Electronic Supplementary Information

for

"CLICKable" azide-functionalized phosphonates for the surface-modification of molecular and solid-state metal oxides

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1. Instrumentation

X-ray diffraction: Single-crystal X-ray diffraction studies were performed on a Agilent SuperNova CCD Single-crystal X-ray diffractometer equipped with a graphite monochromator using $Mo_{K\alpha}$ radiation (wavelength $\lambda(Mo_{K\alpha}) = 0.71073$ Å).

UV-Vis and emission spectroscopy: UV-Vis spectroscopy was performed on a Varian Cary 50 spectrophotometer or JASCO V-670 spectrophotometer. All systems were used with standard cuvettes (d = 10.0 mm).

Elemental analysis: CHN analysis was performed on a Elementar vario MICRO cube.

FT-IR spectroscopy: FT-IR spectroscopy was performed on a Shimadzu FT-IR 8400 spectrophotometer (KBr pellet) or on a Bruker Tensor 27 FT-IR spectrophotometer including a Platinum ATR unit. Signals are given as wave numbers in cm^{-1} using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak and b = broad.

^{1}H- and ^{31}P-NMR spectroscopy: ^{1}H- and ^{31}P-NMR spectra were recorded at ambient temperature, unless otherwise stated, with a Bruker 400 MHz spectrometer. All spectra were referenced to the corresponding solvent residual signal.

Scanning Electron Microscopy / Energy dispersive X-ray spectroscopy: SEM-EDX was performed on a Zeiss Scanning Electron Microscope Leo 1550 VP equipped with an Oxford Instruments EDX system. Samples were measured at 10 KeV acceleration voltage.

Thermogravimetric analysis was performed on a Netzsch TG 209 F1 Libra thermobalance at a heating rate of 5 K min^{-1} under a flow of O_2.

General remarks: All chemicals were purchased from Sigma Aldrich, ABCR or ACROS and were of reagent grade. The chemicals were used without further purification unless stated otherwise. The copper(I) catalyst for the [3+2] cycloaddition of azides and terminal alkynes (CLICK reaction) was synthesized according to literature synthesis.[1]

2. Synthetic section

2.1. Synthesis of 4-aminobenzyl phosphonic acid (1)

Diethyl 4-aminobenzyl phosphonate (0.5 g, 2.06 mmol) was dissolved in aqueous hydrochloric acid (50 mL, 6 M) and stirred at 100 °C for 24 h. The resulting solution was cooled to room temperature and the solvent was removed under reduced pressure. The crystalline product was obtained in nearly quantitative yield and dried under vacuum. **Yield:** 0.37 g (2.0 mmol, 97% based on diethyl 4-minobenzylphosphonate).

^{1}H NMR (400 MHz, MeOH-d$_4$): δ (ppm) = 7.48 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz, 2 H), 7.35 (dd, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2 Hz, 2 H), 3.22 (d, $^2J_{H,H}$ = 22 Hz, 2 H).

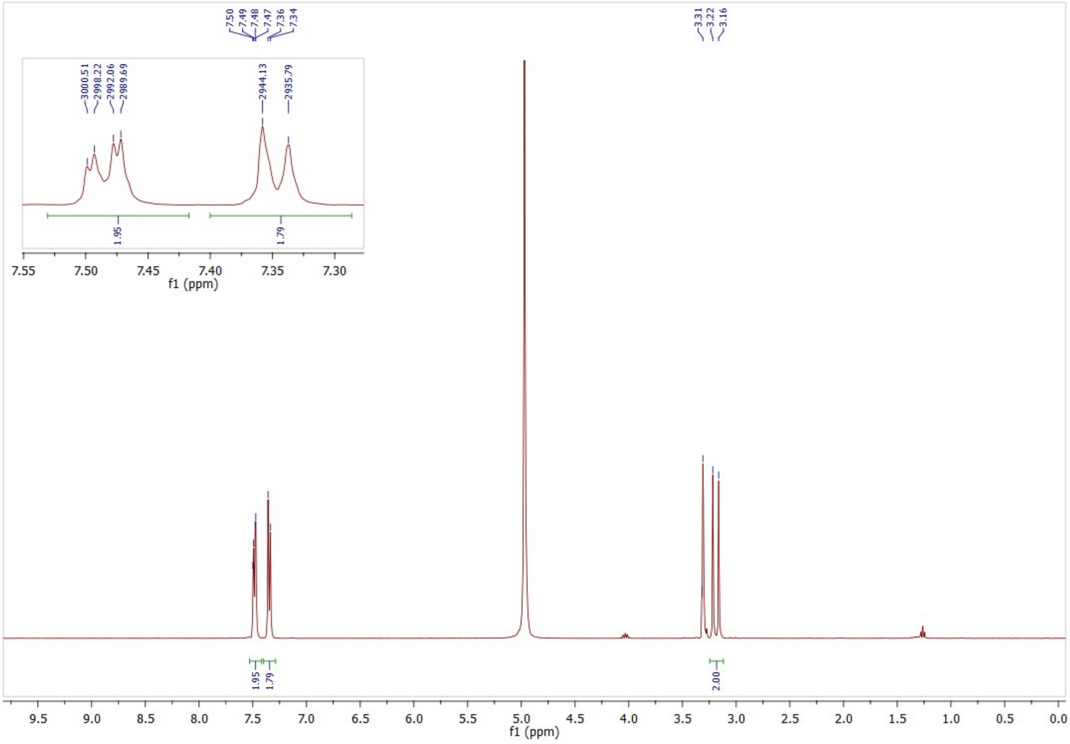

Figure 1: ^{1}H-NMR spectrum of **1** in MeOH-d$_4$.

^{31}P NMR (400 MHz, MeOH-d$_4$): δ (ppm) = 23.08.

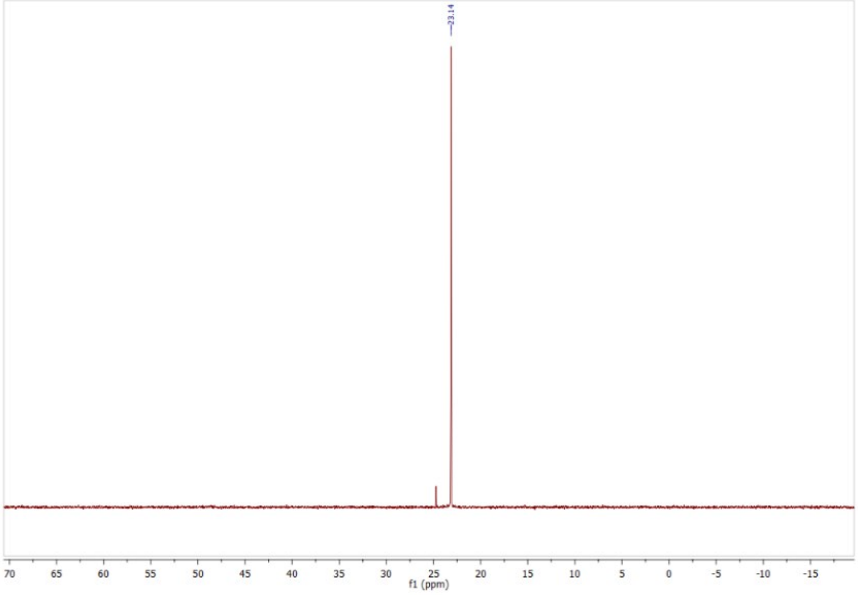

Figure 2: ^{31}P-NMR spectrum of **1** in MeOH-d$_4$.

2.2. Synthesis of 4-azidobenzyl phosphonic acid (2)

1 (0.37 g, 2.0 mmol) was dissolved in water (16 mL) by addition of aqueous HCl (9 mL, 12 M). The resulting solution was cooled (ice bath) and a solution of sodium nitrite (0.35 g, 5.07 mmol) in water (5 mL) was added dropwise. After stirring for 30 min, a solution of sodium azide (0.32 g, 4.92 mmol) in water (2 ml) was slowly added to the cooled reaction mixture. The solution was stirred for 2 h and allowed to warm to room temperature. The solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (Interchim PuriFlash instrument equipped with normal phase silica column SIHP-JP, 25 g, 30 µm particle size) using a mixed eluent (MeOH:EtOH, 2:1, v:v). The pure brown product was dried under vacuum. **Yield:** 0.43 g (2.0 mmol, quantitative yield based on **1**).

Elemental analysis in wt.-% for $C_7H_8N_3PO_3$ (calcd.): C 39.22 (39.44), H 3.42 (3.78), N 19.59 (19.72).

^{1}H NMR (400 MHz, MeOH-d$_4$): δ (ppm) = 7.28 (d, $^3J_{H;H}$ = 8 Hz, 2 H); 7.93 (d, $^3J_{H;H}$ = 8 Hz, 2 H); 3.05 (d, $^2J_{H;H}$ = 21 Hz, 2 H).

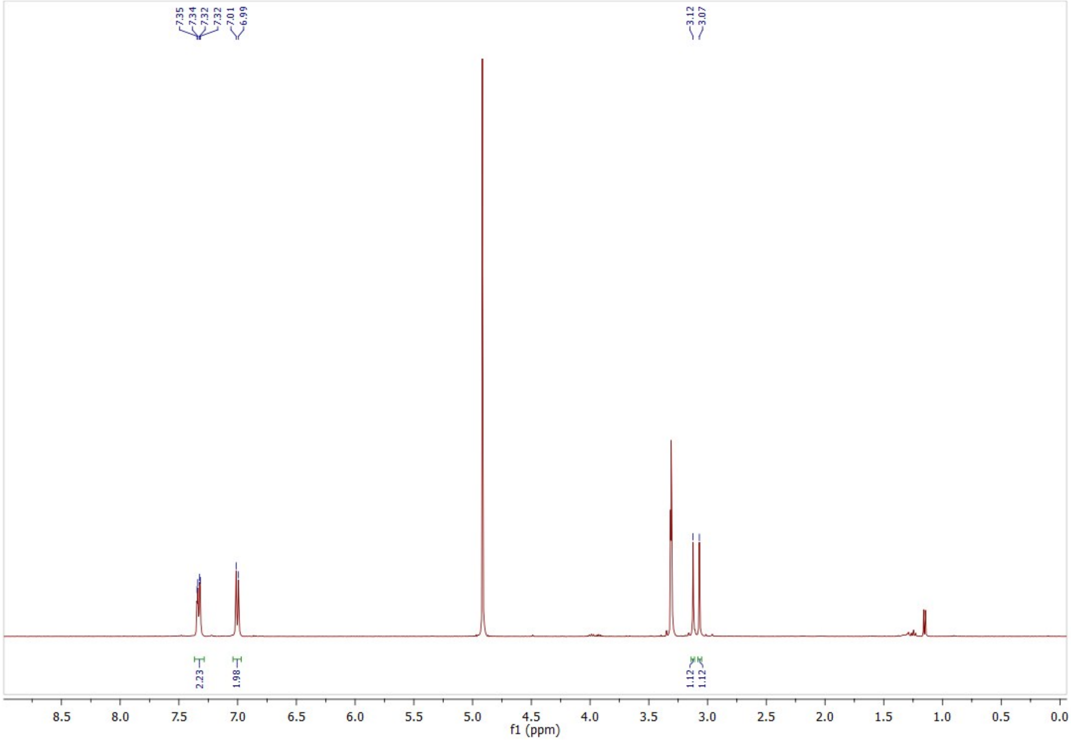

Figure 3: ^{1}H-NMR spectrum of **2** in MeOH-d$_4$.

^{31}P NMR (400 MHz, MeOH-d$_4$): δ (ppm) = 23.71.

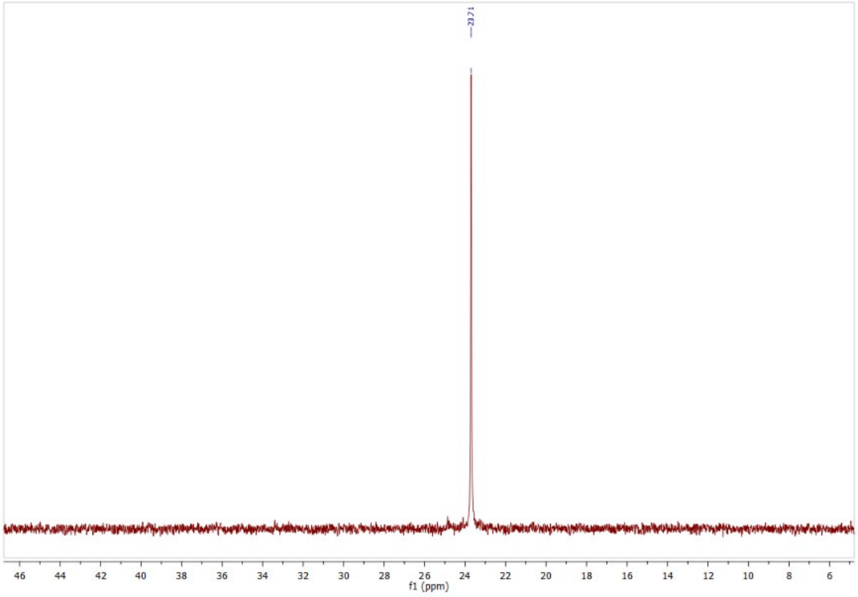

Figure 4: ^{31}P-NMR spectrum of **2** in MeOH-d4.

IR (KBr, $\tilde{\nu}$ [cm^{-1}]): 2793; 2400; 2253; 2118; 1602; 1580; 1506; 1421; 1400; 1264; 1209; 1151; 1102; 998; 945; 835; 815; 788; 708; 643; 554; 468; 429.

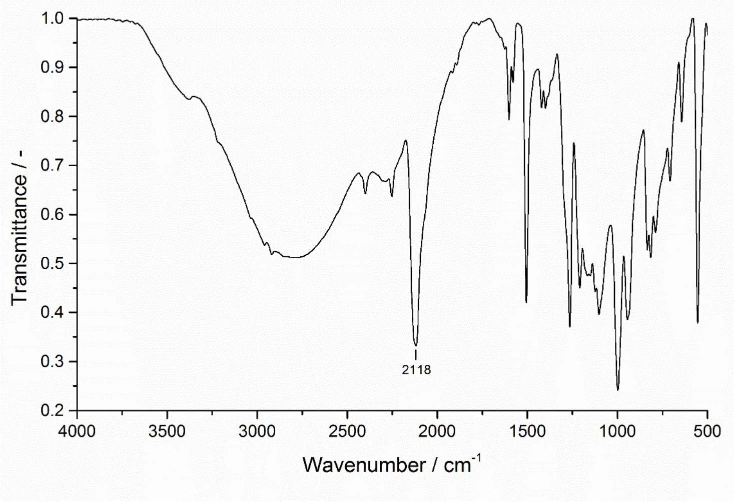

Figure 5: FT-IR spectrum of **2** (KBr pellet).

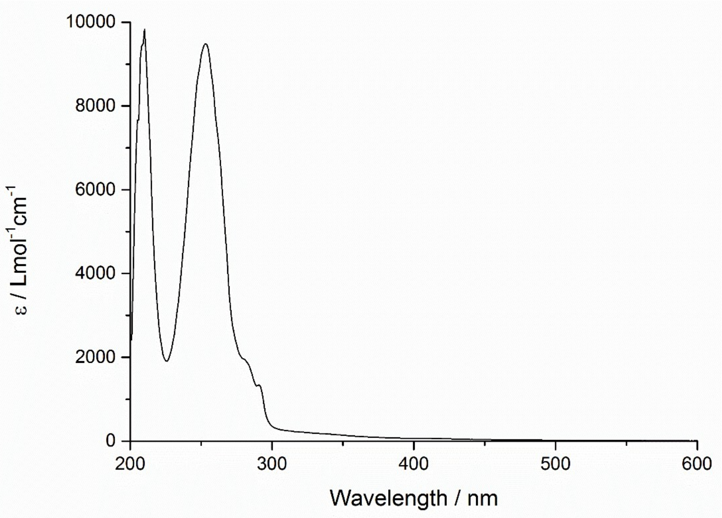

Figure 6: UV-Vis absorption spectrum of **2** in MeOH ([**2**] = 2.3×10^{-4} M).

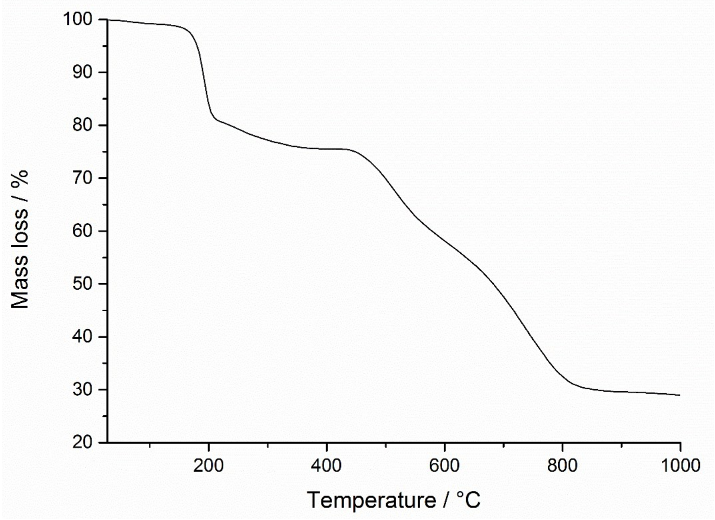

Figure 7: Thermogravimetric analysis of **2.**

2.3. Synthesis of $Rb_4[Mo_5O_{15}(O_3PCH_2PhN_3)_2]$ x *ca.* 8 H_2O (3)

Compound **3** was synthesized according to a modified literature procedure.[2] Na_2MoO_4 x $2H_2O$ (0.15 g, 0.73 mmol) and **2** (62.0 mg, 0.29 mmol) were dissolved in H_2O (8.75 mL). After addition of aqueous HCl (250 µL, 3 M), the solution was refluxed for 30 min. An aqueous solution (125 µL) of $RbNO_3$ (0.35 g, 2.4 mmol) was added and the solution was cooled to room temperature. Pale brown block crystals suitable for single crystal X-ray analysis were obtained overnight. **Yield:** 115.2 mg (0.08 mmol, 28 % based on **2**)

Elemental analysis in wt.-% for $C_{14}H_{28}N_6Mo_5O_{29}P_2Rb_4$ (calcd.): C 10.35 (10.33), H 1.71 (1.73), N 5.17 (5.16).

Note that the elemental analysis indicates the presence of 8 water molecules, giving the final sum formula of $Rb_4[Mo_5O_{15}(O_3PCH_2PhN_3)_2]$ x *ca.* 8 H_2O. Single crystal XRD analysis of **3** only allowed the identification of 7 water molecules (in addition, diffuse water molecules were observed but could not be unambiguously assigned).,

^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 7.79 (dd, $^4J_{H;H}$ = 8 Hz, 2 H); 6.89 (d, $^3J_{H;H}$ = 8 Hz, 2 H); 3.33 (s, 1 H), 3.33 (s, 1H).

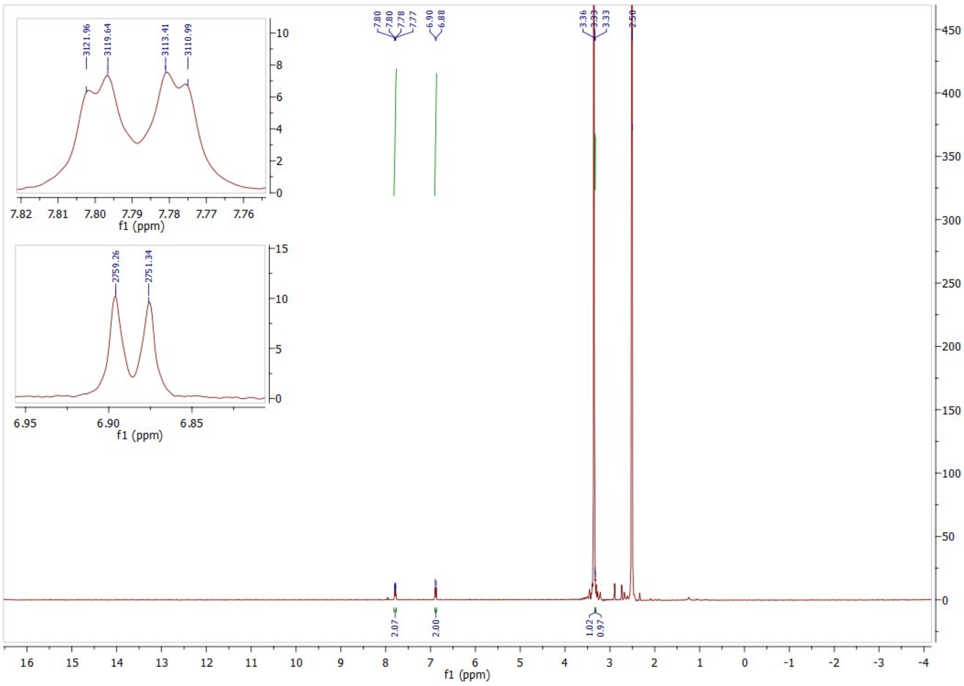

Figure 8: ^{1}H-NMR spectrum of **3** in DMSO-d$_6$.

^{31}P NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 23.74.

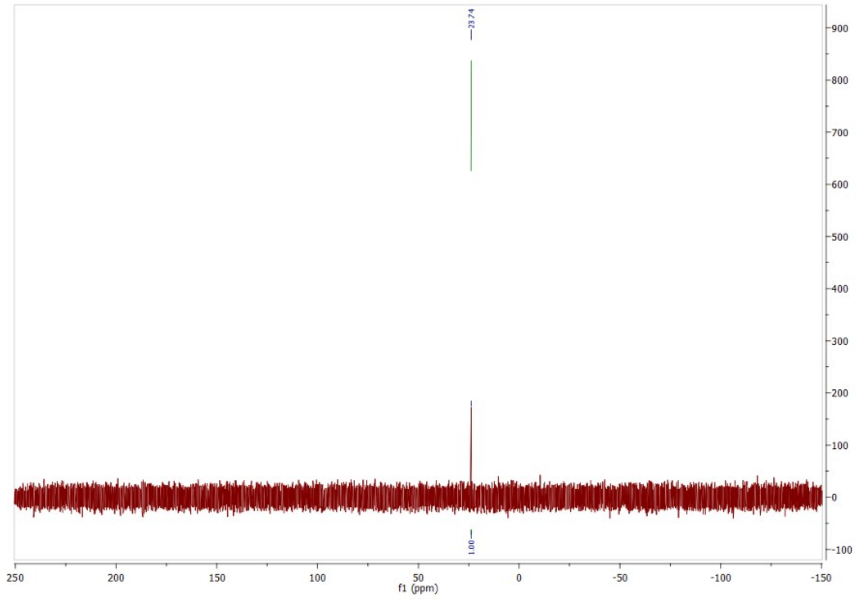

Figure 9: ^{31}P-NMR spectrum of **3** in DMSO-d$_6$.

IR (ATR, $\tilde{\nu}$ [cm^{-1}]): 2361; 2125; 1606; 1506; 1307; 1282; 1243; 1139; 1105; 1090; 1037; 1019; 980; 919; 899; 852; 834; 792; 765.

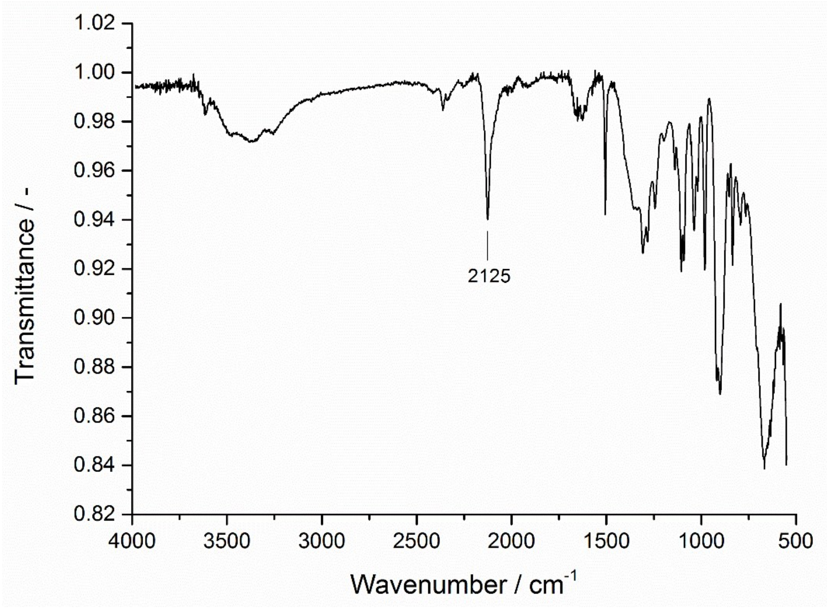

Figure 10: IR spectrum of **3**.

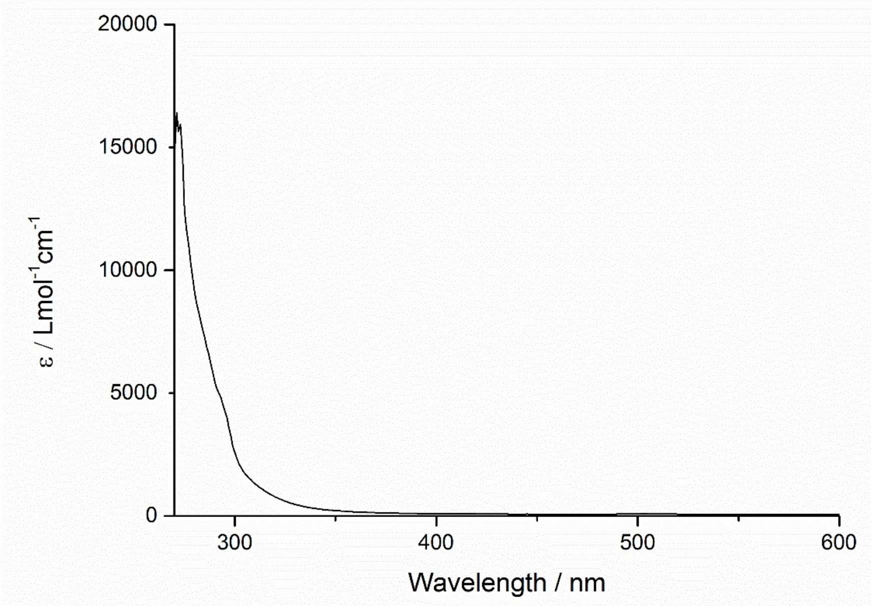

Figure 11: UV-Vis absorption spectrum of **3** in DMSO ([**3**] = 2.3 x 10^{-4} M).

Single crystal X-ray diffraction

Single-crystal structure determination: Suitable single crystals of **3** were grown and mounted onto the end of a microloop using Fomblin oil. X-ray diffraction intensity data were measured at 150 K on a Agilent SuperNova CCD diffractometer [λ(Mo-K_α) = 0.71073 Å] equipped with a monochromator optics. Structure solution and refinement was carried out using the SHELX-2013 package[3] *via* Olex2.[4] Corrections for incident and diffracted beam absorption effects were applied using empirical methods.[5] Structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Crystal data, data collection parameters and refinement statistics are listed in Table **S1**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk. CCDC reference number 1495857 (**3**).

Table S1: Crystallographic data for compound **3**

Compound	**3**
CCDC reference no	1495857
Empirical formula	$C_{14}H_{26}Mo_5N_6O_{28}P_2Rb_4$
Formula weight	1609.93
Temperature / K	150(2)
Crystal system	monoclinic
Space group	$P2_1$
a / Å	10.7278(3)
b / Å	14.7418(3)
c / Å	13.2364(3)
α / °	90
β / °	107.779(3)
γ / °	90
Volume / Å^3	1993.3(8)
Z	2
ρ_{calc} / mg/mm^3	2.682
μ / mm^{-1}	6.564
F(000)	4016.0
Crystal size / mm^3	0.12 × 0.10 × 0.04
2Θ range for data collection	6.8 to 52.6°
Completeness	99.7 %
Reflections collected	10336
Independent reflections	6485 [R_{int} = 0.0449]
Goodness-of-fit on F^2	1.038
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0465, wR_2 = 0.1147
Final R indexes [all data]	R_1 = 0.0513, wR_2 = 0.1188
Largest diff. peak/hole / e Å^{-3}	1.58/-1.35

2.4. Preparation of the azide-functionalized TiO_2

To a solution of **2** (12.3 mg, 0.06 mmol) in MeOH (6 mL), TiO_2 powder (250 mg, type Degussa P25) was added and stirred at 40 °C for 19 h. The resulting suspension was centrifuged and the residual concentration of the supernatant solution was determined by UV-Vis absorption spectroscopy. The decrease in absorbance indicates adsorption of *ca*. 88% of **2** on TiO_2. Leaching of **2** from the composite was studied by stirring the material in MeOH (2.5 mL) for 5 h followed by centrifugation and UV-Vis spectroscopic analysis of the solution, see below.

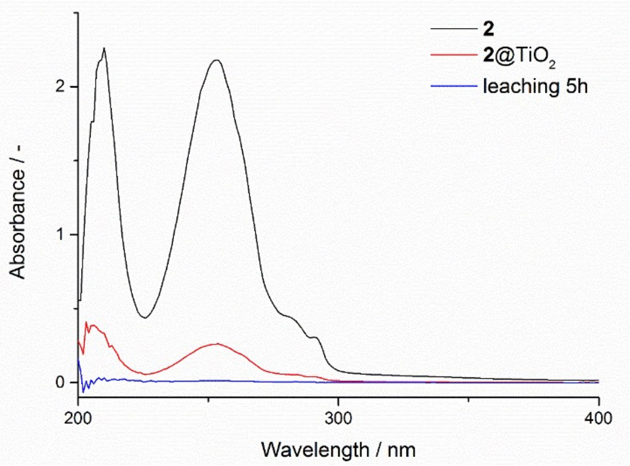

Figure 12: UV-Vis absorption spectrum of **2** in MeOH ([**2**]$_{\text{initial}}$ = 2.3 x 10^{-4} M) before (black) and after (red) adsorption on TiO_2 ([**2**]$_{19h}$ = 0.27 x 10^{-4} M). The stability of adsorbed **2** on TiO_2 was tested by leaching experiments in MeOH (blue); no leaching was detected.

2.5. CLICK reaction

Azide-modified TiO_2 (**2**@TiO_2, 50 mg, containing 0.21 mmol of **2**) and copper(I) catalyst (Bis[*N,N'*-bis(2,4,6-trimethylphenyl)-1,2-ethanediylidenediamine]copper(I) tetrafluoroborate (6.7 mg, 10.3 µmol, 5 mol%) were suspended in methanol (5 mL). Phenyl acetylene (22.7 µL, 0.21 mmol, 1 eq.) was added and the suspension was stirred at 40 °C for 19 h. After centrifugation, the functionalized TiO_2 was washed with acetone, dried under vacuum and analysed using ATR-FT-IR, TGA and SEM-EDX, see main manuscript.

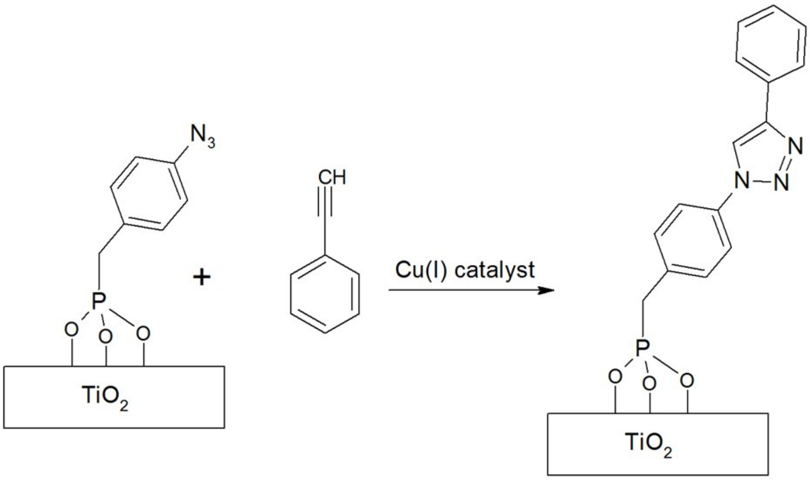

Figure 13: Illustration of the CLICK reaction of **2**@TiO_2 with phenyl acetylene catalyzed by a Cu(I) catalyst (see above for details).

3. Literature

1 C. L. Foster, C. A. Kilner, M. Thornton-Pett and M. A. Halcrow, *Acta Crystallogr. C*, 2000, **56**, 319–320.

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4 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

5 R. H. Blessing, *Acta Crystallogr. A.*, 1995, **51**, 33–38.