Electronic Supplementary Material (ESI) for Dalton Transactions
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SUPPLEMENTARY MATERIAL to the paper:

Copper perchlorate and tetrafluoridoborate compounds with the ligand 1,4,5-triazanaphthalene. Gradual transformation of mononuclear Cu(II) compounds via polynuclear mixed-valence Cu(II)/Cu(I) species to dinuclear Cu(I); syntheses, characterizations and X-ray structures.

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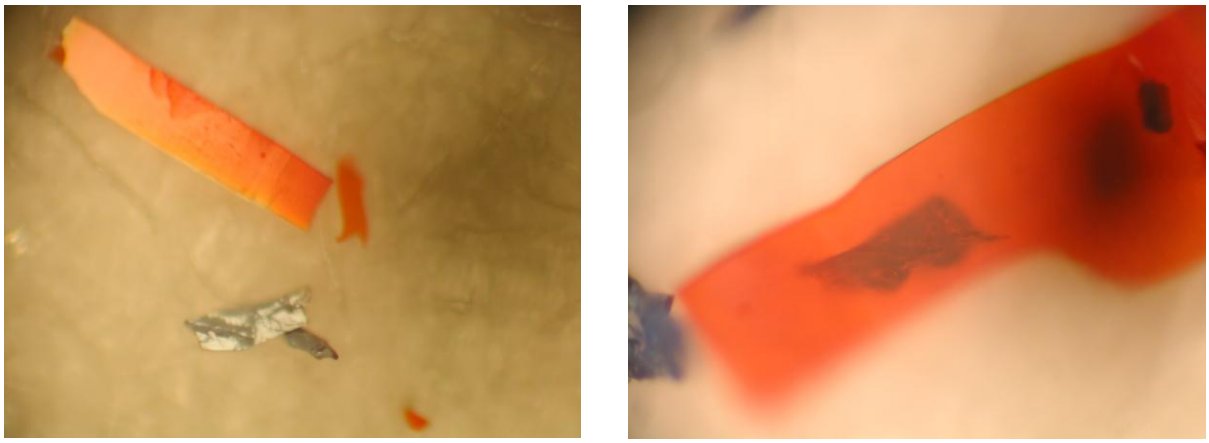

Figure S1: Photo 1, microscope camera snapshots showing the colour change from red to blue crystals or vice versa.

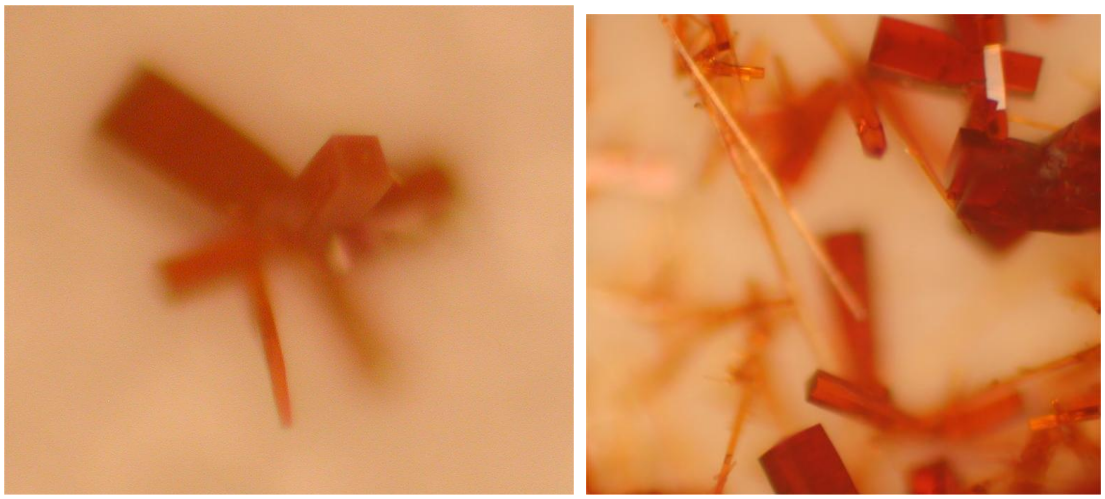

Figure S2: Photo 2. Example of microscope camera snapshot showing the red crystals of **5** and **5**A as a block-like and a needle-like form.

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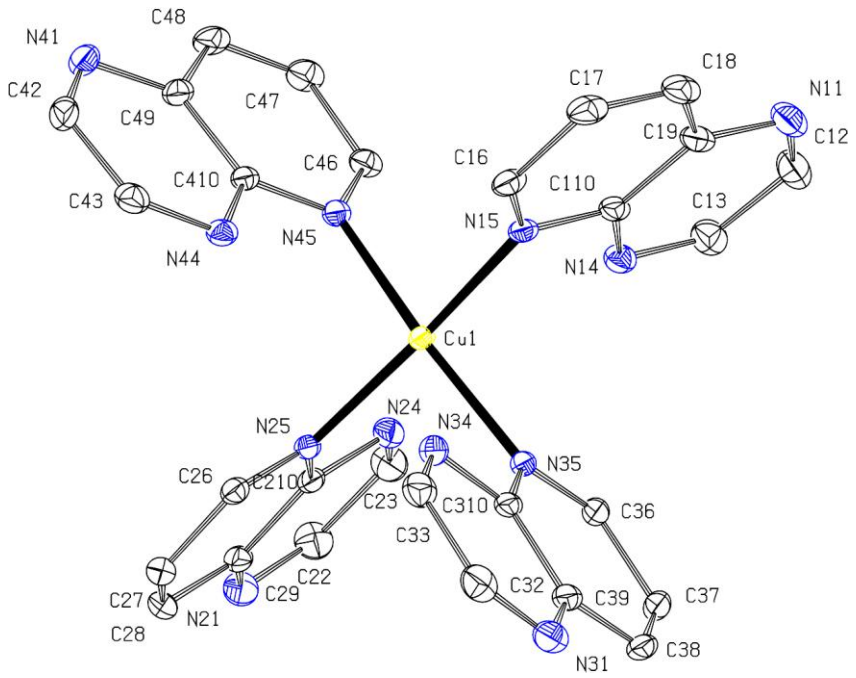

Figure S3: Atomic displacement plot (30% probability level) of the molecular structure of the purple compound $[Cu(tan)_4](BF_4)_2(CH_3OH)_{1.5}(H_2O)$ (**3**). Hydrogen atoms, anions and non-coordinating methanol and water molecules are omitted for clarity.

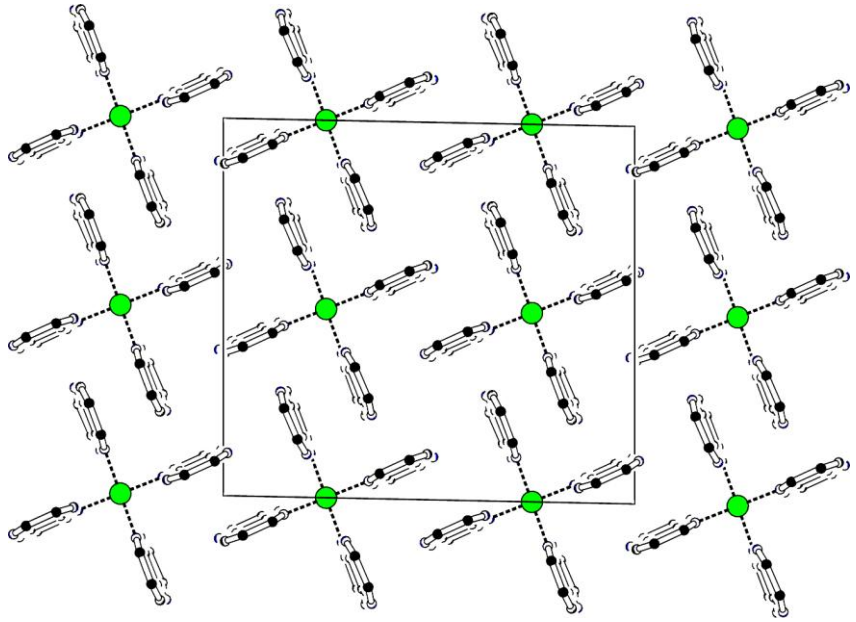

Figure S4. Packing figure of compound **2** along Y axis. Hydrogen atoms, anions and water molecules are omitted for clarity.

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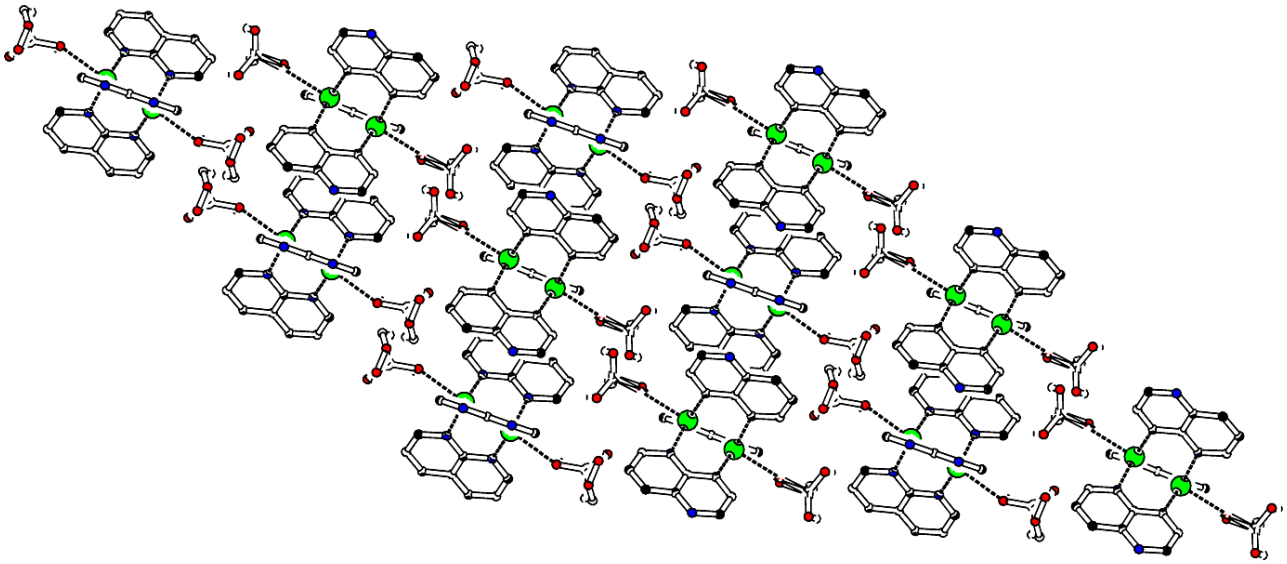
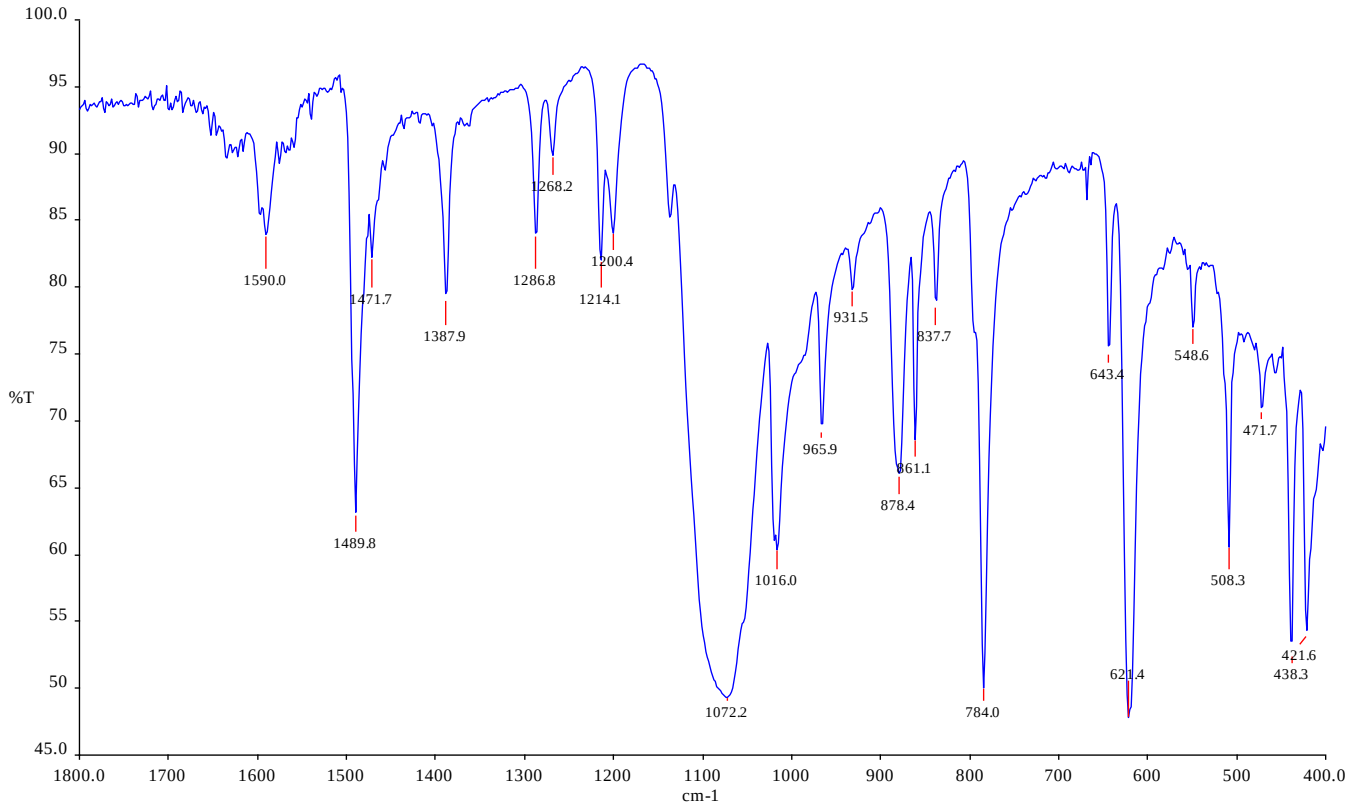


Figure S5. Packing figure of compound **7** along Y axis. Hydrogen atoms are omitted for clarity.

Figure S6: IR Spectra in the range 1800-400 cm^{-1} for compounds **2, 4, 5, 6** and **7**.



Compound $[Cu(tan)_4](ClO_4)_2(H_2O)_2$ (**2)** blue

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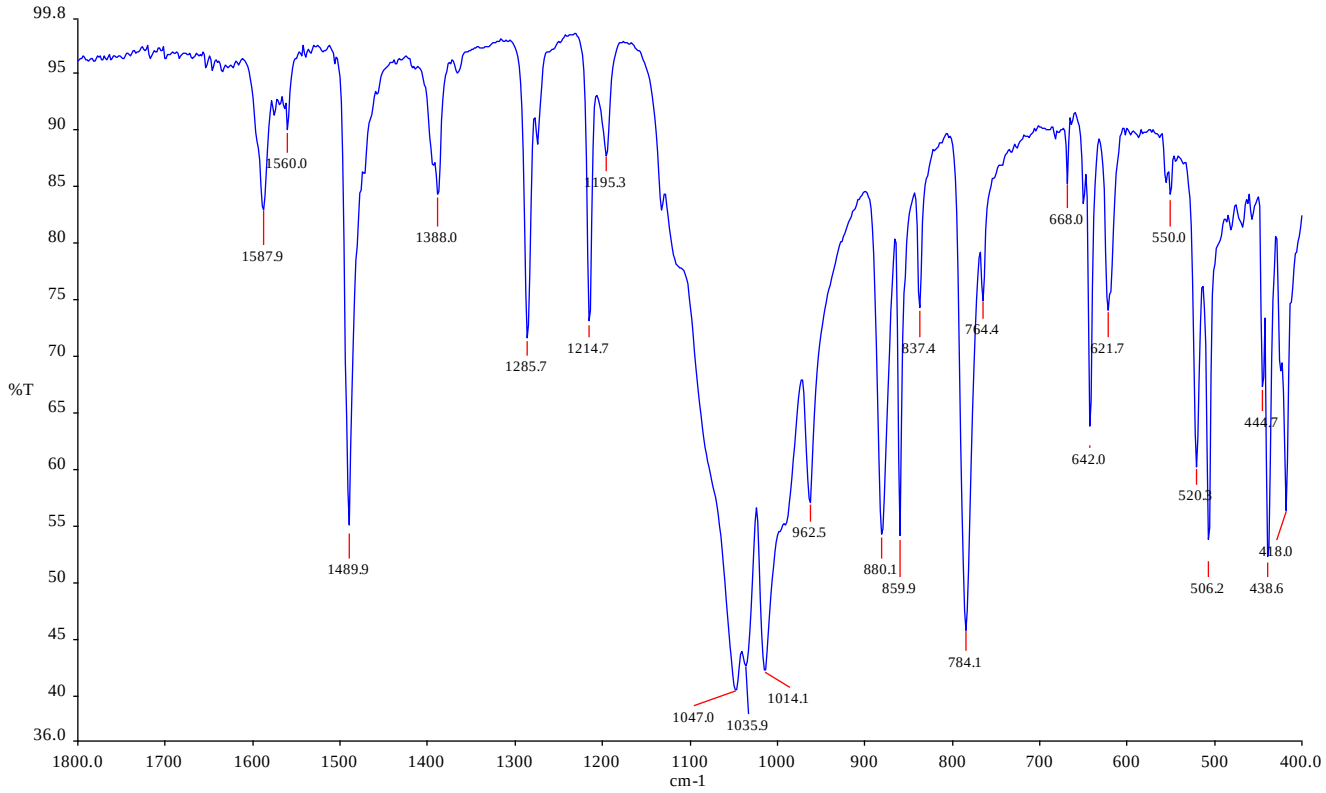
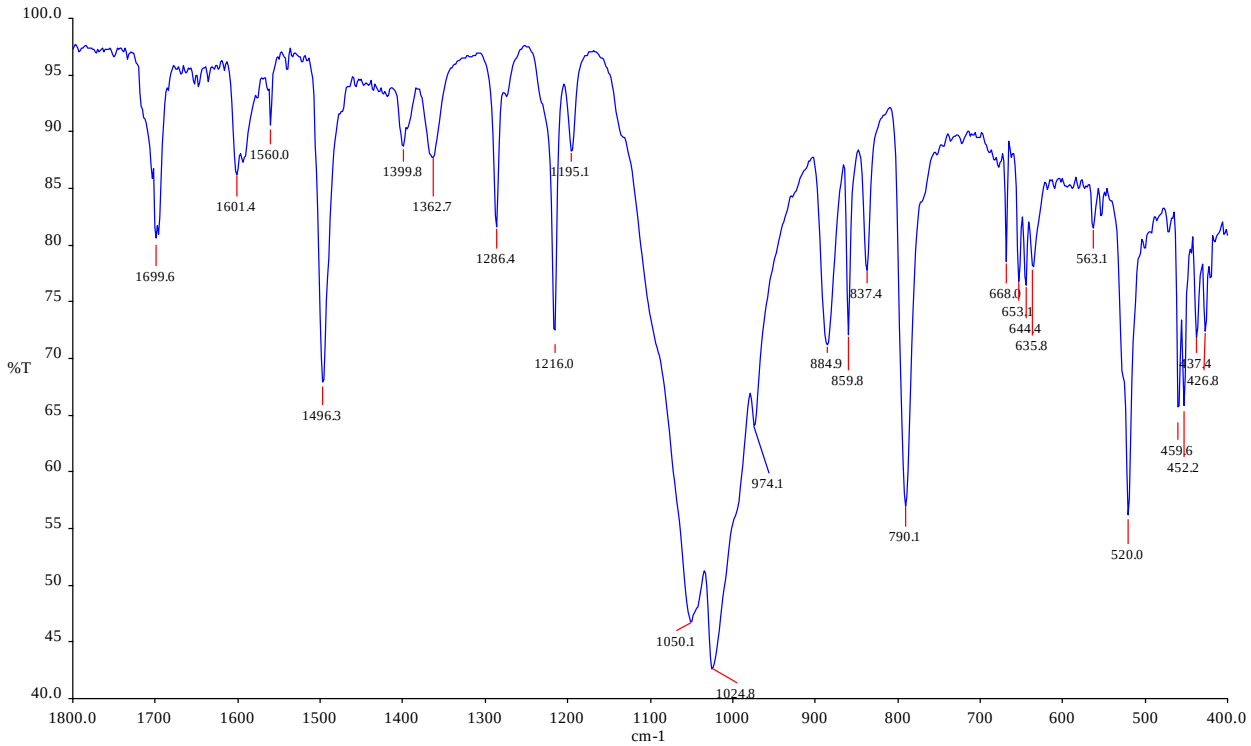


Compound $[Cu(tan)_4](BF_4)_2(H_2O)_2$ (**4)** blue



Compound $[Cu_2(tan)_4]_n(BF_4)_{3n}(H_2O)_{6n}$ (**5/5A**) red

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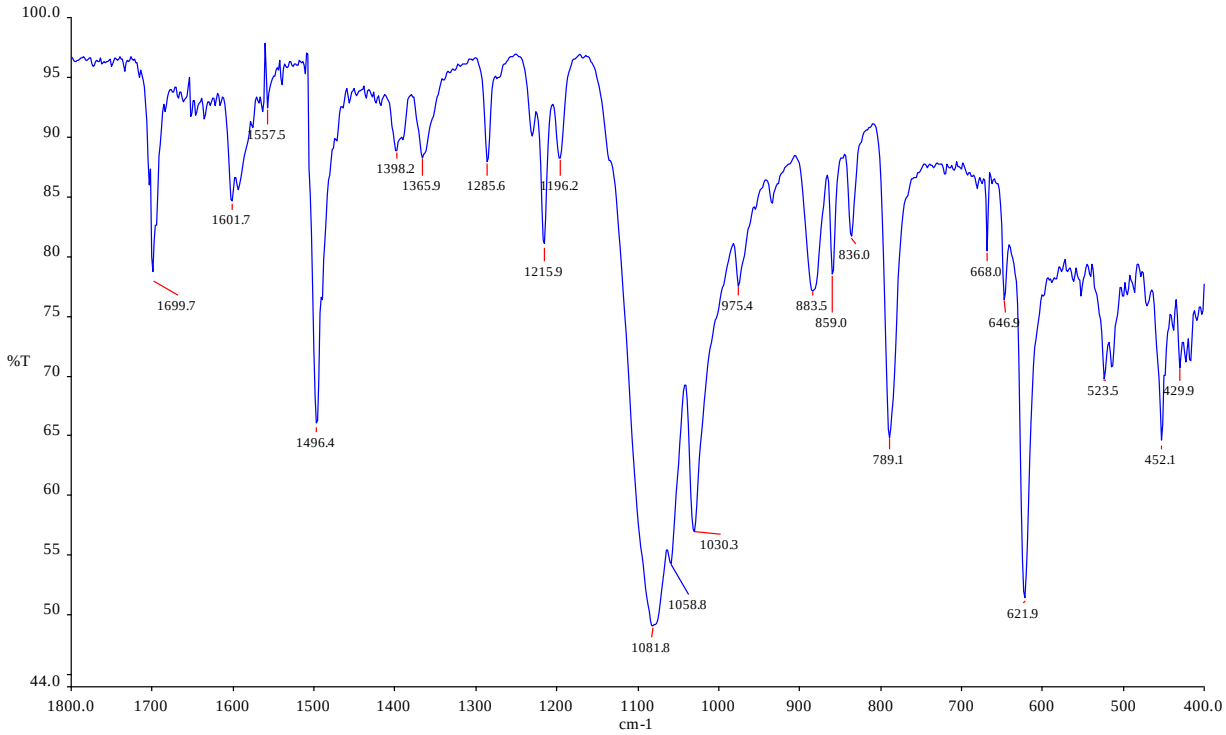
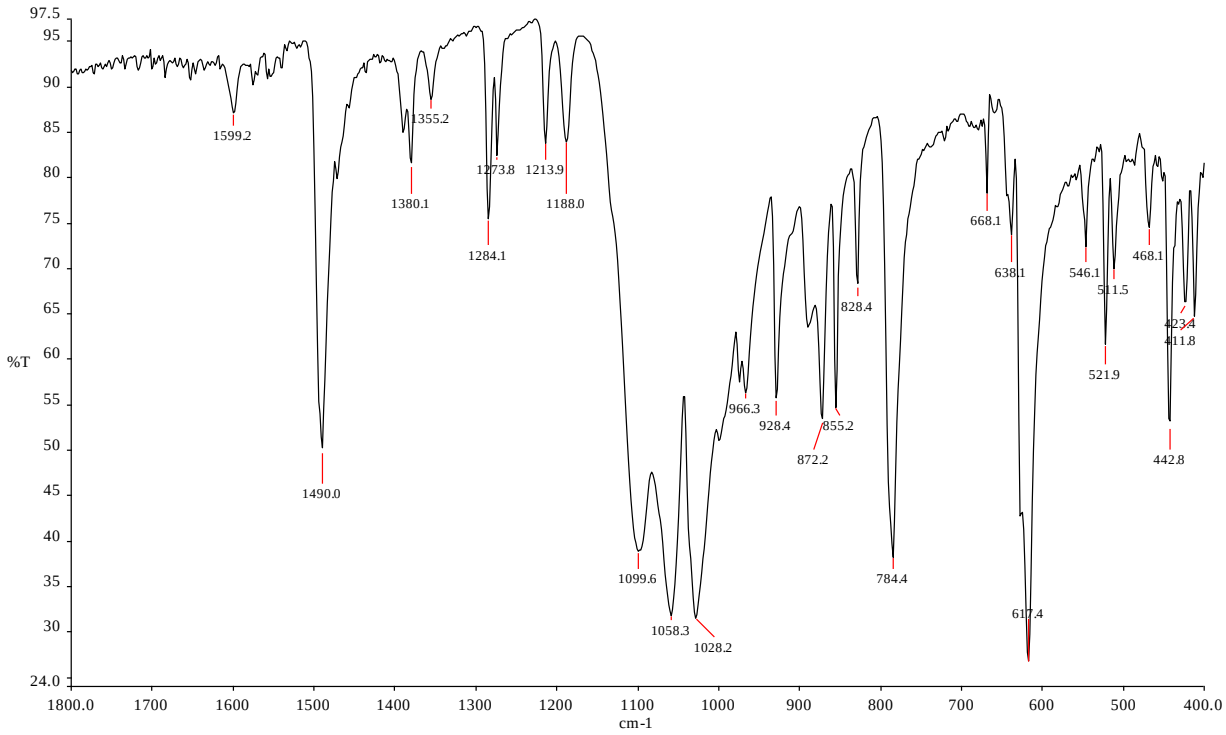


Compound $[Cu_2(tan)_4]_n(ClO_4)_{3n}(H_2O)_{6n}$ (**6/6A**) red (from ref. 1)



Compound $[Cu_2(tan)_3](ClO_4)_2]$ (**7**) red.

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Table S1. IR data of the Cu compounds with the ligand tan.

Compound	colour	IR [a]	anions
free ligand		1010 875 775 641 490 425 400	
2. $[Cu(tan)_4](ClO_4)_2(H_2O)_2$ *	blue	1016 878 784 643 621 508 438 421	1072(br)
4. $[Cu(tan)_4](BF_4)_2(H_2O)_2$	blue	1014 880 784 642 622 506 438 418	1036 1047
5/5A.$[Cu_2(tan)_4]_n(BF_4)_{3n}(H_2O)_{6n}$ **	red	1024 885 790 653 644 520 460 452 437 427	1050
6/6A$[Cu_2(tan)_4]_n(ClO_4)_{3n}(H_2O)_{6n}$ **	red	1030 883 789 622 524 514 452 429(w) 422(w) 417(w)	1059
7. $[Cu_2(tan)_3](ClO_4)_2$	red	1028 872 784 617 522 512 443 423(w) 412(w)	1058 1100

br = broad; w = weak; * = X-ray structure done, ** = X-ray structure done, the X-ray crystal structures, with crystals directly from the mother liquid have the formula $[Cu_2(tan)_4]_n(BF_4)_{3n}$ (**5**), $[Cu(tan)_4]_n(BF_4)_{3n}(CH_3OH)_n(H_2O)_{5n}$ (**5A**), $[Cu_2(tan)_4]n(ClO_4)_{3n}$ (**6**) and $[Cu_2(tan)_4]_n(ClO_4)_{3n}(CH_3OH)_{2n}$ (**6A**), the dry compounds have the formula shown in this table (see experimental section)
[a] = strongest peaks of the ring vibration [2, 3]

References:

1. G. A. van Albada, M. Ghazzali, K. Al-Farhan, I. Mutikainen and J. Reedijk, *Inorg. Chem. Commun.*, 2011, **14**, 162-165.
2. W. L. Armarego, G. B. Barlin and E. Spinner, *Spectrochim. Acta*, 1966, **22**, 117-&.
3. H. J. Stoklosa, J. R. Wasson, E. V. Brown, H. W. Richardson and W. E. Hatfield, *Inorg. Chem.*, 1975, **14**, 2378-2382.