\text{-}Cl) + x\ (CH_3)_3Si\text{-}S\text{-}Si\text{-}(CH_3)_3 \rightarrow (CuS)_x + x\ (CH_3)_3SiCl$
overall: $x\ CuCl_2 + x\ (CH_3)_3Si\text{-}S\text{-}Si\text{-}(CH_3)_3 \rightarrow (CuS)_x + 2x\ (CH_3)_3SiCl$

Table S1: Elemental analysis of selected subset of samples from different synthetic routes shown in Figure 1. Cu/S ratios are calculated from EDS data except † (CHNS data).

	Synthetic Variables	EDS			CHNS		Cu/S ratio
		Cu at%	S at%	Cl at%	C wt%	S wt%	
Route (1): Neat	RT	64±6	35±4	1±1	0.7±0.3	19.4±0.6	1.8±0.3
	70 °C	70±5	29±5	0±1	0.4±0.3	19.8±0.6	2.0±0.1†
Route (2):RT, CH_3CN	5 min	68±4	30±4	2±1			2.2±0.4
	5 h	67±5	32±5	1±1			2.1±0.4
	7 d	67±3	31±3	2±1	0.7±1.1	19.0±1.8	2.1±0.3
Route (5): RT, $CHCl_3$	0.2 M, 7 d	68±3	31±3	1±1	0.1±0.6	18.8±0.9	2.2±0.3
	0.4 M, 7 d	67±4	31±3	3±2	0.8±0.7	18.9±1.1	2.1±0.3
	0.9 M, 7 d				0.7±0.5	18.2±0.8	2.2±0.1†

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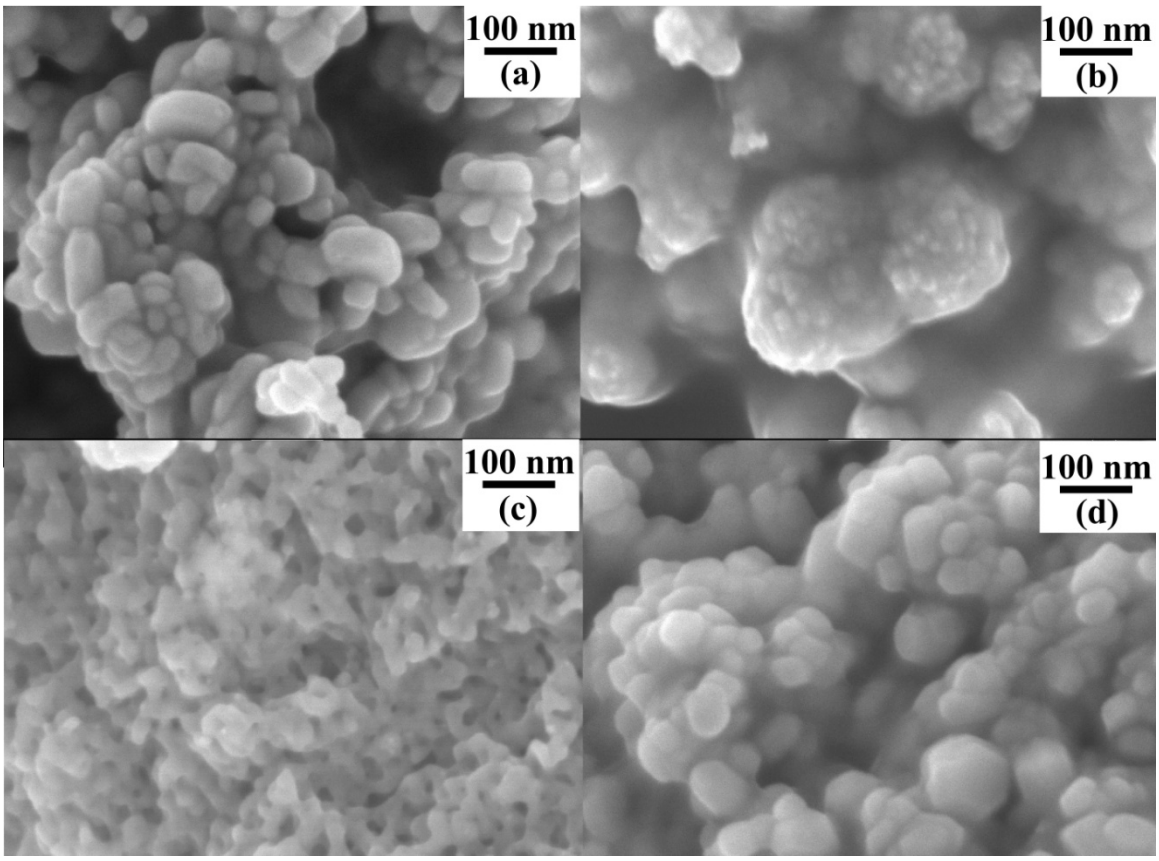

Figure S1. SEM images of copper sulfides prepared by reactions of CuCl with HMDST in chloroform at RT: a) 0.2 M HMDST, 1.5 h, b) 0.4 M HMDST, 1.5 h and in acetonitrile c) 0.2 M HMDST, 1 d and d) 0.2 M HMDST, 7d. a) and d) consist of α-chalcocite, and b) and c) consist of β-chalcocite.

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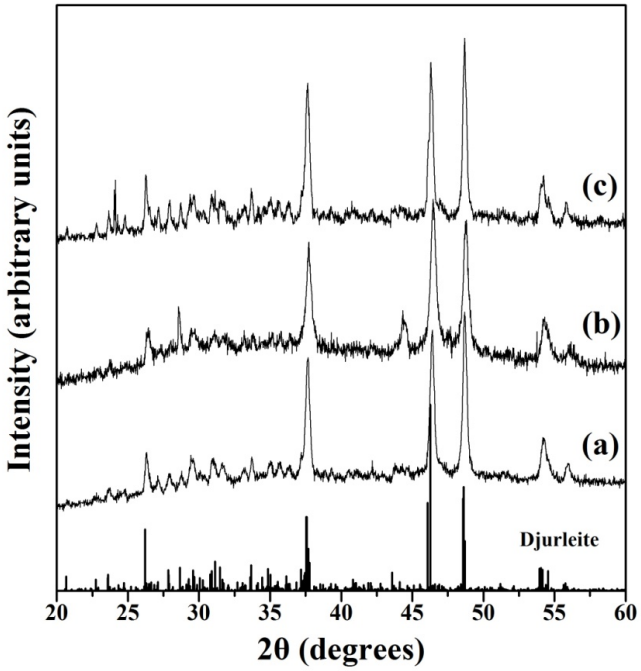

Figure S2. PXRD patterns of djurleite synthesized by reactions of CuCl and HMDST in acetonitrile for 7 d at: a) 70 °C with 0.4 M HMDST, b) 70 °C with 0.9 M HMDST and c) 130 °C with 0.9 M HMDST. Lines indicate peak positions of djurleite (PDF card 71-1383).

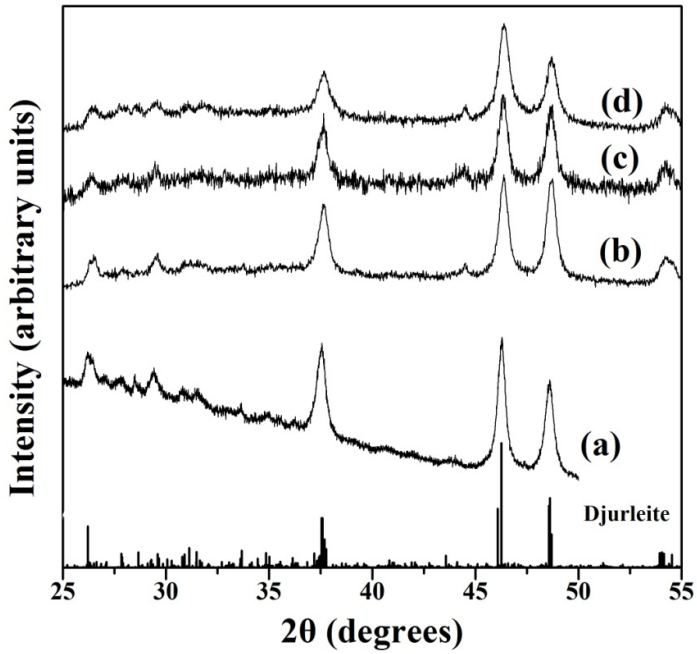

Figure S3. PXRD patterns of copper sulfides prepared by reactions of CuCl and HMDST in chloroform at 70 °C for 7 d with a) and b) 0.2 M HMDST, collected on capillary and flat stages, respectively, c) 0.4 M HMDST and d) 1.0 M HMDST. c) and d) were collected on a flat stage. The PDF card for djurleite is 71-1383.

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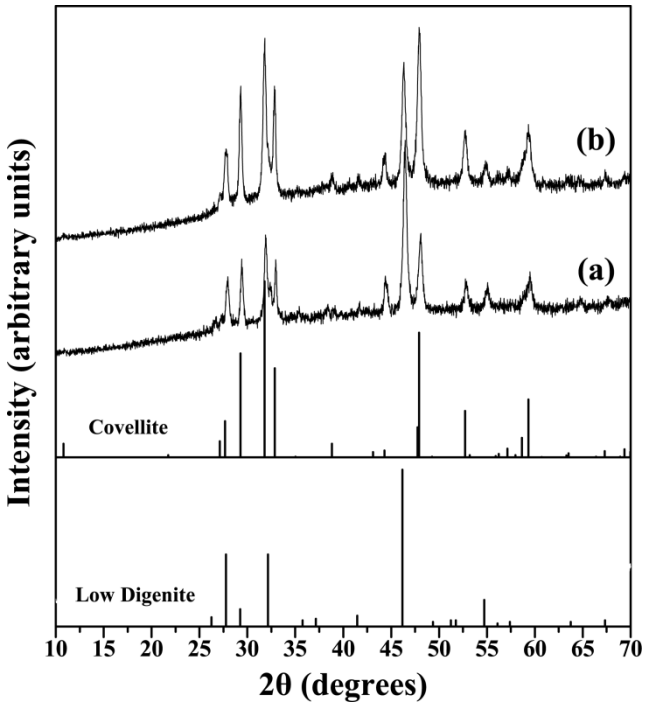

Figure S4. PXRD patterns of copper sulfides prepared by reactions of CuCl with 0.4 M HMDST in chloroform at 130 °C for a) 7 d and b) 15 d. Lines indicate PDF cards of low digenite (PDF card 47-1748, bottom) and covellite (PDF card 78-0877, top).

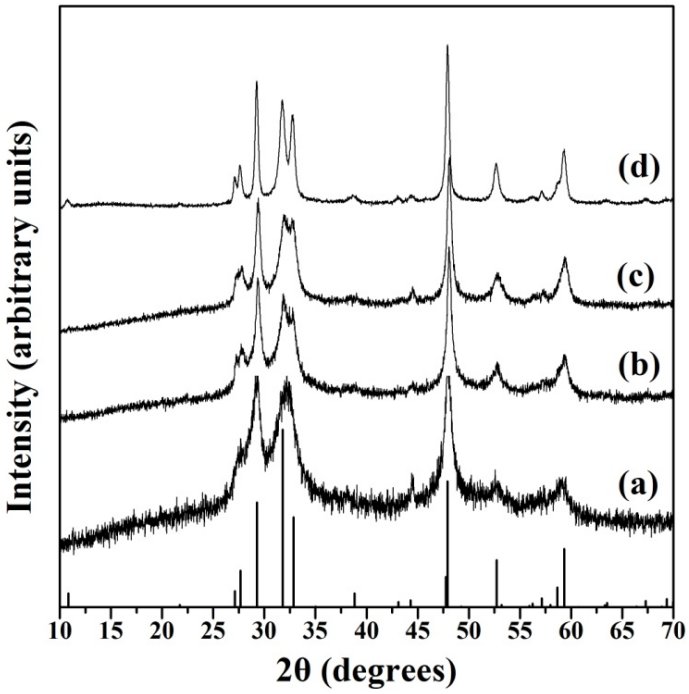

Figure S5. PXRD patterns of covellite prepared by reaction of $CuCl_2$ with 0.4 M HMDST a) in $CHCl_3$ at RT, and in CH_3CN at b) RT, c) 70 °C and d) 130 °C. Lines indicate peak positions of covellite (PDF card 78-0877).

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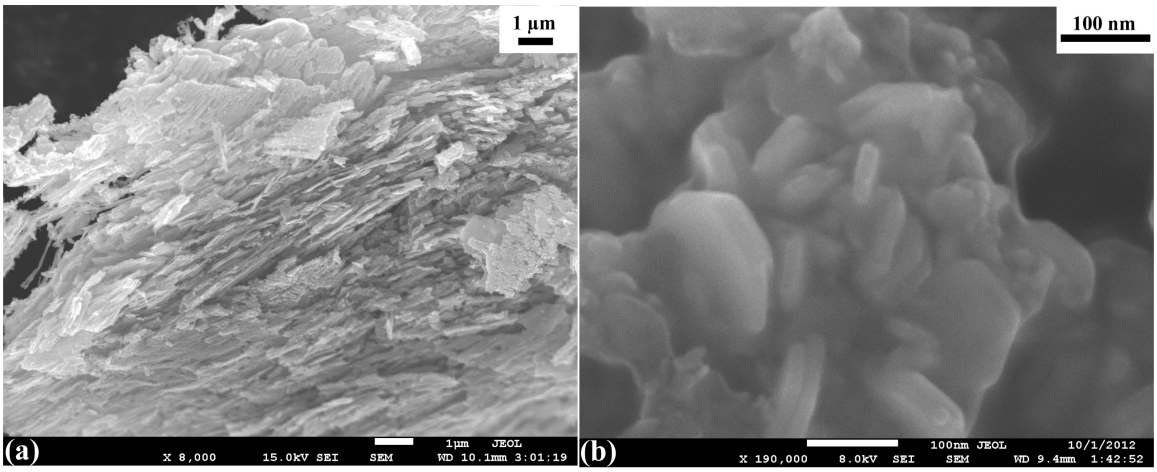

Figure S6. SEM images of covellite prepared by reactions of $CuCl_2$ and HMDST with a) 0.9 M HMDST in chloroform at 70 °C for 7 d and b) 0.9 M HMDST in acetonitrile at RT for 4 d.

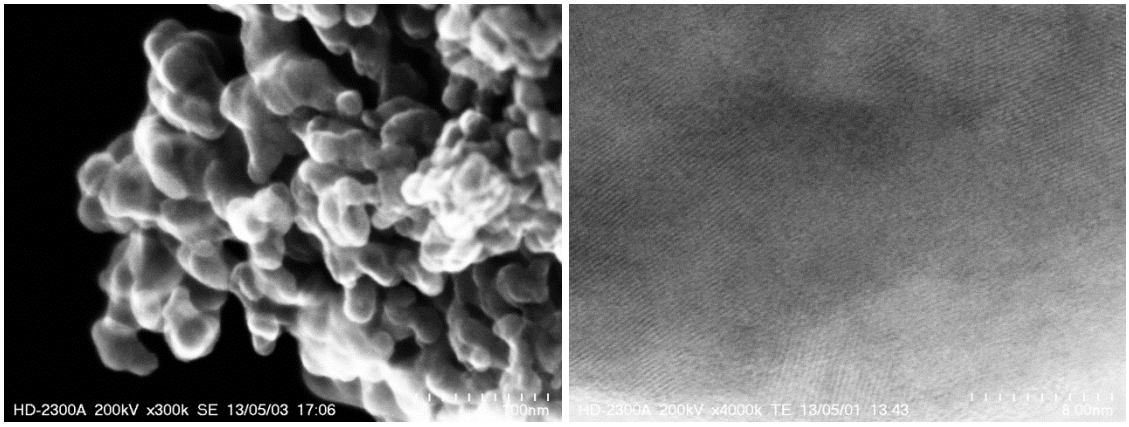

Figure S7. STEM images of samples prepared at RT with XRD patterns displaying phases between α-chalcocite and djurleite. This is corroborated by the high magnification image, which shows multiple orientations of lattice fringes.

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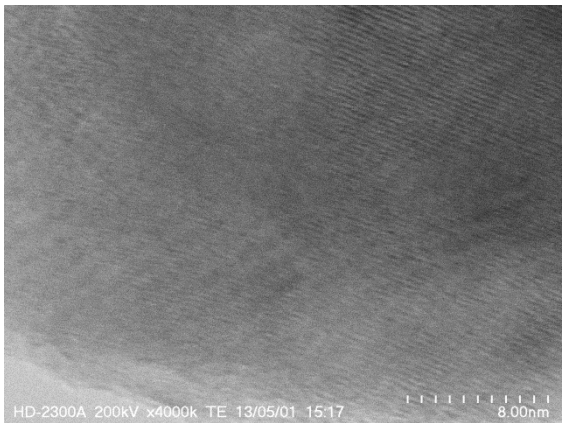

Figure S8. STEM image of a sample prepared with CuCl and HMDST in CH_3CN at RT for 7 d. This sample consists of fully formed djurleite, and lattice fringes extend in the same direction over significant length scales.

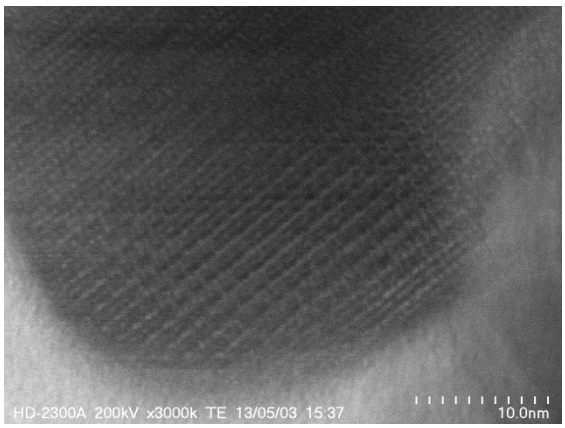

Figure S9. STEM image of a sample prepared with CuCl and high [HMDST] in CH_3CN at RT for 5 h. The XRD pattern of this sample showed well crystallized phase pure α-chalcocite at the time of recovery, and slow conversion to djurleite afterwards. This image was taken six months after preparation, when the sample consisted of a mixture of α-chalcocite and djurleite.