Electronic Supplementary Information

Synthesis, characterisation and evaluation of a novel copper-64 complex with selective uptake on EMT-6 cells under hypoxic conditions

James C. Knight,[a] Melinda Wuest,[a] Fawaz A. Saad,[b] Monica Wang,[a] David W. Chapman,[a] Hans-Soenke Jans,[a] Suzanne E. Lapi,[c] Benson M. Kariuki,[d] Angelo J. Amoroso,*[d] and Frank Wuest*[a]

[a] *Department of Oncology, University of Alberta, Edmonton, AB, T6G 1Z2, Canada. Tel: +1 780 989 8150; E-mail: wuest@ualberta.ca*

[b] *College of Applied Science, Chemistry Department, Umm Al-Qura University (UQU), Makkah, Saudi Arabia. E-mail: fasaad@uqu.edu.sa*

[c] *Department of Radiology, Washington University School of Medicine, 510 S. Kingshighway Blvd, St. Louis, MO 63110, United States. Fax: 314 362 9940; Tel: 314 362 4696; E-mail: lapis@mir.wustl.edu*

[d] *Cardiff University of Wales – Department of Chemistry, Main Building, Park Place, Cardiff, CF10 3AT, United Kingdom. Fax: +44 (0)29 208 74030; Tel: +44 (0)29 208 74077; E-mail: amorosoaj@cardiff.ac.uk*

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1. Experimental section

1.1 Infrared spectra

According to the literature, the amide carbonyl stretch appears at ~1620-1670 cm^{-1}. Similarly, in the infrared spectrum of MTUBo, a carbonyl stretch is observed at 1671 cm^{-1} (Table 1). Even though the carbonyl does not directly co-ordinate to the copper cation, it appears to be at lower energy when the ligand co-ordinates to copper perhaps due to the formation of a stronger intramolecular hydrogen bond within the thiourea arm. A strong peak at 1331 cm^{-1}, assigned to the ν(C=S) stretch also shifted to lower energy (1261 cm^{-1}) upon co-ordination of the sulfur atom to the metal which reduces the bond order and thus weakens the C=S bond. The shift of the pyridine ring vibration at around 1600 cm^{-1} and 1450 cm^{-1} indicates co-ordination from the pyridine ring nitrogens. Two characteristic unsplit infrared active bands at ~1090 cm^{-1} and ~625 cm^{-1} are indicative of ionic perchlorate (T_d symmetry).[1,2] All of these features are consistent with the X-ray diffraction data.

Table 1: IR Stretching Frequencies of L[1] and complexes*

Compound	ν(C=O)	ν(C=S)	ν(O-H)	ν(C=N), ν(C=C)	ν(Cl-O)
MTUBo	1671(s)	1331(s)	3431(br)	1540(s), 1455(s)	-
Cu-MTUBo	1609(s)	1261(s)	3416(br)	1539(s), 1433(s)	1088(s), 625(s)

*IR spectra measured as KBr discs

1.2 Electronic absorption spectra

The electronic spectra of MTUBo and Cu-MTUBo have been measured and the data are presented in Table 2. The electronic absorption spectrum for MTUBo contains two strong peaks between 268 nm and 310 nm characteristic of intra-ligand pyridyl π-π* transitions. The copper compound features an N_4S_1 chromophore surrounding the Cu^{II} centre and exhibits an approximately C_{3v} symmetry in the solid state forming a trigonal bipyramidal geometry. According to crystal field theory, the trigonal bipyramidal geometry is not Jahn-Teller active as the odd electron is in a non-degenerate orbital. There are two transitions that would occur in such geometry: $d_{xz}, d_{yz} \rightarrow dz^2$ at higher energy and $d_{xy}, d_x{}^2$-$y^2 \rightarrow dz^2$. Thus, two peaks are observed for Cu-MTUBo (15,850 and 12,165 cm^{-1}) and these transitions may be labelled as ($d_{xz}, d_{yz} \rightarrow d_z{}^2$) and ($d_{xy}, d_x{}^2$-$y{}^2 \rightarrow d_z{}^2$), respectively. Additionally, the slight shoulder at ~950 nm suggests that perhaps in solution the compound has a different structure to that in the solid state. However, this spectral pattern is typical of a five co-ordinate copper (II) complex with a trigonal bipyramidal based geometry.[3,4] While the bands at 15,850 and 12,160 cm^{-1} are tentatively assigned to $^2A_1' \rightarrow {}^2E''$ and the symmetry allowed $^2A_1' \rightarrow {}^2E'$ transitions respectively in D_{3h} symmetry,[5] the little shoulder at ~950 nm does suggest a lower symmetry.

Table 2: Electronic spectral assignments for MTUBo and Cu-MTUBo [a]

Compound	π-π* transitions / λ (nm)	MLCT / λ (nm)	d-d transitions / λ (nm)	Δ (cm^{-1})
MTUBo	268(62,300), 310(33,500)	-	-	-
Cu-MTUBo	255(13,100), 280(8,500)	326(8,700), 353(5,460)	631(95), 822(140), 950(115)	10,530

[a] Performed in CH_3CN solution at room temperature; Numbers in parentheses indicate molar absorption coefficients ε $(M^{-1}cm^{-1})$.

2. Supporting Figures
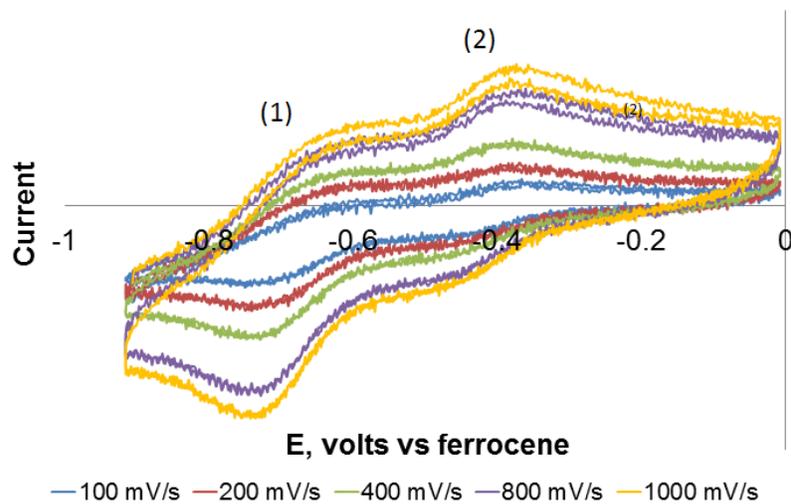
Fig. S1 Cyclic voltammogram of Cu-MTUBo complex.
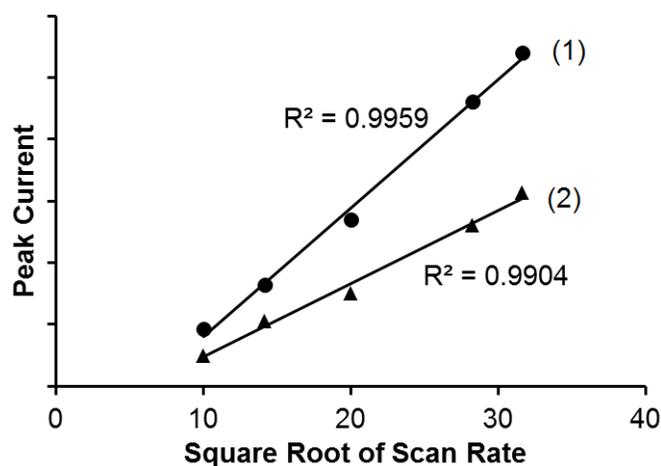
Fig. S2 Peak current *versus* square root of scan rate for Cu-MTUBo complex.
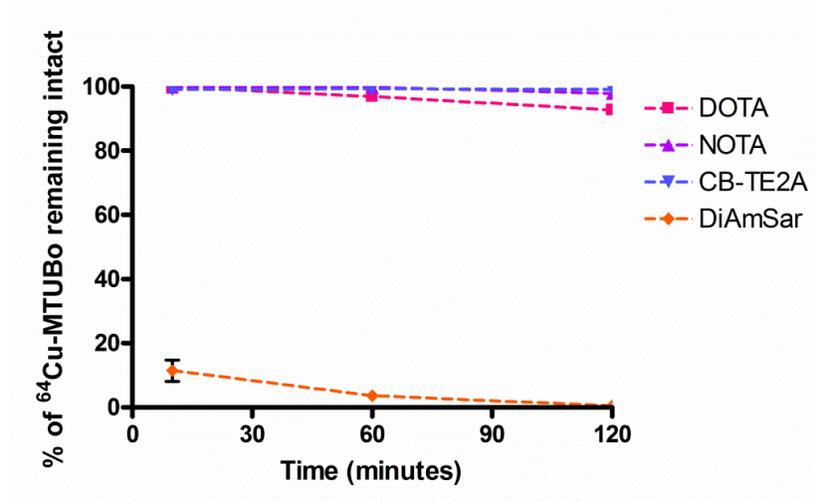
Fig. S3 Challenging ^{64}Cu-MTUBo with DOTA, NOTA, CB-TE2A, and DiAmSar.

References:

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