

Supporting Information (SI) for

Copper(II)-Mediated Oxidative Transformation of *vic*-Dioxime to Furoxan: Evidence for a Copper(II)-Dinitrosoalkene Intermediate

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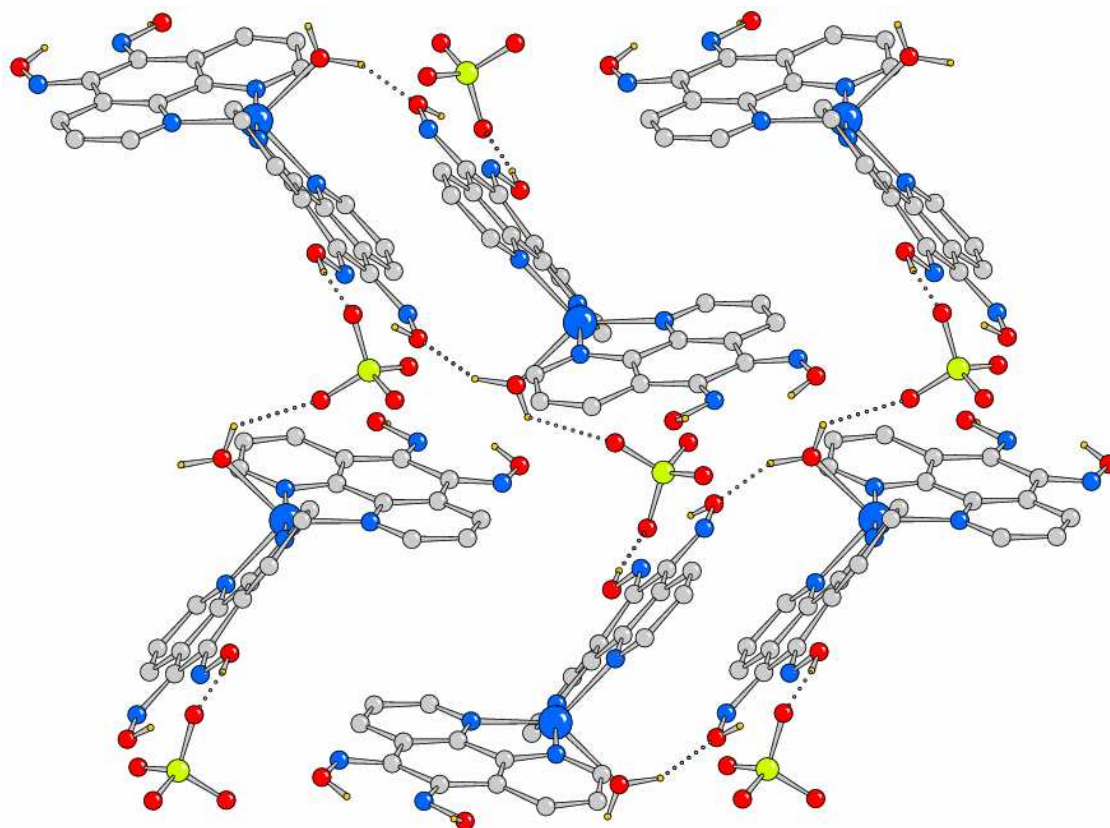


Figure S1. Two-dimensional hydrogen-bonded network involving the complex cations of **1**, water molecules and perchlorate counterions.

Kinetic measurements in the presence of external substrates: An acetonitrile solution (3.0 mL) of $[\text{Cu}(\text{HDMG})_2]$ (0.25 mM) was taken in a cuvette of 1 cm pathlength. The cuvette was placed in the sample holder of the diode-array spectrometer maintained at -20°C using a cryostat. An acetonitrile solution of copper(II) perchlorate hexahydrate (3 equivalent) was then added to the cuvette using a microlitre syringe. Formation of the blue intermediate was monitored at -20°C . When the peak at 615 nm was reached at the

maximum absorbance, ten equivalents of intercepting agent were added and the decay of the peak at 615 nm was monitored.

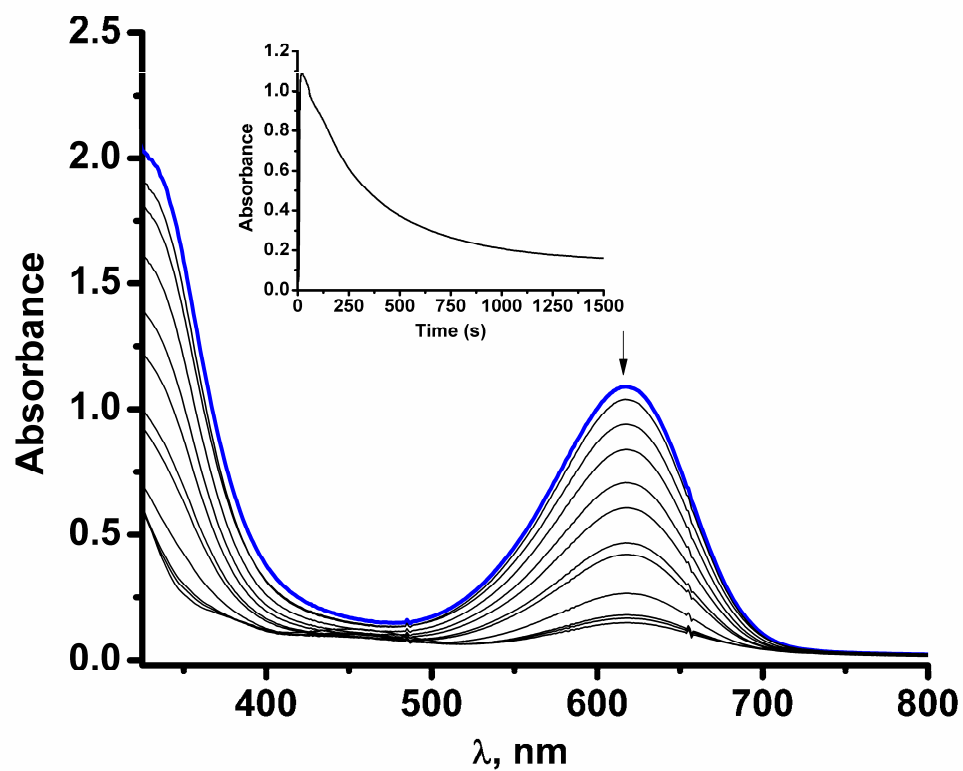


Figure S2. Decay of the intermediate at 615 nm generated from $[\text{Cu}(\text{HDMG})_2]$ in the presence of 10 equivalents of TEMPOH.

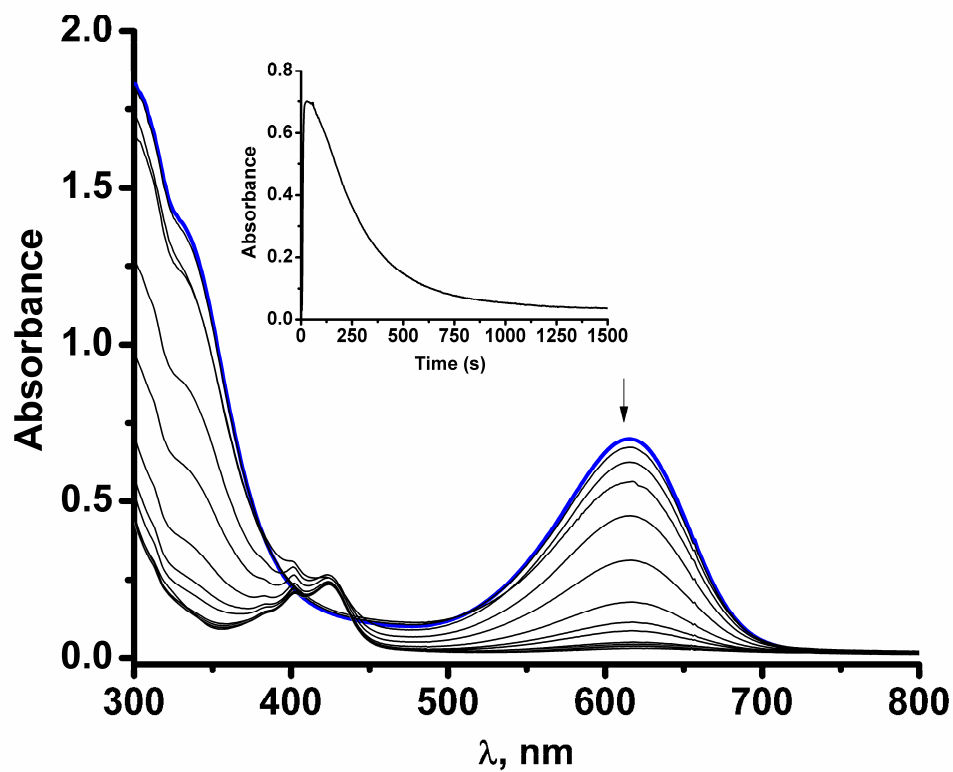


Figure S3. Decay of the intermediate at 615 nm generated from $[\text{Cu}(\text{HDMG})_2]$ in the presence of 10 equivalents of 2,4,6-tri-*tert*-butylphenol.

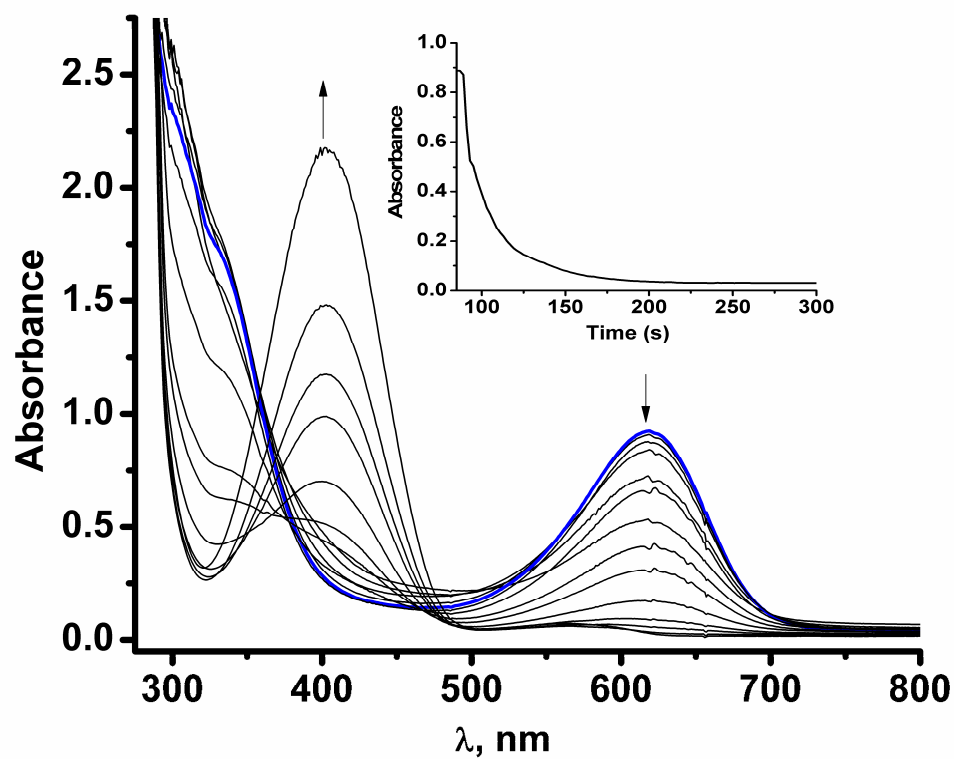
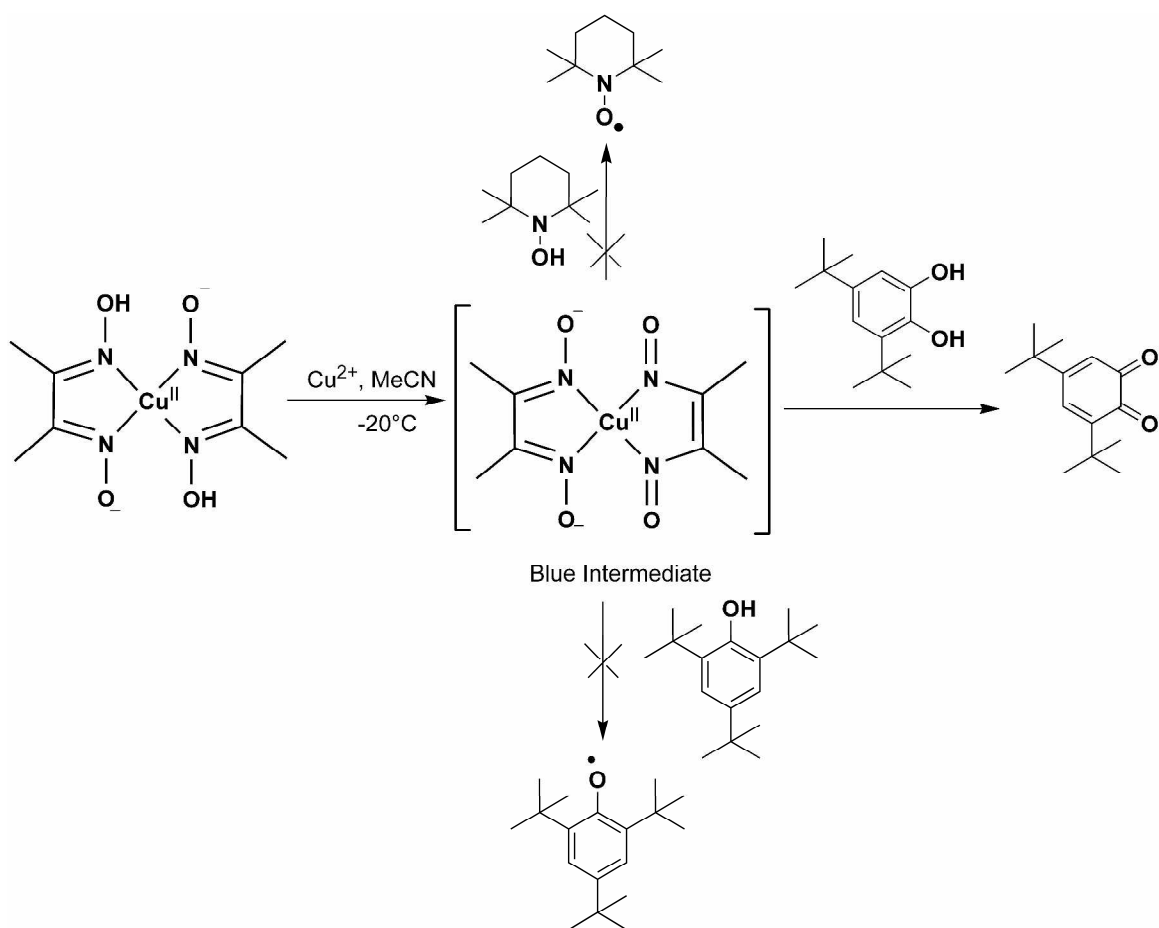


Figure S4. Decay of the intermediate at 615 nm generated from $[\text{Cu}(\text{HDMG})_2]$ in the presence of 10 equivalents of 3,5-di-*tert*-butylcatechol. The peak at 400 nm indicates the formation of 3,5-di-*tert*-butylquinone.



Scheme S1. Reaction of blue intermediate with different intercepting reagents.