Electronic Supplementary Material (ESI) for Chemical Communications


# CuAAC click functionalization of azide-modified nanodiamond with a photoactivatable CO releasing molecule (PhotoCORM) based on $[Mn(CO)_3(tpm)]^+$

**Gregor Dördelmann,[a] Thomas Meinhardt,[b] Thomas Sowik,[a] Anke Krueger,[b*] and Ulrich Schatzschneider[a*]**

[a]Institut für Anorganische Chemie,
Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Fax: +49 931 3184605
eMail: ulrich.schatzschneider@uni-wuerzburg.de

[b]Institut für Organische Chemie,
Julius-Maximilians-Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany
Fax: +49 931 3184606
eMail: krueger@chemie.uni-wuerzburg.de

**Supporting Information**

## Experimental

### General remarks

Reactions were carried out in oven-dried Schlenk glassware under an atmosphere of pure nitrogen and reaction vessels were protected from light by wrapping them with aluminium foil if necessary. IR spectra were recorded on a Bruker Tensor 27 IR spectrometer equipped with a Pike MIRacle Micro ATR accessory. The manganese determination was carried out by the Labor für Mikroanalytik und Thermoanalyse of the Universität Duisburg-Essen using a M-Series atomic absorption spectrometer (AAS) from Thermo Electron. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a Hitachi H-8100 microscope equipped with an EDX spectrometer from Oxford Instruments operating at an accelerating voltage of 200 keV. Samples were prepared by dispersing a small amount of the functionalized nanoparticles in methanol (5 mL), followed by sonication for 30 min and deposition on copper grids covered with a carbon film. UV/Vis spectra were recorded on a Jasco V-670 and measured in a Hellma quartz cuvette ($d$ = 1 cm).

### Synthesis

**Precursors.** The azide-functionalized detonation nanodiamond (**1**) was produced as recently reported.[1] Its surface loading with azide groups was 0.25 mmol $g^{-1}$ as measured by thermogravimetry. The manganese carbonyl complex $[Mn(CO)_3(tpm^{C\equiv CH})]PF_6$ (**2**) was prepared according to the literature.[2]

**Functionalized nanodiamond (3).** A Schlenk flask was charged with azide-functionalized detonation nanodiamond (**1**, 21.3 mg, equivalent to 0.005 mmol of surface azide groups) and a mixture of *N*,*N*-dimethylformamide (0.8 mL) and water (0.2 mL) was added. Then, the nanodiamonds were suspended by sonication for 15 min and degassed by bubbling with nitrogen. A tenfold excess of $[Mn(CO)_3(tpm^{C\equiv CH})]PF_6$ (**2**) (28.3 mg, 0.050 mmol) was added to the suspension. Subsequently, copper(II) sulfate pentahydrate (5.0 mg; 0.020 mmol, 40 mol-%) and sodium ascorbate (8.0 mg, 0.040 mmol; 80 mol-%) were added under a flow of nitrogen. The mixture was stirred for 72 h under a dinitrogen atmosphere with exclusion of light. Then, the suspension was added to a crystallizing dish charged with methanol (40 mL). The resulting slurry was centrifuged (5 min at 11000 rpm) and the resulting pellet redispersed in methanol (30 mL) by sonication for 5 min. This washing step (centrifugation and washing with methanol) was then repeated three

times, followed by another washing with water (3 × 30 mL). Lyophilization of the resulting pellet gave $[Mn(CO)_3(tpm)]^+$-functionalized detonation nanodiamond (**3**) as a dark brown powder. Yield: 18.7 mg. IR (ATR, $cm^{-1}$): 3400, 2950, 2885, 2051 (C≡O), 1961 (C≡O), 1718, 1654, 1363, 1320, 1110, 822. Elemental analysis (%): Mn 0.47. TEM: crystallite size ~10 nm. EDX spectroscopy (keV): 0.29 [$CK_\alpha$], 5.92 [$MnK_\alpha$].

**Myoglobin assay**

To study the CO release properties of the $[Mn(CO)_3(tpm)]^+$-functionalized detonation nanodiamond (**3**) the myoglobin assay was used.[3] This method monitors the change in the Q-band region of the absorption spectrum of deoxy-myoglobin (Mb) vs. carbonmonoxy-myoglobin (MbCO). Carbon monoxide liberated from the nanocarrier binds to Mb to form MbCO and thus, the absorption of Mb at 557 nm decreases while that of MbCO at 540 and 577 nm increases. Thus, horse skeletal muscle myoglobin was dissolved in phosphate buffer (0.1 M, pH 7.3) and placed in a quartz cuvette ($l$ = 1 cm). Then, the solution was degassed by bubbling with dinitrogen for 5 min and the myoglobin reduced by addition of an excess of sodium dithionite (100 µl) in the same solvent to give a total volume of 990 µl. UV/Vis spectra of the solution before and after the reduction step were recorded. Then, the nanoparticles (about 0.5 mg) were dispersed a minimum amount of dimethylsulfoxide and added to give a total volume of 1 mL. The final concentrations were about 1 mM sodium dithionite and 50 µM of myoglobin with $A_{557\ nm} < 1$. The cuvette was sealed with a Teflon plug to prevent reoxidation of Mb as well as an escape of gaseous CO. The sealed cuvette was either kept in the dark as a control or irradiated with a UV hand lamp (Uvitec LF-206.LS, 6 W) at 365 nm, positioned perpendicular to the cuvette at a distance of 5 cm. The irradiation was interrupted in 5 min intervals to take UV/Vis spectra on a Jasco V-670 spectrometer until no more changes in the Q-band region were observed. Finally, the solution was saturated with CO gas by bubbling to test whether conversion to MbCO was complete.

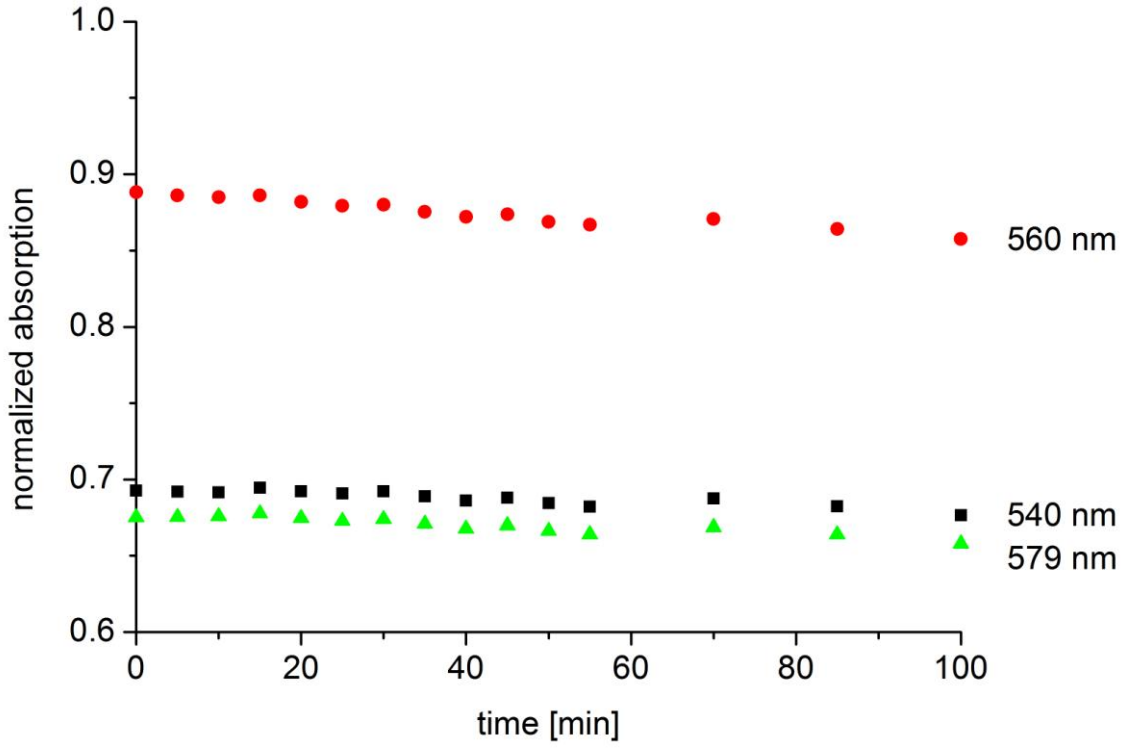


**Fig. S1** Change of the normalized UV/Vis absorption at different wavelengths (540, 560, and 579 nm) of $[Mn(CO)_3(tpm)]^+$-functionalized detonation nanodiamond (**3**) upon incubation under the conditions of the myoglobin assay in the dark (0 to 100 min).

## References

1. T. Meinhardt, D. Lang, H. Dill and A. Krüger, *Adv. Funct. Mater.*, 2011, **21**, 494.
2. H. Pfeiffer, A. Rojas, J. Niesel and U. Schatzschneider, *Dalton Trans.*, 2009, 4292; G. Dördelmann, H. Pfeiffer, A. Birkner and U. Schatzschneider, *Inorg. Chem.*, 2011, **50**, 4362; J. Niesel, A. Pinto, H. W. Peindy N'Dongo, K. Merz, I. Ott, R. Gust and U. Schatzschneider, *Chem. Commun.*, 2008, 1798.
3. A. J. Atkin, J. M. Lynam, B. E. Moulton, P. Sawle, R. Motterlini, N. M. Boyle, M. T. Pryce and I. J. S. Fairlamb, *Dalton Trans.*, 2011, **40**, 5755; S. McLean, B. E. Mann and R. K. Poole, *Anal. Biochem.*, 2012, **427**, 36.