Supporting Information Part 2/1 (SI2/1) for

Accessing Distributions of Exchange and Dipolar Couplings in Stiff Molecular Rulers with Cu(II) centres

K. Keller,[a] I. Ritsch,H. Hintz,[b] M. Hülsmann,[b] M. Qi,[b] F. Breitgoff,[a] D. Klose,[a] Y. Polyhach,[a,*] M. Yulikov,[a,*] A. Godt,[b,*] G. Jeschke[a]

[a]*Laboratory of Physical Chemistry, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich, Switzerland.*
[b]*Faculty of Chemistry and Center for Molecular Materials (CM_2), Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany*

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Supporting Information Part 2/2

1. Nomenclature for the rulers and the synthetic intermediates

The nomenclature used in the following sections for the rulers [Cu-PyMTA]-nitroxide **2_3**, [Cu-PyMTA]-[Cu-PyMTA] **1_n**, and [Cu-TAHA]-[Cu-TAHA] **3** is explained on the examples of ruler [Cu-PyMTA]-nitroxide **2_3** (Figure S1, left) and [Cu-TAHA]-[Cu-TAHA] **3** (Figure S1, right). A very similar nomenclature was introduced earlier.[1]

Ruler [Cu-PyMTA]-nitroxide **2_3** consists of the complex {Cu^{II}(PyMTA)}$^{2-}$, a nitroxide moiety (NO•), and phenylene (P) and ethynylene (E) units. Ruler [Cu-TAHA]-[Cu-TAHA] **3** consists of the complex {Cu^{II}(TAHA)}$^{4-}$, phenylene (P) units, ethynylene (E) units, and a butadiyne unit (B = EE). With Na_2[{Cu^{II}(PyMTA)}-(EP)$_4$-NO•] and H_xNa_{8-x}[{Cu^{II}(TAHA)}-EPBPE-{Cu^{II}(TAHA)}] the constitution of the ruler is described omitting an information on the type of the side chains of the spacer. The information on the concrete side chains is given in the schemes and figures. "PyMTA" and "TAHA" refer to the fully deprotonated ligands. In case of TAHA, we consider the 1,4-disubstituted benzene ring at the spacer's termini as part of the ligating unit and therefore include this moiety into the abbreviation "TAHA". Viguier et al. mentioned the benzene ring separately and wrote of Ph-TAHA.[2]

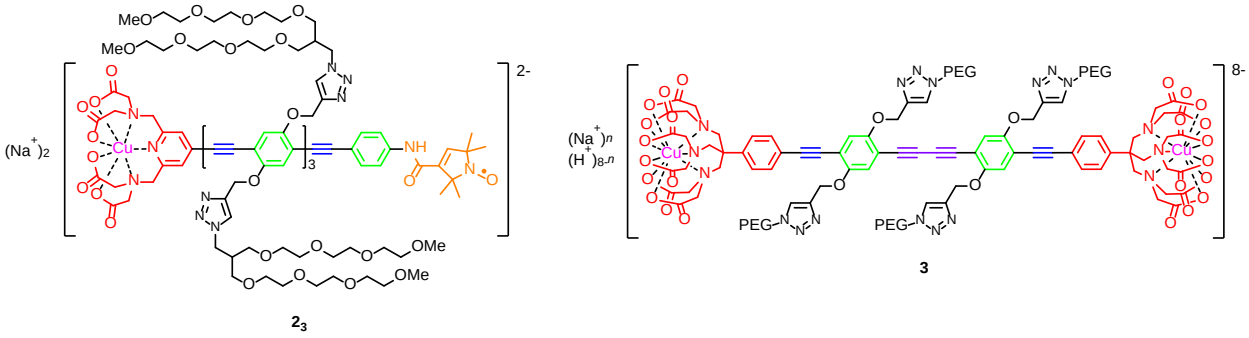


Figure S1. Left: Na_2[{Cu^{II}(PyMTA)}-(EP)$_4$-NO•] **2_3** as an example for the nomenclature of [Cu-PyMTA]-nitroxide, [Cu-TAHA]-nitroxide, and [Cu-PyMTA]-[Cu-PyMTA] rulers and their precursors. Right: H_xNa_{8-x}[{Cu^{II}(TAHA)}-EPBPE-{Cu^{II}(TAHA)}] **3** as an example for the nomenclature of [Cu-TAHA]-[Cu-TAHA] and [Cu-TAHA]-nitroxide rulers and their precursors.

Please, be aware that the naming of the rulers [Cu-PyMTA]-[Cu-PyMTA], [Cu-TAHA]-[Cu-TAHA], [Cu-PyMTA]-nitroxide, and [Cu-TAHA]-nitroxide in the main manuscript is simplified and does not contain information on the protonation degree.

2. Comment on the ^{1}H NMR spectra of H_xNa_{12-x}[TAHA-EPBPE-TAHA] 23

The ^{1}H NMR signals of ruler precursor H_xNa_{12-x}[TAHA-EPBPE-TAHA] **23** show a pH-dependent shift. Additionally, the simultaneous presence of several species differing in the degree of protonation at a given pH make the spectra very complex.

To explore the influence of the pH value on the ^{1}H NMR spectrum, a sample of ruler precursor **23** was treated in the following way: It was dissolved in an aqueous solution of

HCl, then the solvent was removed. Addition of deuterium oxide gave a solution with pD 1.6 which showed the spectrum displayed in the top of Figures S2, S49, and S50. The solvent was evaporated, and the residue was dissolved in a solution of NaOD in D_2O. This provided a solution of pD 5.0 which gave the spectrum shown in the middle of Figures S2, S49, and S50. The solvent was removed and the residue was dissolved in an aqueous solution of HCl. Then, the solvent was removed and the remaining solid was dissolved in deuterium oxide giving a solution with pD 1.3. Its spectrum is shown at the bottom of Figures S2, S49, and S50. More details on this experiment can be found in the synthesis description of H_xNa_{12-x}[TAHA-EPBPE-TAHA] **23**. In Figure S2 the range of 8.5 ppm to 7.0 ppm of ^{1}H NMR spectra of ruler precursor **23** in deuterium oxide at different pD values are shown. From 8.5 ppm to 7.9 ppm triazole proton signals of **23**, and from 7.9 ppm to 7.0 ppm the signals of the aromatic protons of **23** are found. For a detailed assignment of all ^{1}H NMR signals see Figure S52.

The ^{1}H NMR signal patterns of the solutions with pD 1.6 and 1.3 are quite similar to each other, whereas they differ significantly from the signal patterns of the solution with pD 5.0. The experiment proves the reversibility of the spectral changes and indicates that they are caused by protonation/deprotonation of the ruler precursor.

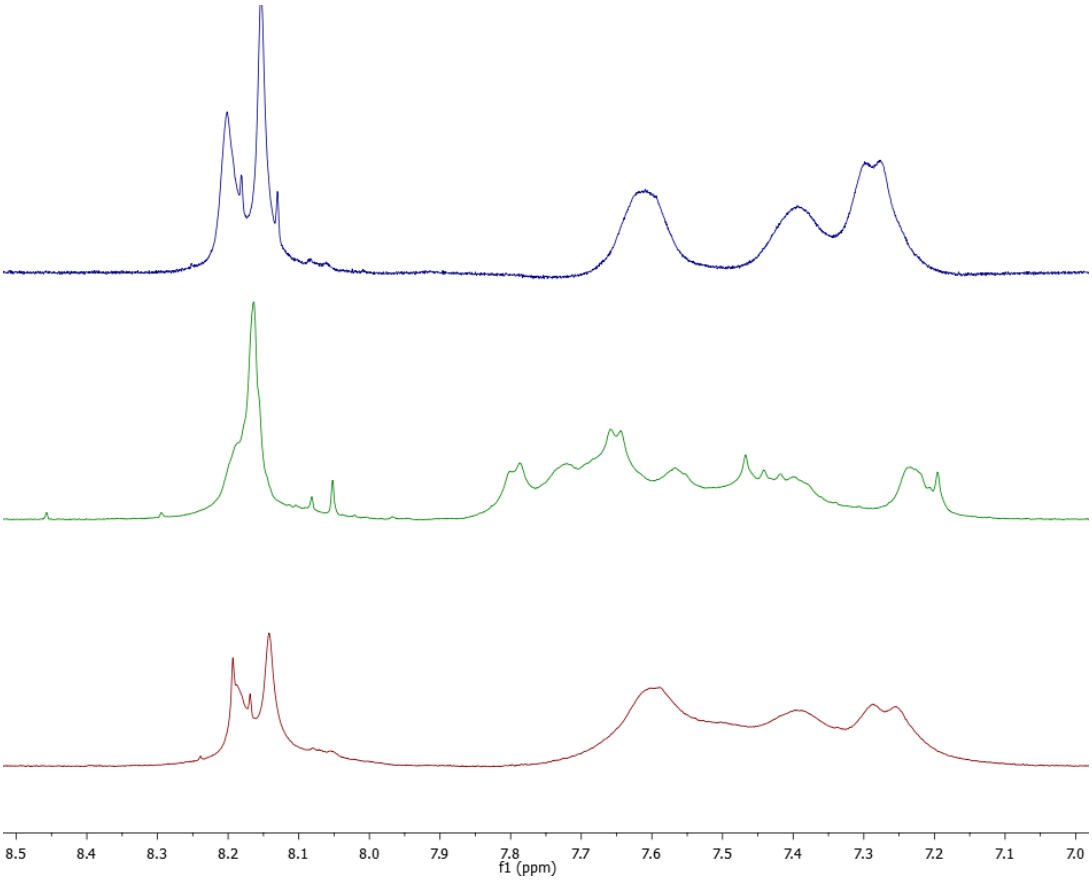
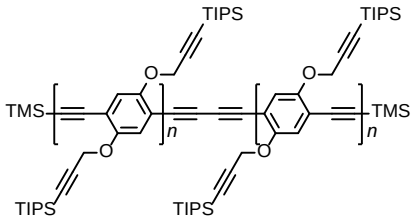


Figure S2. ^{1}H NMR spectra (500 MHz) of solutions of H_xNa_{12-x}[TAHA-EPBPE-TAHA] **23** in D_2O at pD 1.6 (top), pD 5.0 (middle), and pD 1.3 (bottom). The range from 8.5 ppm to 7.0 ppm is shown here. The ranges 10 ppm to 5 ppm and 5 ppm to 0 ppm can be found in figures **S49** and **S50**, respectively.

3. Syntheses of the rulers [Cu-PyMTA]-nitroxide 2_3, [Cu-PyMTA]-[Cu-PyMTA] 1_n with n = 1, 3, 5, and [Cu-TAHA]-[Cu-TAHA] 3

Schemes 1 and 2 given in the main text provide the compound numbers of starting materials and products. Compound numbers of identified side products are given in Figure S3.



24 (n=1)
25 (n=3)

Figure S3. Alkyne dimers $\mathbf{24_1}$ and $\mathbf{24_3}$ are isolated side products of Sonogashira-Hagihara couplings using TMS-EPE-H $\mathbf{8_1}$ and TMS-$(EP)_3$E-H $\mathbf{8_3}$, respectively.

3.1 General

Unless otherwise stated, reactions were performed in dried glassware under argon. Argon was passed through anhydrous $CaCl_2$ prior to its use. Degassed solutions were prepared through applying three freeze-pump-thaw cycles. Solvents were removed at a bath temperature of ~40 °C and reduced pressure. The products were dried at room temperature at ~0.3 mbar. The pH/pD values of the solutions were determined using pH indicator strips (resolution: 0.5 or 0.3 pH).

Unless otherwise stated, commercial solvents and reagents were used. Since all commercial compounds used for syntheses had a purity of >95% their molar amounts used in the syntheses were calculated with their compound masses and were not corrected by the manufacturer specified purities. Sources, purities, and batch numbers of the reagents are given in Table S1. THF (HPLC grade) was dried with sodium/benzophenone prior to its use. For the preparation of aqueous solutions, deionized water was used. Solvents used for extraction and chromatography were of technical grade and were distilled prior to their use. $PdCl_2(PPh_3)_2$ was synthesized according to literature,[3] however using 2.1 times the given amount of methanol. The syntheses of TMS-EPE-H $\mathbf{8_1}$,[4] TMS-$(EP)_3$E-H $\mathbf{8_3}$,[4] PEG-N_3 **14**,[4] 4-iodo-PyMTA ethyl ester (**11**),[5] and {H_4PyMTA}-$(EP)_n$E-{H_4PyMTA} $\mathbf{25}_n$[4] have been reported. The synthesis of 4-iodo-TAHA ethyl ester (**17**) will be published separately.

Column chromatography was carried out on silica gel 60 (0.035−0.070 mm) without applying pressure. In the procedures reported below, the size of the column is given as diameter x length. The material was loaded onto the column dissolved in a small quantity of the eluent. Thin layer chromatography (TLC) was performed on silica gel 60 containing

fluorescent indicator F254. The solid support for the silica gel layer was aluminum foil. The spots were detected with UV light of λ = 254 nm and 366 nm. The compositions of solvent mixtures are given in volume ratios. For preparative HPLC a Phenomenex Luna® Silica(2) column (particle size: 5 µm, pore size 100 Å, column size 21.2 mm x 250 mm) was used.

The ligand content of a material was quantified by quantitative ^{1}H NMR spectroscopy[6] using a capillary filled with a solution of maleic acid in D_2O as the standard. Measurements were carried out in MeOD and with 90 s pulse delay.

NMR spectra were calibrated using the solvent signal as an internal standard [$CDCl_3$: δ (^{1}H) = 7.25, δ (^{13}C) = 77.0; CD_2Cl_2: δ (1H) = 5.32, δ (13C) = 53.8; CD_3OD: δ (1H) = 3.31, δ (^{13}C) = 49.0; D_2O: δ (^{1}H) = 4.79]. Signal assignments are supported by DEPT-135, COSY, HMBC, and HMQC experiments.

ESI MS spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik) equipped with a standard ESI source. Unless otherwise stated, accurate ESI mass measurements were performed using a Q-IMS-TOF mass spectrometer Synapt G2Si (Waters, Manchester, UK) in resolution mode, interfaced to a nano-ESI ion source. Nitrogen served as the nebulizer gas and the dry gas for nano-ESI. Nitrogen was generated by a nitrogen generator NGM 11. Helium 5.0 was used as buffer gas in the IMS entry cell, nitrogen 5.0 was used for IMS. ESI samples were introduced by static nano-ESI using in-house pulled glass emitters. The monoisotopic mass of the compounds is reported.

Table S1. Sources, purities, and batch numbers of commercial compounds used for reactions and preparation of the solutions used for EPR spectroscopical experiments.

compound	manufacturer	purity [%]	batch number
Copper(II) chloride	Fluka	>97%	61173
$[Cu(phen)(PPh_3)_2]NO_3 \cdot 0.5\ CH_2Cl_2$	Aldrich	95	MKAA0733V
Deuterium oxide	Deutero	99.9	B15529
	Roth	99.8	15790
Dichloromethane	VWR	100.0	17F264004
Dichloromethane, dry, over molecular sieve (degassed), < 0.005% H_2O	Acros	99.8	1277573
Diisopropylamine	Merck	≥ 99.0	S4082846429
4-(N,N-Dimethylamino)pyridine	Janssen	---	44411/1
Ethanol	VWR	99.96	16E284008
Ethanol, < 0.003% H_2O	VWR	≥ 99.8	122110449
Hydrochloric acid, 37%	Fisher Scientific	p.A.	1674520
4-Iodoaniline	Acros	99	A0235953
Methanol	VWR	100.0	17G054004
Methanol-d_4	Deutero	99.8	B17240
$Pd_2(dba)_3$	Aldrich	97	A0323562
Piperidine	Alfa Aesar	99	17181722
Potassium carbonate	VWR	100.6	07E020030
Potassium carbonate, anhydrous	Aldrich	99.99	---
Quadrapure BZA	Aldrich	---	BCBF4504V
Quadrapure TU	Aldrich	---	BCBL0423V
Sodium hydroxide	VWR	99.2	13K210004
Sodium deuteroxide, 40% in D_2O	Acros	---	A0333261
Tetra-*n*-butylammonium fluoride, 1 M solution in THF (containing 3.27% H_2O)	Alfa Aesar	---	10176007
2,2,5,5-Tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid	Acros	99	A006034301
Toluene, dry, over molecular sieve	Acros	99.85	1561013
Triphenylphosphane	Merck	≥ 99	S5329270917
Tris(dibenzylideneacetone)dipalladium(0)	Aldrich	---	MKBF1602V

3.2 Synthesis of ruler H_xNa_{8-x}[{Cu^{II}(TAHA)}-EPBPE-{Cu^{II}(TAHA)}] 3

TAHAester-EPE-TMS 18. To a degassed solution of TMS-EPE-H **8_1** (60 mg, 97 µmol) and 4-iodo-TAHA ethyl ester (**17**) (61 mg, 74 µmol) in dry THF (8 mL) and $^iPr_2NH$ (522 µL, 3.71 mmol) was added $PdCl_2(PPh_3)_2$ (2.1 mg, 3.0 µmol) and CuI (1.1 mg, 5.8 µmol). The yellow solution was stirred at room temperature for 21.5 h. All volatiles were evaporated, strictly keeping the reaction mixture under argon. The residual brown oil was dissolved in degassed anhydrous CH_2Cl_2 (7 mL) and metal scavenger QuadraPure TU (120 mg) was added. The yellow suspension was stirred at room temperature for 22.5 h. Metal scavenger QuadraPure BZA (15 mg) was added and the suspension was stirred for another 3 h at room temperature. The metal scavenger QuadraPure BZA did not change its color, which indicated that there had been no free Cu or Pd ions left in the solution. The suspension was filtered through a syringe filter (PTFE membrane, 13 mm diameter, 0.45 µm pore size) and the solvent of the filtrate was removed. The residual orange solid was filtered through silica gel (1.5 cm x 2.0 cm, rinsing with Et_2O). The solvents of the eluate were removed. The components of the residual orange oil were separated by column chromatography (1.5 cm x 28 cm). Eluting with Et_2O/pentane 1:1 gave as a first fraction a mixture (31 mg; R_f = 0.90) of alkyne dimer **24_1** and grease as an orange solid. As the second fraction a mixture (2 mg; R_f = 0.90, 0.59, 0.44) of TAHAester-EPE-TMS **18**, triphenylphosphane oxide and a minor amount of unidentified compounds was obtained as a yellowish solid. As the third fraction a yellow oil (80 mg; R_f = 0.44) was obtained consisting of TAHAester-EPE-TMS **18** (82% yield) and triphenylphosphane oxide in the molar ratio of 98:2. For ^{1}H NMR data of TAHAester-EPE-TMS **18** see Tables S2 and S3. For ^{13}C NMR data of TAHAester-EPE-TMS **18** see Tables S4 and S5. ^{1}H NMR data of alkyne dimer **24_1** agree with previously reported data.[4] MS (ESI; MeCN) of TAHAester-EPE-TMS **18**: *m*/*z* = 1334.8 $[M + Na]^+$.

TAHAester-EPE-H 19. To a colorless suspension of dry K_2CO_3 (14.5 mg, 105 µmol) in anhydrous EtOH (2 mL) was added a yellow solution of a 98:2 mixture (77 mg) of TAHAester-EPE-TMS **18** (58 µmol) and triphenylphosphane oxide (1.1 µmol) in dry THF (4 mL). The suspension consisting of a yellow solution and a colorless solid was stirred at room temperature for 19 h. Subsequently, the suspension was filtered through silica gel (1.0 cm x 1.0 cm, rinsing with Et_2O). The solvents of the eluate were removed. The components of the residual brown oil were separated by column chromatography (1.5 cm x 33 cm). Elution with pentane/Et_2O 4:3 gave a mixture (5 mg; R_f = 0.51) of triphenylphosphane oxide and unidentified compounds as a yellowish solid and TAHAester-EPE-H **19** (68 mg, 95%, R_f = 0.23) as a yellow oil. For ^{1}H NMR data see Tables S2 and S3. For ^{13}C NMR data see Tables S4 and S5. MS (ESI; MeCN): *m*/*z* = 1240.6 $[M + H]^+$, 1262.6 $[M + Na]^+$.

TAHAester-EPBPE-TAHAester 20. The reaction was performed in air. To a solution of TAHAester-EPE-H **19** (68 mg, 55 µmol) in dry THF (5 mL) and $^iPr_2NH$ (385 µL, 2.74

mmol) was added $PdCl_2(PPh_3)_2$ (1.57 mg, 2.23 µmol) and CuI (0.85 mg, 4.5 µmol). The greenish solution was stirred at room temperature for 23 h. TLC proved the reaction to be complete (Et_2O/pentane 2:1, R_f(**19**) = 0.70; R_f(**20**) = 0.43). All volatiles were removed at room temperature and reduced pressure. After ventilation the flask with argon the residual yellow oil was dissolved in degassed anhydrous CH_2Cl_2 (10 mL) and metal scavenger QuadraPure TU (90 mg) was added. The yellow suspension was stirred at room temperature for 17.5 h. Metal scavenger QuadraPure BZA (20 mg) was added and the suspension was stirred for another 4 h at room temperature. The metal scavenger QuadraPure BZA did not change its color, which indicated that there had been no free Cu or Pd ions left in the solution. The suspension was filtered through a syringe filter (PTFE membrane, 13 mm diameter, 0.45 µm pore size) and the solvent of the filtrate was removed. The components of the residual yellow oil were separated by column chromatography (1.5 cm x 37 cm). Eluting with Et_2O/pentane 4:3 gave as a first fraction a mixture (2 mg; R_f = 0.59, 0.50) of triphenylphosphane oxide, grease and unidentified compounds as a yellowish solid. As the second fraction TAHAester-EPE$_2$PE-TAHAester **20** (57 mg, 84%, R_f = 0.23) was obtained as a yellow oil. For ^{1}H NMR data see Tables S2 and S3. For ^{13}C NMR data see Tables S4 and S5. MS (ESI; MeCN): *m*/*z* = 1239.7 $[M + 2H]^{2+}$, 1250.7 $[M + H + Na]^{2+}$, 1261.7 $[M + 2Na]^{2+}$.

Desilylated TAHAester-EPBPE-TAHAester 21. To a solution of TAHAester-EPBPE-TAHAester **20** (57 mg, 23 µmol) in dry THF (5 mL) was added a 1.0 M solution of Bu_4NF in THF (138 µL, 138 µmol). Immediately after addition of Bu_4NF the color of the reaction solution had changed from yellow to orange. The solution was stirred at room temperature for 75 min. It was filtered through silica gel (2 cm x 1.5 cm, rinsing with THF). Solvent removal from the eluate gave a yellow oil (60 mg) consisting of desilylated TAHAester-EPBPE-TAHAester **21** accompanied by TIPS-F and/or TIPS-OH, and a Bu_4N salt. For ^{1}H NMR data see Tables S2 and S3.

PEGylated TAHAester-EPBPE-TAHAester 22. PEG-N_3 **14** (34 mg, 80 µmol) and material (35 mg; containing ~ 13 µmol desilylated TAHAester-EPBPE-TAHAester **21**) that had been obtained by desilylation of TAHAester-EPBPE-TAHAester **20** (see above) were dissolved in dry toluene (10 mL) and the solution was degassed. $[Cu(phen)(PPh_3)_2]NO_3 \bullet 0.5\ CH_2Cl_2$ (1.85 mg, 2.12 µmol) was added. The yellow solution was stirred at 30 °C for 69.5 h. After cooling to room temperature, metal scavenger QuadraPure TU (40 mg) was added. The yellow suspension was stirred at room temperature for 67 h. Metal scavenger QuadraPure BZA (15 mg) was added and the suspension was stirred for another 7.5 h at room temperature. The metal scavenger QuadraPure BZA did not change its color, which indicated that there had been no free Cu ions left in the solution. The solution was decanted off from the scavenger and the solvent was removed. The residual yellow oil was filtered through silica gel (2 cm x 2 cm, rinsing with CH_2Cl_2/EtOH 9:1). After removal of the solvent from the eluate, the components of the residual yellow/brown oil were

separated by preparative HPLC (isocratic run with CH_2Cl_2/EtOH 94.7:5.3, flow rate of 20 mL/min; 62 mg of the yellow/brown oil dissolved in CH_2Cl_2 (820 µL) were injected). This gave PEGylated TAHAester-EPBPE-TAHAester **22** (37 mg, 78% over 2 steps; R_f = 0.52) containing a trace of grease at a retention time of 7.6 min. For ^{1}H NMR data see Tables S2 and S3. For ^{13}C NMR data see Tables S4 and S5. MS (ESI; MeCN): *m*/*z* = 1795.9 $[M + 2Na]^{2+}$.

Ruler precursor H_xNa_{12-x}[TAHA-EPBPE-TAHA] 23. The reaction was performed in air. To a solution of PEGylated TAHAester-EPBPE-TAHAester **22** (36 mg, 10 µmol) in EtOH (3.0 mL) was added a 0.10 M aqueous solution of NaOH (2.44 mL, 244 µmol). The yellow solution was stirred at room temperature for 44 h. The pH was lowered to 7.0 by addition of a 0.10 M aqueous solution of HCl (1300 µL, 130.0 µmol). Removal of the solvents gave a yellowish solid. The ^{1}H NMR spectrum revealed an incomplete ester hydrolysis. The solid was dissolved in water (2000 µL) and a 0.10 M aqueous solution NaOH (610 µL, 61.0 µmol) was added. The solution was stirred at room temperature for 45 h. The pH was lowered to 7.0 by addition of a 0.10 M aqueous solution of HCl (450 µL, 45.0 µmol). After removal of the solvent a yellowish solid was obtained. Again, the ^{1}H NMR spectrum revealed an incomplete ester hydrolysis. The solid was dissolved in water (2000 µL) and a 0.10 M aqueous solution of NaOH (610 µL, 61.0 µmol) was added. The solution was stirred at room temperature for 48 h. The pH was lowered to 7.0 by addition of 0.10 M aqueous solution of HCl (600 µL, 60.0 µmol). ^{1}H NMR spectroscopy showed a complete ester hydrolysis. After removal of the solvent, the yellowish solid was dissolved in water (2000 µL) and the pH was lowered to 3.0 by addition of a 0.10 M aqueous solution of HCl. After removal of the solvent the yellowish solid was dissolved in a 0.10 M aqueous solution of HCl (2.0 mL, 0.20 mmol). After removal of the solvent, the yellowish solid was dissolved in a 0.10 M solution of NaOD in D_2O (600 µL, 60.0 µmol) giving an orange solution of pD 5.0. After removal of the solvent, the yellowish solid was dissolved in an 0.10 M aqueous solution of HCl (2.0 mL, 0.20 mmol). After removal of the solvent, a yellow solid (40 mg) consisting of H_xNa_{12-x}[TAHA-EPBPE-TAHA] **23** and NaCl was obtained. A part of this compound (32.644 mg) was suspended in MeOD (500 µL) giving a mixture of an orange solution and a colorless solid. The solution was decanted off and the solvent was removed. The content of the structural motive $[TAHA\text{-}EPBPE\text{-}TAHA]^{12-}$ in the remaining solid was determined by quantitative ^{1}H NMR spectroscopy to be 4.4 µmol (54% yield). For ^{1}H NMR data see Figure S28. Accurate MS (ESI; H_2O/MeOH): *m/z* calcd for $[M - 2H]^{2-}$, $C_{148}H_{218}N_{18}O_{60}^{2-}$, 1603.7286; found, 1603.7240; M = H_{12}[TAHA-EPBPE-TAHA].

Ruler H_xNa_{8-x}[{Cu^{II}(TAHA)}-EPBPE-{Cu^{II}(TAHA)}] 3. A stock solution (500 µL) of ruler precursor H_xNa_{12-x}[TAHA-EPBPE-TAHA] **23** (22.83 mg containing 4.437 µmol of the structural motive $[TAHA\text{-}EPBPE\text{-}TAHA]^{12-}$) in D_2O was prepared. A part of this stock solution (180.3 µL containing 1.60 µmol of the structural motive $[TAHA\text{-}EPBPE\text{-}TAHA]^{12-}$) was mixed with a 0.05 M solution of $CuCl_2$ in D_2O (28.8 µL, 1.44 µmol) and then a solution

of 0.10 M NaOD in D_2O (110 µL, 11.0 µmol) was added to raise the pH of the solution to pH 7. The solution was diluted with D_2O up to a total volume of 320 µL. A part of the thus obtained solution (300 µL containing 1.50 µmol of the structural motive [TAHA-EPBPE-TAHA]$^{12-}$) was mixed with a 0.05 M solution of $CuCl_2$ in D_2O (27.0 µL, 1.35 µmol) and then a solution of 0.10 M NaOD in D_2O (25 µL, 2.5 µmol) was added to raise the pH of the solution to pH 7. The solution was diluted with D_2O up to a total volume of 375 µL to obtain a 4.0 mM yellowish solution of H_xNa_{8-x}[{Cu^{II}(TAHA)}-EPBPE-{Cu^{II}(TAHA)}] **3** in D_2O containing NaCl.

3.3 Synthesis of ruler Na_2[{Cu^{II}(PyMTA)}-$(EP)_4$-NO• 2_3

I-P-NO• 7. To an ice-bath cooled solution of 2,2,5,5-tetramethyl-3-pyrrolin-1-oxyl-3-carboxylic acid (**6a**) (168 mg, 0.91 mmol) and 4-(N,N-dimethylamino)pyridine (257 mg, 2.29 mmol) in anhydrous CH_2Cl_2 (10 mL) was added thionyl chloride (64.6 µL, 0.89 mmol) whereupon the solution immediately changed its color from yellow to red. Five min later the ice bath was removed and the solution was stirred for 65 min at room temperature. A solution of 4-iodoaniline (100 mg, 0.46 mmol) in anhydrous CH_2Cl_2 (10 mL) was added and the orange solution was stirred at room temperature for another 65 min. It was filtered through silica gel (2 cm × 6 cm, rinsing with Et_2O). The yellow band and the eluate ahead of it were collected and the orange band was left on the silica gel. The solvents of the complete eluate were removed. Column chromatography (2 cm × 28 cm, CH_2Cl_2/Et_2O 20:1) of the residual yellow solid (209 mg; applied to the silica gel column as a solution in $CDCl_3$) gave I-P-NO• **7** (172 mg, 98%; R_f = 0.20) together with a small amount of CH_2Cl_2 (ca. 7 mol%) as a yellow solid. Ahead of this material, three yellow bands were eluted giving a yellow film (3 mg) of unidentified compounds. For ^{1}H NMR data of I-P-NO• **7** see Tables S2 and S3. MS (ESI, positive mode; MeCN): *m/z* = 393.4 [M - CH_3 + Na]$^+$, 408.1 [M + Na]$^+$. MS(ESI, negative mode; MeCN): *m/z* = 383.9 [M - H]$^-$, 419.9 [M + ^{35}Cl]$^-$, 421.9 [M + ^{37}Cl]$^-$.

TMS-$(EP)_4$-NO• 9. To a degassed solution of TMS-$(EP)_3$E-H **8_3** (200 mg, 120 µmol) and a 96:4 mixture (51 mg) of I-P-NO• **7** (0.13 mmol) and CH_2Cl_2 (5 µmol) in dry THF (7 mL) and piperidine (0.60 mL, 6.1 mmol) were added $Pd_2(dba)_3$ (11.17 mg, 12.20 µmol), PPh_3 (12.74 mg, 48.56 µmol) and CuI (6.26 mg, 32.9 µmol). The yellow solution was stirred at room temperature for 45 h, whereupon the solution became turbid. All volatiles were evaporated. The residual brown oil was filtered through silica gel (2 cm x 3 cm, rinsing with Et_2O). The solvents of the eluate were removed. The components of the residual brown solid were separated by column chromatography (3 cm x 40 cm). Eluting with CH_2Cl_2/Et_2O 50:1 gave as a first fraction a mixture (7 mg; R_f = 0.83) of alkyne dimer **24_3**, grease, triphenylphosphane oxide and a minor amount of unidentified compounds as a yellow solid. As the second fraction a mixture (35 mg; R_f = 0.81, 0.50, 0.36, 0.24) of TMS-$(EP)_4$-NO• **9** and residuals of the $Pd_2(dba)_3$ catalyst was obtained as an orange solid. As

the third fraction TMS-(EP)$_4$-NO• **9** (178 mg, 77%, R_f = 0.24) was obtained as a yellow solid. Residual I-P-NO• **7** was not eluted (R_f = 0.08). For ^{1}H NMR data of TMS-(EP)$_4$-NO• **9** see Tables S2 and S3. For ^{13}C NMR data of TMS-(EP)$_4$-NO• **9** see Tables S4 and S5. ^{1}H NMR data of alkyne dimer **24$_3$**[4] agree with previously reported data. MS (ESI; CH_2Cl_2/MeCN) of TMS-(EP)$_4$-NO• **9**: *m*/*z* = 1915.1 $[M - H]^-$, 1951.0 $[M + Cl]^-$. Accurate MS (ESI) of a sample obtained in another experiment with identical NMR data: *m/z* calcd for $[M+Na]^+$ $C_{116}H_{171}N_2O_8Si_7Na^+$, 1939.1313; found 1939.1289.

H-(EP)$_4$-NO• 10. The reaction was performed under argon but the glassware had not been dried. To a solution of TMS-(EP)$_4$-NO• **9** (150 mg, 78.2 µmol) in MeOH (6 mL) and CH_2Cl_2 (6 mL) was added K_2CO_3 (16 mg, 0.12 mmol). The suspension consisting of a yellow solution and a colorless solid was stirred at room temperature for 14.5 h. Et_2O (40 mL) and H_2O (10 mL) were added. The organic phase was separated, and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined organic phases were dried over $MgSO_4 \cdot x\ H_2O$ and filtered. The solvents of the filtrate were removed. The components of the residual yellow solid were separated by column chromatography (3 cm x 21 cm). Elution with CH_2Cl_2/Et_2O 50:1 gave H-(EP)$_4$-NO• **10** (131 mg, 91%; R_f = 0.26) as a yellow solid. For ^{1}H NMR data see Tables S2 and S3. For ^{13}C NMR data see Tables S4 and S5. MS (ESI; MeCN): *m*/*z* = 1867.3 $[M + Na]^+$.

PyMTAester-(EP)$_4$-NO• 12. To a degassed solution of H-(EP)$_4$-NO• **10** (83 mg, 0.045 mmol) and 4-iodo-PyMTA ethyl ester (**11**) (35.5 mg, 0.058 mmol; The material contained ca. 4 mol% 4-chloro-PyMTA ethyl ester) in THF (3 mL) and ^{i}Pr$_2$NH (340 µL, 2.42 mmol) were added $Pd_2(dba)_3$ (4.76 mg, 5.2 µmol), CuI (2.21 mg, 11.6 µmol), and PPh_3 (5.73 mg, 21.8 µmol). The reaction mixture was stirred at room temperature for 3 d. A precipitate had formed within the first 18 h. 2-Methylbut-3-yn-2-ol (5.0 µL, 0.051 mmol) was added and the suspension was stirred for another 22 h. All volatiles were removed at room temperature and reduced pressure avoiding exposure to air. The residue was dissolved in degassed anhydrous CH_2Cl_2 (3 mL), and metal scavenger QuadraPure TU (208 mg) was added. The suspension was stirred at room temperature for 23 h. Metal scavenger QuadraPure BZA (5 mg) was added, and the suspension was stirred for another 1 h at room temperature. The suspension was filtered through silica gel (2 cm × 3 cm, rinsing with CH_2Cl_2/EtOH 10:0.5 (20 mL)). The solvent of the eluate was removed. Column chromatography (2 cm × 40 cm, CH_2Cl_2/Et_2O/EtOH 10:4:0.2) of the residual yellow-brown solid (147 mg) gave first a yellow-brown solid (65 mg) containing, among other components, the product of oxidative alkyne dimerization of H-(EP)$_4$-NO• **10**, i.e. •ON-(PE)$_4$(EP)$_4$-NO•, and second PyMTAester-(EP)$_4$-NO• **12** in mixture with unidentified components as a yellow film (52 mg; R_f = 0.39). The latter fraction was submitted to preparative HPLC. HPLC gave a yellow film (46 mg) which consisted of PyMTAester-(EP)$_4$-NO• **12** (44% yield) and a small amount of another compound containing the PyMTA ethyl ester moiety (about 5 mol%), probably 4-chloro-PyMTA ethyl ester which had been a contaminant in the starting material 4-iodo-PyMTA ethyl ester (**11**). Details

for this HPLC run: The material was loaded onto the column as a solution in CH_2Cl_2. Linear gradients in combination with isocratic elution with a flow rate of 15 mL/min at room temperature and UV detection at 240 nm. The mobile phase consisted of CH_2Cl_2 and EtOH with the following percentages of EtOH: start: 1.3%; 0-25 min, 1.3→5.9%; 25-30 min, 5.9%. The eluate between 10.4 and 12.1 min was collected. For ^{1}H NMR see Tables S2 and S3. For ^{13}C NMR data see Tables S4 and S5. MS (ESI; MeCN): *m*/*z* = 2325.4 $[M]^+$, 2348.4 $[M + Na]^+$.

Desilylated PyMTAester-(EP)$_4$-NO• 13. To a solution of PyMTAester-(EP)$_4$-NO• **12** (45.1 mg, 19.4 µmol; containing about 6 mol% of another compound with a PyMTA ethyl ester moiety as mentioned above) in THF (5 mL) was added *n*-Bu_4NF (1 M in THF; 140 µL, 140 µmol) whereupon the reaction solution changed its color immediately from yellow to orange-brown. The solution was stirred at room temperature for 10 min. Filtration through silica gel (1 cm × 6 cm, rinsing with dry THF (12 mL)) and removal of the solvent from the eluate gave a yellow solid (29 mg) consisting of desilylated PyMTAester-(EP)$_4$-NO• **13**, the above mentioned accompanying compound with a PyMTA ethyl ester moiety, and TIPS-F and/or TIPS-OH. For ^{1}H NMR data see Tables S2 and S3.

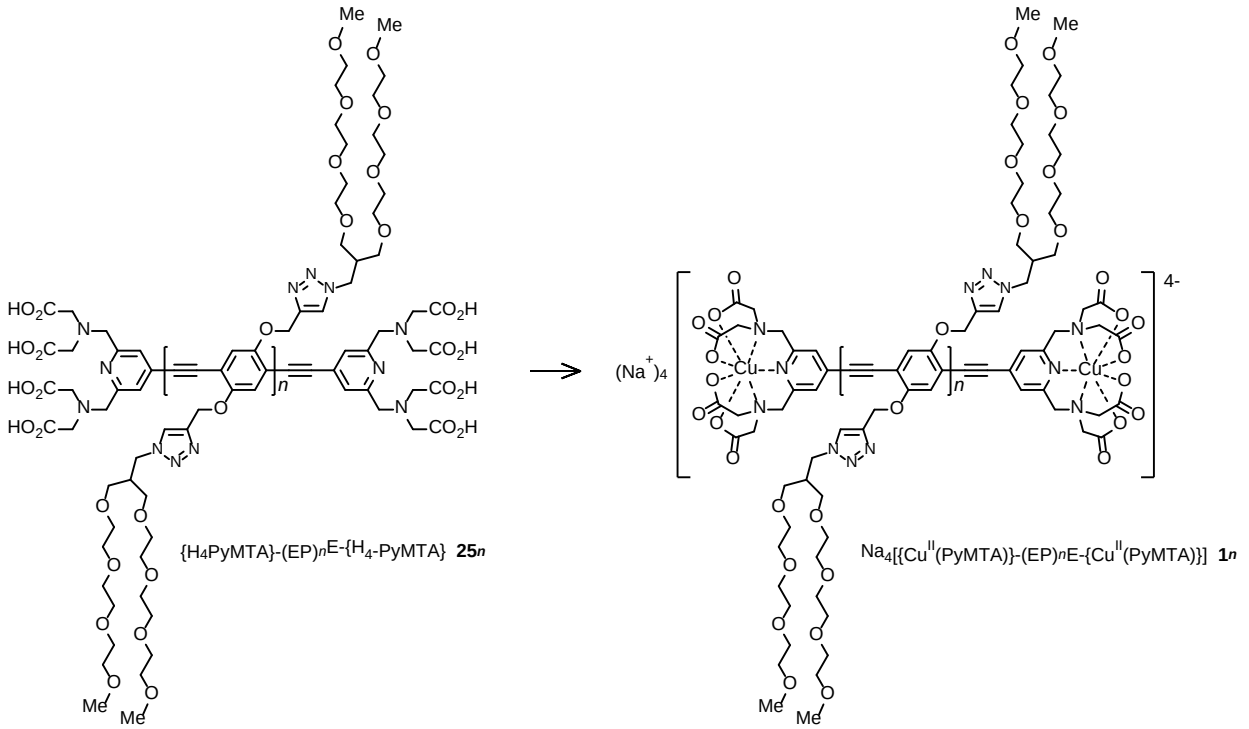
PEGylated PyMTAester-(EP)$_4$-NO• 15. PEG-N_3 **14** (59.7 mg, 0.141 mmol) and the material (29 mg, max. 19.4 µmol PyMTAester-(EP)$_4$-NO• **13**) that had been obtained by desilylation of PyMTAester-(EP)$_4$-NO• **12** as described above, were dissolved in anhydrous toluene (4 mL) and the solution was degassed. $[Cu(phen)(PPh_3)_2]NO_3$ • 0.5 CH_2Cl_2 (2.775 mg, 3.3 µmol) was added. The reaction mixture was stirred for 3 d at 40 °C, during which time it turned from a brownish suspension into a brown solution. Metal scavenger QuadraPure TU (66 mg) was added at room temperature and the suspension was stirred for 23 h. Then, metal scavenger QuadraPure BZA (9 mg) was added, and the suspension was stirred for another 3 h at room temperature. The suspension was filtered through silica gel (1.5 cm × 2.5 cm, rinsing with CH_2Cl_2/EtOH 5:1 (10 mL)). The solvent was removed from the eluate. Preparative HPLC on silica gel of the residual yellow oil (92 mg) gave PyMTAester-(EP)$_4$-NO• **15** (51 mg, 67% in reference to PyMTAester-(EP)$_4$-NO• **12**) as a yellow film. Details for the HPLC run: The material was loaded onto the column as a solution in CH_2Cl_2. Linear gradients with a flow rate of 15 mL/min at room temperature and UV detection at 220 nm were used. The mobile phase consisted of CH_2Cl_2 and EtOH with the following percentages of EtOH: 0-10 min, 5%; 10-20 min, 5→10%; 20-30 min, 10→20%; 30-40 min, 20%. The eluate between 21.7 and 23.0 min was collected. For ^{1}H NMR data see Tables S2 and S3. For ^{13}C NMR data see Tables S4 and S5. MS (ESI; THF): *m*/*z* = 1987.1 $[M + 2Na]^{2+}$, 1995.1 $[M + Na + K]^{2+}$, 2003.1 $[M + 2K]^{2+}$.

Ruler precursor $(H^+)_2(Na^+)_2$[PyMTA-(EP)$_4$-NO•]$^{4-}$ 16. PyMTAester-(EP)$_4$-NO• **15** (47.1 mg, 12.0 µmol) was dissolved in EtOH (4.0 mL) and an aqueous solution of NaOH (1 M in millipore water; 71.9 µL, 71.9 µmol) was added. The reaction mixture was stirred at

room temperature for 18 h. Because the mixture became slightly cloudy, water (0.5 mL) was added and the resulting solution was stirred at room temperature for another 1.5 h. An aqueous solution of HCl (0.1 M; 215 µL, 21.5 µmol) was added to adjust the pH to about 7.1. All volatiles were removed at room temperature and reduced pressure. The ^{1}H NMR spectrum of the obtained material showed that the saponification was incomplete. Therefore, the material was dissolved in EtOH (4 mL) and an aqueous solution of NaOH (0.1 M; 400 µL, 40 µmol) was added. After 12 h at room temperature, an aqueous solution of HCl (0.1 M; 250 µL, 25 µmol) was added to adjust the pH to about 6.9. All volatiles were removed at room temperature and reduced pressure. HPLC gave $(H^+)_{4-x}(Na^+)_x$[PyMTA-$(EP)_4$-NO•]$^{4-}$ **16** (37 mg) as a yellow wax. The content of the structural motive [PyMTA-$(EP)_2$-NO•]$^{4-}$ in this solid was determined by quantitative ^{1}H NMR spectroscopy, to be 8.08 µmol (67% yield). Details for the HPLC run: The material was loaded onto the column as a solution in H_2O. Linear gradients with a flow rate of 12 mL/min at room temperature and UV detection at 210 nm were used. The mobile phase consisted of H_2O and MeCN with the following percentages of MeCN: start, 15%; 0-5 min, 15→20%; 5-15 min, 20%→80%; 15-25 min, 80%. The eluate between 14.8 and 15.8 min was collected. For ^{1}H NMR data see Tables S2 and S3.

Ruler $(Na^+)_2$[Cu(II)-PyMTA]-$(EP)_4$-NO•] 2$_3$. With $(H^+)_2(Na^+)_2$[PyMTA-$(EP)_4$-NO•]$^{4-}$ **16** a solution in D_2O (4040 µL) was prepared being 2 mM in respect to the structural motive [PyMTA-$(EP)_2$-NO•]$^{4-}$ (8.08 µmol). To a part of this solution (525 µL containing 1.05 µmol of the structural motive [PyMTA-(EP)2-NO•]$^{4-}$) was added a solution of $CuCl_2$ in D_2O (5 mM; 200 µL, 1 µmol). Then a solution of NaOD in D_2O (50 mM; 50 µL, 2.5 µmol) was added. The solution was diluted with D_2O (225 µL) to a total volume of 1000 µL to obtain a 1 mM solution of $(Na^+)_2$[Cu(II)-PyMTA]-$(EP)_4$-NO•] **2$_3$**. The pD value of the solutions was about 7-8. MS (ESI; D_2O/MeCN): *m*/*z* = 1938.3 [M + D - 2Na]$^{2-}$.

3.4 Synthesis of the rulers Na_4[{Cu^{II}(PyMTA)}-(EP)$_n$E-{Cu^{II}(PyMTA)}] **1$_n$** with n = 1, 3, 5



Scheme S1. Preparation of the rulers Na_4[{Cu^{II}(PyMTA)}-(EP)$_n$E-{Cu^{II}(PyMTA)}] **1$_n$** with n = 3, 5.

Ruler Na_4[{Cu^{II}(PyMTA)}-EPE-{Cu^{II}(PyMTA)}] 1$_1$. A solution of $CuCl_2$ in D_2O (0.05 M, 129.5 µL, 6.475 µmol) was added to a solution of {H_4PyMTA}-EPE-{H_4PyMTA} **25$_1$**** (16.35 mM, 200 µL, 3.270 µmol). To this green-blue solution a solution of NaOD in D_2O (1.0 M, 25 µL, 25 µmol) and a solution of NaOD in D_2O (0.1 M, 21 µL, 2.1 µmol) was added to rise the pH of the solution to pH 7.1. The solution was diluted with D_2O (278.5 µL) to obtain a 5.0 mM solution of Na_4[{Cu^{II}(PyMTA)}-EPE-{Cu^{II}(PyMTA)}] **1$_1$** in D_2O. MS (ESI): m/z = 967.3 $[M - 4Na + 2H]^{2-}$.

Ruler Na_4[{Cu^{II}(PyMTA)}-(EP)$_3$E-{Cu^{II}(PyMTA)}] 1$_3$. {H_4PyMTA}-(EP)$_3$E-{H_4PyMTA} **25$_3$**** (2.110 mg, 0.5374 µmol) was dissolved in D_2O (1000 µL). A solution of $CuCl_2$ in D_2O (0.05 M, 20.96 µL, 1.048 µmol) was added whereupon the color of the solution changed from yellow to yellow green. A solution of NaOD in D_2O (0.10 M, 30 µL, 3.0 µmol) was added to raise the pH of the solution to pH 8.2 whereupon the color of the solution changed from yellow green to green. The solution was diluted with D_2O (292.6 µL) to obtain a 400 µM solution of Na_4[{Cu^{II}(PyMTA)}-(EP)$_3$E-{Cu^{II}(PyMTA)}] **1$_3$** in D_2O. MS (ESI): Because of the high molecular weight of this compound and therefore the broad isotopic distribution, the most abundant mass is reported instead of the monoisotopic mass; m/z = 1011.2 $[M - 4Na]^{4-}$, 1348.9 $[M - 4Na + H]^{3-}$, 2023.6 $[M - 4Na + 2H]^{2-}$, 2034.6 $[M - 3Na + H]^{2-}$, 2045.6 $[M - 2Na]^{2-}$.

Ruler $Na_4[\{Cu^{II}(PyMTA)\}\text{-}(EP)_5E\text{-}\{Cu^{II}(PyMTA)\}]$ $\mathbf{1_5}$. $\{H_4PyMTA\}\text{-}(EP)_5E\text{-}\{H_4PyMTA\}$ $\mathbf{25_5}$**** (3.156 mg, 0.5228 µmol) was dissolved in D_2O (750 µL). A solution of $CuCl_2$ in D_2O (0.05 M, 20.39 µL, 1.012 µmol) was added whereupon the color of the solution changed from yellow to yellow green. A solution of NaOD in D_2O (0.10 M, 35 µL, 3.5 µmol) was added to raise the pH of the solution to pH 8.2 whereupon the color of the solution changed from yellow green to green. The solution was diluted with D_2O (501 µL) to obtain a 400 µM solution of $Na_4[\{Cu^{II}(PyMTA)\}\text{-}(EP)_5E\text{-}\{Cu^{II}(PyMTA)\}]$ $\mathbf{1_5}$ in D_2O. MS (ESI): Because of the high molecular weight of this compound and therefore the broad isotopic distribution, the most abundant mass is reported instead of the monoisotopic mass; *m/z* = 1539.3 $[M - 4Na]^{4-}$, 2052.6 $[M - 4Na + H]^{3-}$.

****The ruler precursors $\mathbf{25_n}$ were prepared through basic hydrolysis of the corresponding esters followed by protonation using proton exchange resin.[4] For calculating their molar amount, we assumed that the ligating moiety is uncharged, i.e. it contains four acidic protons. Therefore we use here the formula $\{H_4PyMTA\}\text{-}(EP)_nE\text{-}\{H_4PyMTA\}$ despite the material may be better represented with $\{H_{4-x}Na_xPyMTA\}\text{-}(EP)_nE\text{-}\{H_{4-x}Na_xPyMTA\}$.

4. NMR data

Influence of the nitroxide radical on the NMR spectra

As found earlier, the nitroxide influences the NMR signals of carbon and proton atoms in a distance dependent way.[1] In Figure S4 the structure of the nitroxide unit of compounds **7**, **9**, **10**, **12**, **13**, **15** and **16** is highlighted with colors: The signals of the proton or carbon atoms in the area marked with red are not found in the NMR spectra. The signal of the carbon atom in the yellow marked area is only found occasionally and, if observed, the intensity of this signal is very low. The signals of the protons and carbon atoms in the green highlighted area are observed: Proton signals are broad, the signals of the carbon atoms *ortho* and *para* to NH show low intensity, and the intensity of the signal of the carbon atoms *meta* to NH is only slightly reduced.

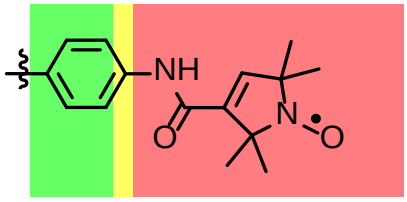


Figure S4. Nitroxide unit of compounds **7**, **9**, **10**, **12**, **13**, **15** and **16**. Hydrogen and carbon atoms, whose NMR signals are affected by the unpaired electron spin, are highlighted with colors.

Table S2. ^{1}H NMR (500 MHz) data: Signals with a chemical shift above 4 ppm.

compound, solvent	$C_{triaz}H$	H_{benz} *meta* to N	H_{benz} *ortho* to N	$C_{Py}H$	H_{benz} *ortho* to $C(CH_2)_3$	H_{benz} *meta* to $C(CH_2)_3$	H_{benz} *ortho* to OCH_2	$C_{benz}OCH_2$	$N_{triaz}CH_2$	CH_2CH_3	$C_{Py}CH_2$ (s)
7 $CDCl_3$	---	7.71 (s, 2H)	7.32 (br s, 2H)	---	---		---	---	---	---	---
9 $CDCl_3$	---	7.54 (br s, 2H)[#]		---	---		7.34 (s, 1H), 7.27 (s, 2H), 7.26 (s, 1H), 7.21 (s, 1H), 7.16 (s, 1H)	4.85 (s, 2H), (4.840 (s), 4.838 (s), large overlap, together 4H), 4.82 (s, 2H), 4.81 (s, 2H), 4.76 (s, 2H)	---	---	---
10 CD_2Cl_2	---	7.55 (br s, 3H)[#]		---	---		7.35 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.27 (s, 1H), 7.22 (s, 2H)	(4.873 (s), 4.869 (s), 4.866 (s), large overlap, together 6H), 4.85 (s, 2H), 4.84 (s, 2H), 4.80 (s, 2H)	---	---	---
12 CD_2Cl_2	---	7.56 (br s), overlap with $C_{Py}H$, together 5.2H[##]		7.54 (s), overlap with H_{benz} *ortho* and *meta* to N, together 5.2H[##]	---		7.35 (s, 2H), 7.30 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.23 (s, 1H)	(4.88 (s with shoulder), 4.87 (s), large overlap, together 10H), 4.84 (s, 2H)	---	4.15 (q, 8H, ^3J = 7.1 Hz)	4.01 (s, 4H)
13 CD_2Cl_2	---	7.60 (br s), overlap with $C_{Py}H$, together 3.4H[##]		7.60 (s), overlap with H_{benz} *ortho* and *meta* to N, together 3.4H[##]	---		7.24 (s, 1H), 7.23 (s, 3H), 7.22 (s, 1H), 7.21 (s, 1H)	4.873, 4.868, 4.866, 4.861, 4.853, 4.848, 4.843, 4.839, all s with large overlap, together 12H	---	4.15 (q, 8H, ^3J = 7.1 Hz)	4.00 (s, 4H)
15 CD_2Cl_2	7.943 (s, 1H), 7.938 (s, 2H), 7.91 (s, 1H), 7.88 (s, 1H), 7.84 (s, 1H)	7.47 (br s), overlap with $C_{Py}H$, together 3.2H[##]		7.53 (s), overlap with H_{benz} *ortho* and *meta* to N, together 3.2H[##]	---		7.30 (s, 1H), 7.280 (s, 1H), 7.276 (s, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 7.17 (s, 1H)	5.30 (s, 2H), 5.26 (s, 6H), 5.25 (s, 2H), 5.23 (s, 2H)	4.51 (s, 1H), 4.49 (s, 1H), 4.48 (s, 5H), 4.46 (s, 5H)	4.14 (q, 8H, ^3J = 7.1 Hz)	4.00 (s, 4H)
16 CD_3OD	8.22 (s, 1H), 8.21 (m, 1H), 8.20 (s, 1H), 8.17 (s, 1H), 8.16 (s, 1H), 8.15 (s, 1H), 8.12 (s, 1H)	7.47 (br s), overlap with $C_{Py}H$, together 1.5H[##]		7.52 (s), overlap with H_{benz} *ortho* and *meta* to N, together 1.5H[##]	---		7.38 (s, 1H), 7.36 (s, 1H), 7.32 (s, 1H), 7.31 (s, 1H), 7.30, (s, 1H), 7.23 (br s, 1H)	5.35 (s, 2H), 5.31 (s, 2H), 5.30 (s, 4H), 5.28 (s, 4H)	(4.57 (s), 4.56 (s), large overlap, together 4H), (4.53 (s), 4.52 (s), 4.51 (s), large overlap, together 8H)	---	4.36 (br s, 1H)[#]
18 CD_2Cl_2	---	---	---	---	7.41 (s, 4H)		7.21 (s, 1H), 7.20 (s, 1H)	4.80 (s, 2H), 4.77 (s, 2H)	---	4.05 (q, 12H, ^3J = 7.2 Hz)	---
19 CD_2Cl_2	---	---	---	---	7.41 (s, 4H)		7.25 (s, 1H), 7.24 (s, 1H)	4.80 (s, 2H), 4.79 (s, 2H)	---	4.05 (q, 12H, ^3J = 7.1 Hz)	---
20 CD_2Cl_2	---	---	---	---	7.42 (s, 8H)		7.28 (s, 2H), 7.26 (s, 2H)	4.83 (s, 4H), 4.81 (s, 4H)	---	4.06 (q, 24H, ^3J = 7.1 Hz)	---
21 CD_2Cl_2	---	---	---	---	7.45 (AA'BB' spin system, 8H)*		7.19 (s, 2H), 7.17 (s, 2H)	4.81 (d, 4H, ^4J = 2.4 Hz), 4.79 (d, 4H, ^4J = 2.4 Hz)	---	4.07 (q, 24H, ^3J = 7.0 Hz)	---
22 CD_2Cl_2	7.93 (s, 2H), 7.91 (s, 2H)	---	---	---	7.41 (s, 8H)		7.24 (s, 2H), 7.21 (s, 2H)	5.25 (s, 4H), 5.23 (s, 4H)	4.51 (t like**, 8H)	4.06 (q, 24H, ^3J = 7.1 Hz)	---

benz = benzene; Py = pyridine; triaz = triazole. *The signal has a quartet-like appearance. **The signal with triplet-like appearance consists of two overlapping dubletts. [#]An integral of 4H is expected. Precise integration is impossible because of signal broadness. [##]An integral of 6H is expected. Precise integration is impossible because of signal broadness.

Table S3. ^{1}H NMR (500 MHz) data: Signals with a chemical shift below 4 ppm.

compound, solvent	OCH_2CH_2	$CHCH_2O$	$C{\equiv}CH$	CH_2CO	$C(CH_2)_3$	OMe	$CHCH_2O$	CH_2CH_3	$SiCHMe_2$	$SiMe_3$
7 $CDCl_3$	---	---	---	---	---	---	---	---	---	---
9 $CDCl_3$	---	---	---	---	---	---	---	---	1.049, 1.046, 1.041, 1.035, 1.033, 1.028, all s with large overlap, together 126H	0.25 (s, 9H)
10 CD_2Cl_2	---	---	3.40 (s, 1H)	---	---	---	---	---	1.07, 1.06, 1.05*^{4}, all s with large overlap, together 126H	---
12 CD_2Cl_2	---	---	---	3.59 (s, 8H)	---	---	---	1.26 (t, 12H, ^3J = 7.1 Hz)	1.073, 1.067, 1.061*^{2}, 1.056, 1.053, all s with large overlap, together 126H	---
13 CD_2Cl_2	---	---	2.71 (t, 1H, ^4J = 2.2 Hz), (2.674, 2.669, 2.664, all s with large overlap, together 5H)	3.59 (s, 8H)	---	---	---	1.26 (t, 12H, ^3J = 7.1 Hz)	---	---
15 CD_2Cl_2	3.7 – 3.4 (several m overlapping with CH_2CO, together 152H)	3.4 – 3.3 (several m, together 24H)	---	3.59 (s, 8H) overlap with OCH_2CH_2	---	3.29 (s, 18H), 3.28 (s, 18H)	2.5 – 2.4 (m, 5H), 2.36 (br s, 1H)	1.25 (t, 12H, ^3J = 7.1 Hz)	---	---
16 CD_3OD	3.8 – 3.4 (several m overlapping with CH_2CO, together 152H)	3.4 – 3.32 (several m, together 24H)	---	3.60 (s, 8H) overlap with OCH_2CH_2	---	3.293, 3.288, both s with large overlap, together 36H	2.52 – 2.35 (m, 6H)	---	---	---
18 CD_2Cl_2	---	---	---	3.36 (s, 12H)	3.27 (s, 6H)	---	---	1.21 (t, 18H, ^3J = 7.2 Hz)	1.06 (s, 21H), 1.05 (s, 21H)	0.25 (s, 9H)
19 CD_2Cl_2	---	---	3.39 (s, 1H)	3.36 (s, 12H)	3.27 (s, 6H)	---	---	1.21 (t, 18H, ^3J = 7.1 Hz)	1.050 (s), 1.049 (s), all s with large overlap, together 42H	---
20 CD_2Cl_2	---	---	---	3.37 (s, 24H)	3.28 (s, 12H)	---	---	1.22 (t, 36H, ^3J = 7.1 Hz)	1.07 (s, 42H), 1.05 (s, 42H)	---
21 CD_2Cl_2	---	---	2.65 (t, 2H, ^4J = 2.4 Hz), 2.64 (t, 2H, ^4J = 2.4 Hz)	3.37 (s, 24H)	3.28 (s, 12H)	---	---	1.22 (t, 36H, ^3J = 7.0 Hz)	---	---
22 CD_2Cl_2	3.6 – 3.4 (several m, together 96H)	3.4 – 3.3 (several m overlapping with CH_2CO, together 40H)	---	3.36 (24H) overlap with $CHCH_2O$	3.27 (s, 12H)	3.29 (s, 12H), 3.28 (s, 12H)	2.48 (oct like with shoulders, 4H)	1.21 (t, 36H, ^3J = 7.1 Hz)	---	---

*^{n} means the signal has *n*-fold intensity compared to the other signals in the series.

Table S4. ^{13}C NMR (125 MHz) data: Signals with a chemical shift above about 90 ppm.

compound solvent	CO_2	$\underline{C}_{Py}CH_2$	$C_{benz}O$	$\underline{C}_{benz}C_q$	$\underline{C}$=CH of triazole	$C_{benz}N$	C_{Py} *para* to N	$C_{benz}H$ *meta* to $C_{benz}N$	$C_{benz}H$ *ortho* / *meta* to C_q	C=$\underline{C}$H of triazole	C_{Py} *meta* to N	C_{benz} *para* to C_q	$C_{benz}H$ *ortho* to $C_{benz}N$	C_{benz} *para* to $C_{benz}N$	$C_{benz}H$ *ortho* to $C_{benz}O$	$\underline{C}_{benz}C\equiv C$ (*benz* = substituted alkoxybenzene)	$CH_2\underline{C}\equiv C$	$TMS\underline{C}\equiv\underline{C}$	$C_{benz}\underline{C}\equiv\underline{C}C_{benz}$ (*benz* = substituted alkoxybenzene)	$CH_2C\equiv\underline{C}$	$C_{benz}\underline{C}\equiv\underline{C}$ *para* to $C_{benz}N$
9 $CDCl_3$	---	---	150.4, [150.07, 150.05*^{2}, 150.01, 149.98]	---	---	131.7**	---	130.1	---	---	---	---	120.4**	118.0**	117.6, 117.2, [116.99, 116.97], 116.5, 116.1	112.2, [112.08, 112.07], 112.0, 111.9, 111.8	99.3, 99.23, 99.16*^{2}, 98.99*^{2}, 98.0*^{2}, 92.1, [88.9, 88.84, 88.82, 88.78], 87.8, 87.7, [87.64, 87.62], 87.5, 87.2, 83.3				
10 CD_2Cl_2	---	---	151.9, 151.3, 151.2*^{3}, 151.1	---	---	133.7**	---	131.3	---	---	---	---	122.1**	118.8**	119.1, 118.3, 118.1*^{2}, 117.3*^{2}	113.8, 113.4, 113.2, 113.12, 113.06, 111.9	100.6, 100.5*^{3}, 100.4, 100.2	---	93.5, [90.11, 90.08, 90.03], 89.8, [89.04, 89.01], [88.96, 88.94, 88.92], 88.7, 84.3 or 82.5		
12 CD_2Cl_2	170.8	158.6	152.6, [152.4, 152.33*^{2}, 152.30], 152.2	---	---	not found	132.1	not found$^{\%}$	---	---	122.9	---	120.7**	119.44**	119.6, 119.37, [119.21, 119.20], [118.46, 118.38]	115.1, 114.5, 114.3, 114.2, 114.1, 113.1	101.7, 101.6*^{3}, 101.5, 101.4	---	91.5, 91.2, [91.12, 91.06], 90.2, [90.13, 90.10], [90.02, 89.99], 89.8		94.5, 89.2 or 85.4
15 CD_2Cl_2	170.9	158.9	153.7, 153.6, [153.41, 153.38], 153.2, 153.1	---	143.7, [143.00*^{3}, 142.96], 142.9	not found	132.1	131.8	---	[125.14*^{3}, 125.09, 125.05], 124.3	123.0	---	120.5**	118.8**	119.2, 119.0, 118.7, 118.5, [118.1, 118.0]	115.5, 114.8*^{2}, [114.74, 114.71], 113.5	---	---	91.9, 91.7, [91.6, 91.5]	---	95.1, 89.4 or 85.4
18 CD_2Cl_2	171.8	---	153.0, 152.7	145.3	---	---	---	---	131.7, 127.3	---	---	121.2	---	---	119.7, 119.2	114.8, 114.4	102.0	100.9, 100.8	---	90.4, 90.3	---
19 CD_2Cl_2	171.8	---	153.4, 152.6	145.4	---	---	---	---	131.7, 127.3	---	---	121.2	---	---	119.9, 118.9	115.2, 113.1	102.0, 101.9	---	---	90.5, 90.4	---
20 CD_2Cl_2	171.8	---	154.3, 152.5	145.5	---	---	---	---	131.8, 127.3	---	---	121.1	---	---	119.7, 118.8	115.9, 112.7	101.9, 101.8	---	---	90.8, 90.6	---
22 CD_2Cl_2	171.8	---	155.0, 153.3	145.5	143.2, 143.0	---	---	---	131.8, 127.3	125.7, 125.5	---	121.0	---	---	119.2, 118.0	116.1, 112.5	---	---	---	---	---

benz = benzene; *Py* = pyridine; *triaz* = triazole; C_q = quarternary C of $C(CH_2)_3$. Signals reported in brackets [ ] overlap. *^{n} means the signal has *n*-fold intensity compared to the other signals in the series. **Broad signal with very low intensity. $^{\%}$ It is assumed that the signal of $C_{benz}H$ *meta* to $C_{benz}N$ is covered by the signal of C_{Py} *para* to N.

Table S5. ^{13}C NMR (125 MHz) data: Signals with a chemical shift below about 90 ppm.

compound, solvent	$C_{benz}C{\equiv}C$ *para* to C_q	$C_{Py}C{\equiv}C$	$C_{benz}C{\equiv}C$ *para* to C_q	$C_{Py}C{\equiv}C$	$C{\equiv}CH$	$C{\equiv}C\text{-}C{\equiv}C$	OCH_2CH_2	$CHCH_2O$	$C_{triaz}CH_2$	CH_2CH_3	C_qCH_2	$C_{Py}CH_2$	OMe	$CH_2C{\equiv}C$	CH_2CO	C_q	$N_{triaz}CH_2$	$CHCH_2O$	$CHMe_2$	CH_2CH_3	$CHMe_2$	$SiMe_3$
9 $CDCl_3$	---	---	---	---	---	---	---	---	---	---	---	---	---	[56.10, 56.05, 56.02]	---	---	---	---	[16.09, 16.08, 16.06]	---	8.6	-2.5
10 CD_2Cl_2	---	---	---	---	84.3 or 82.5, 78.4	---	---	---	---	---	---	---	---	[57.4, 57.3], 57.2	---	---	---	---	[17.22, 17.20, 17.18]	---	[9.96, 9.93, 9.91]	---
12 CD_2Cl_2	---	92.7	---	89.2 or 85.4	---	---	---	---	---	60.38	---	59.5	---	[58.25*^{2}, 58.21*^{2}, 58.15], 58.0	54.7	---	---	---	[18.22*^{2}, 18.20]	14.0	11.00 with shoulder at 10.98	---
15 CD_2Cl_2	---	93.0	---	89.4 or 85.4	---	---	([71.94, 71.89], [70.59, 70.52, 70.50, 70.47], 70.4, 70.3)[a]	[68.94, 68.92*^{4}, 68.88]	64.2, [63.9, 63.8*^{3}], 63.6	60.5	---	59.7	(58.8, [58.63, 58.60])[b]	---	54.8	---	[48.67*^{2}, 48.65*^{2}, 48.61, 48.57]	40.73, [40.65*^{3}, 40.62*^{2}]	---	14.1	---	---
18 CD_2Cl_2	95.2	---	85.7	---	---	---	---	---	---	60.6	59.9	---	---	58.4, 58.3	56.1	49.2	---	---	18.7	14.4	[11.49, 11.47]	0.0
19 CD_2Cl_2	95.3	---	85.6	---	83.0, 79.8	---	---	---	---	60.6	59.9	---	---	58.4, 58.3	56.1	49.1	---	---	18.7	14.4	11.5	---
20 CD_2Cl_2	95.9	---	85.7	---	---	79.5	---	---	---	60.6	59.9	---	---	58.4, 58.3	56.1	49.2	---	---	18.7	14.4	[11.49, 11.47]	---
22 CD_2Cl_2	96.1	---	86.0	---	---	79.9, 79.5	72.2*^{2}, [70.97, 70.95], [70.88*^{2}, 70.86*^{2}], 70.71*^{2}, [70.62, 70.61]	[69.27, 69.25]	63.8, 63.6	60.6	59.9	---	58.9	---	56.1	49.2	[48.934, 48.925]	[41.00, 40.95]	---	14.4	---	---

benz = benzene; *Py* = pyridine; *triaz* = triazole; C_q = quarternary C of $C(CH_2)_3$. Signals reported in brackets [ ] overlap. *^{n} means the signal has *n*-fold intensity compared to the other signals in the series. [a]It could not be determined how many carbon atoms of **15** are represented by an individual signal. In total, the signals belong to 72 carbon atoms. [b]It could not be determined how many carbon atoms of **15** are represented by an individual signal. In total, the signals belong to 12 carbon atoms.

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