Supporting Information

Assembly of linear chains consisting of alternating silica beads and zeolite L crystals by nitroxide exchange reactions

Maike Becker, Luisa De Cola* and Armido Studer*

1.1 Abbreviations

Ac	acetyl	mQ	ultra pure water
APES	3-aminopropyltriethoxysilane	MS	mass spectrometry
APMS	3-aminopropyldimethylmethoxysilane	MTBE	*tert*-butylmethylether
aq.	aqueous	n_e	number of channel entrances
Ar	aryl, aromatic	NEt_3	triethylamine
Boc	*tert*-butyloxycarbonyl	NHS	*N*-hydroxysuccinimide
conc.	concentrated	NMR	nuclear magnetic resonance
d	day(s)	ppm	parts per million
DCE	1,2-dichloroethane	*p*-TosMIC	*para*-tosylmethylisocyanate
dest.	distilled	quant.	quantitative
DMF	*N*,*N*-dimethylformamide	r/min	rounds per minute
DMSO	dimethylsulfoxide	rt	room temperature
Element. Anal.	elemental analysis	s	second(s)
eq	equivalent	sat.	saturated
ESI	MS: electrospray ionisation	Si-NP	silica nanoparticles
Et_2O	diethylether	TEG	tetraethylene glycol
EtOAc	ethylacetate	TEMPO	2,2,6,6-tetramethylpiperidin-*N*-oxyl radical
GC	gas chromatography	T	temperature
GP	general procedure	t	time
h	hour(s)	TBDMSCl	*tert*-butyldimethylsilylchlorid
HRMS	high resolution MS	^{t}Bu	*tert*-butyl
IR	infrared spectroscopy	Tf	triflate
J	NMR: coupling constant	THF	tetrahydrofurane
M	molar, molarity	TLC	thin layer chromatography
min	minute(s)	TMS	tetramethylsilyl
Mp	melting point	TMSCl	trimethylsilylchloride

1.2 Techniques and materials

Reagents were purchased from *ABCR*, *Aldrich*, *Acros Organics, Fluka, Lancaster, Merck* or *TCI* and used as received. Triethylamine was distilled over CaH_2 and stored under argon. **Solvents** that were used for reactions with oxygen and/or moisture sensitive starting materials, intermediates or products were dried by standard procedures, stored under argon and cooling or freshly distilled prior to use: benzene (Na); CH_2Cl_2 (P_2O_{10}); Et_2O (1. KOH, 2. K/Na-alloy); THF (1. KOH, 2. Na, 3. K); 1,2-dichloroethane (CaH_2) and 1,2-dimethoxyethane (CaH_2). DMF (99.8%, *AcroSeal*®, *Extra Dry over Molecular Sieve*), toluene (99.85%, *AcroSeal*®, *Extra Dry over Molecular Sieve*), methanol (99.8%, *AcroSeal*®, *Extra Dry over Molecular Sieve*) and hexanes (97%, *AcroSeal*®, *Extra Dry over Molecular Sieve*) were purchased from *Acros Organics*. The solvents used for oxygen sensitive radical reactions were degassed by three freeze cycles or by bubbling of argon through the reaction mixture for three minutes prior to the reaction. **Reactions** with oxygen and/or moisture sensitive starting materials, intermediates or products were conducted using *Schlenk* technique in glassware that was dried with a heat gun under high vacuum and flooded with argon prior to the reaction. Solvents and liquid reagents were measured with syringes and injected into the reaction tube through a septum plug. The reaction process was observed by TLC if possible. **Thin layer chromatography (TLC)** was conducted with glass plates from *Merck (Silica 60, F254)*. UV-active compounds were detected with an UV-lamp (λ = 254 nm). Additionally, the chromatograms of all compounds were made by dipping of the plates into a dip solution and subsequent warming with a heat gun. *Potassium permanganate-dip solution:* 5 g $NaHCO_3$, 1.5 g $KMnO_4$, 400 mL H_2O. **Flash chromatography (FC)** was conducted on *Silica 60* (grit size 40–63 µm) from *Merck* with an argon pressure of *ca.* 0.4 bar. The solvents used for FC were technical grade and were distilled prior to use. Diethylether was distilled over $FeSO_4$ and KOH, MTBE was distilled over KOH. EtOAc, acetone, dichloromethane, methanol and pentane were distilled without a drying agent. **Ultra pure water** (18.2 mQ) was generated with an *Eliga Maxima*. **Centrifugations** were performed with a microprocess guided centrifuge *Labofuge 200* from *Heraeus*. The maximum RZB value is 3030 g (referring to the radius of the device) and the driving speed can be varied from 1600 r/min to 5300 r/min.

1.3 Analytical methods

Melting points were determined with an *SMP 10* from *Stuart Scientific* and are uncorrected. **IR spectra** were recorded with a *Digilab FTS 4000* equipped with a *Specac MKII Golden Gate Single Reflection ATR System* or with a *Bruker IFS 28*. The absorption bands are specified in wave numbers (cm^{-1}) with following abbreviations for their intensity: *br* = broad signal, *s* = strong, *m* = medium, *w* = weak. **^{1}H-NMR spectra** were recorded in the NMR spectroscopy lab of the Organic Institute of the *Westfälische Wilhelms-Universität* Münster (Münster University) in deuterated solvents with a *Varian 600 "unity plus"* (600 MHz; at 300 K), an *AV 400* (400 MHz; at 300 K) or a *DPX 300* (300 MHz; at 298 K) from *Bruker* with a preset pulse program. The chemical shifts δ in ppm are stated in relation to the resonance signal of the ^{1}H-nuclei of tetramethylsilane (δ = 0.00 ppm). For a calibration of the spectra we correlated the resonance signal of the residual solvent protons with the value reported in the literature[1] (δ_{CHCl3} = 7.26 ppm, δ_{CDHCl2} = 5.32 ppm). The multiplicities of the resonance signals are abbreviated with *s* (singlet), *d* (doublet), *t* (triplet), *q* (quintet), or *m* (multiplet). Broad signals are abbreviated with *br s* (broad signal). Coupling constants *J* are specified in Hz. **^{13}C-NMR spectra** were recorded in the NMR spectroscopy lab of the Organic Institute of the *Westfälische Wilhelms-Universität* Münster (Münster University) in deuterated solvents with a *Varian 600 "unity plus"* (150 MHz; at 300 K), an *AV 400* (100 MHz; at 300 K) or a *DPX 300* (75 MHz; at 298 K) from *Bruker* with a preset pulse program. The chemical shifts δ in ppm are stated in relation to the residual resonance signal of the internal standard tetramethylsilane (δ = 0.00 ppm). For a calibration of the spectra we used the deuterium coupled resonance signal of the particular solvent. 90° DEPT-^{13}C- and 135° DEPT-^{13}C-spectra were recorded, as well as H,H-COSY (GCOSY) or C,H-correlation experiments (GHSQC, GHMBC) were performed as a further tool for the interpretation of the ^{13}C-NMR spectra, if necessary. **Mass spectra** were recorded in the mass spectrometry lab of the Organic Institute of the *Westfälische Wilhelms-Universität* Münster (Münster University) as electrospray ionisation spectra (ESI spectra) with a *Bruker Daltonics MicroTof* (exact mass) or a *Waters-Micromass Quattro LC-Z* (nanospray). The detected signals *m/z* are specified in u. **Elemental analyses** were recorded in the analytical lab of the Organic Institute of the *Westfälische Wilhelms-Universität* Münster (Münster University) with a *Vario EL III*

from *Elementar-Analysensysteme GmbH*, Hanau. **Gas chromatography (GC)** was performed with a *Hewlett Packard 6890* chromatograph with a *Hewlett Packard HP-1* column (25 m×0.32 mm, film thickness 0.25 µm) or a *HP-5* column (30 m×0.32 mm, film thickness 0.25 µm) by using H_2 (*ca.* 1 bar) as a carrier gas. **Fluorescence microscopy** images were recorded with an epi-fluorescence microscope *Olympus Reflected Fluorescence System CKX41*, which was equipped with excitation and emission filters and connected to a *Kappa Opto-Electronics* camera. The images were arranged as they were seen through the microscope. **Zetapotential measurements** were recorded with a *DTS Zetasizer Nano ZS* from *Malvern* or a *Delsa Nano C Particle Analyzer* (*Zetasizer*) from *Beckman Coulter*. The measurements were performed in double distilled water at room temperature in a cell purged with dry methanol prior to the measurements. For interpretation the *Smoluchowski* equation was applied. **X-Ray photoelectron spectra (XPS)** were recorded by *Dr. Andreas Schäfer* and *Dr. Torsten Reuter* (*nanoAnalytics GmbH*) with an *ESCALAB 250* (*Thermo VG Scientific*). For primary radiation monochromatic Al K_α X-rays (15 kV, 150 W) with a ray diameter of *ca.* 500 µm was chosen. A copper standard was used for the calibration of the analyzer´s transmission function. The charge compensation was conducted with a flood gun (e^- energy *ca.* 6 eV/0.05 mA) if necessary. For interpretation of the spectra the energy was set up with the carbon main peak at 285 eV. General spectra were measured with a pass energy of 80 eV and high resolution spectra with 30 eV. To improve the signal to noise ratio a magnetic lense was applied. Quantitative data for the surface composition was calculated according to the *Scofield* factors from the general spectra. The error (statistic and systematic) kann be estimated to be around *ca.* 10%.

1.4 General Procedures (GP)

General procedure for alkoxyamine synthesis (GP1)

According to a literature procedure by *Matyjaszewski*[2], $Cu(OTf)_2$ (1 mol-%) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (4 mol-%) were suspended in benzene under argon in a sealed tube (1.25 mL/mmol nitroxide). Nitroxide (1.21 eq), bromide (1.0 eq) and copper powder (1.05 eq) were dissolved in benzene and added. The reaction mixture was stirred at 55-75 °C for 17 h. Solids were removed by filtration over silica gel and washed several times with CH_2Cl_2. The crude product was purified by FC to give the corresponding alkoxyamine.

General procedure for the *Jones* oxidation of alcohols (GP2)

According to a literature procedure by *Jones*[3], the corresponding alcohol (1.0 eq) was dissolved in acetone and cooled with an ice bath to 0 °C. At this temperature *Jones* reagent (2.6 M, CrO_3 in H_2SO_4/H_2O (1:3.3), 2.0 eq) was slowly added and the reaction mixture was stirred for 1 h at 0 °C. Afterwards, surplus CrO_3 was reduced by the addition of 2-propanol and the reaction mixture was stirred at rt for further 30 min. H_2O was added and the aqueous layer was extracted with CH_2Cl_2 (3×). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by FC.

General procedure for the dye loading of the zeolites by cation exchange (GP3)

The synthetic cylindric zeolite L crystals utilized for this work were either prepared according to a literature procedure[4] or purchased from *Zeochem* (0.2-0.5 µm) or *Süd-Chemie* (1.0-1.5 µm). The crystals had an average length of either 1.0 µm or 3.0 µm and an average diameter of *ca.* 1.0 µm.

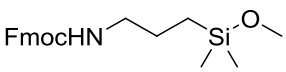
For the dye loading of the zeolite L channels according to a literature procedure by *Calzaferri*[5] the crystals were suspended in a sealed tube in H_2O (mQ, c = 10 mg/mL). A dye stock solution (0.1 mM in H_2O (mQ), pyronine Y (green) or oxazine 1 (red)) was added, the crystals were suspended by ultrasonication (3 min) and the reaction mixture was stirred for 15 h at 100 °C. The suspension was centrifuged (2×15 min, 5300 r/min), the supernatant solvent was removed and the residue was washed with H_2O (mQ) and centrifuged until the supernatant solution was colourless. The dye loaded zeolite L crystals were dried *in vacuo*.

General procedure for the preparation of the active esters for the surface modification (GP4)

For further functionalization the surface amino groups were reacted with the active esters of the corresponding carboxylic acids. For the activation, the carboxylic acid (75 µmol) was added to a solution of EDCI×HCl (50 µmol) and NHS (82.5 µmol) in DMF (2 mL) and the reaction mixture was stirred for 24 h at rt. The active ester was obtained in solution and therefore directly further reacted.

General procedure for the entrance functionalization of zeolite L (GP5)

Fmoc protection of APMS (GP5a)



Fluorenylmethoxycarbonyl-*N*-hydroxysuccinimide (1.5 eq) was dissolved in CH_2Cl_2 (c = 15 mg/mL) in a teflon Erlenmeyer flask and APMS (1.0 eq) was added. The reaction mixture was stirred for 1 h at rt. The protected silane was obtained in solution and therefore directly further reacted.

Entrance functionalization of the zeolite L crystals with amino groups (GP5b)

The zeolite L crystals were suspended in dry hexanes (c = 33 mg/mL) and FmocAPMS (1.0 eq) was added. The reaction mixture was stirred for 24 h at 60 °C in a teflon centrifuge tube. After cooling to rt the crystals were centrifuged (15 min, 5300 r/min), the supernatant solvent was removed and the residue was suspended in DMF (c = 50 mg/mL). Afterwards, piperidine was added in ecxess (c = 125 mg/mL) and the reaction mixture was again stirred for 1 h at rt. Purification was performed by centrifugation (3×10 min, 5300 r/min) and washing with DMF. The crystals were dried *in vacuo*.

Table 1: XPS-analysis of the NH_2-functionalization of zeolite L.

Functionalization	O 1s %	C 1s %	Si 2p %	N 1s %	Al 2p %
unfunctionalized	54.1	8.4	21.0	1.6	6.3
NH_2	31.4	37.5	16.6	10.5	2.1

The success of the functionalization was verified with zetapotential measurements of the zeolite surfaces. The zetapotential of the entrance modified NH_2-zeolite crystals was determined with -46.8 mV in comparison to -60.9 mV of the unmodified surface.

Entrance functionalization of the zeolite L crystals with the active esters (GP5c)

The NH_2-functionalized zeolite L crystals were suspended in DMF (c = 20 mg/mL) by ultrasonication (3 min). A solution of the corresponding active ester in DMF was

added to the reaction mixture and then stirred for 24 h at rt. Purification was performed by centrifugation (15 min, 5300 r/min) and the supernantant solvent was removed. The residue was washed by three purification cycles with Et_2O. The functionalized crystals were dried *in vacuo*.

*Table 2: XPS-analysis of the alkoxyamine conjugates **2**.*

Funktionalization	O 1s %	C 1s %	Si 2p %	N 1s %	Al 2p %
unfunctionalized	54.1	8.4	21.0	1.6	6.3
alkoxyamine zeolites **2**	33.0	37.9	15.2	5.8	3.2

The zetapotential measurements for the entrance functionalization gave values that changed from -60.9 mV for the unfunctionalized crystals to -49.1 mV for the entrance modified alkoxyamine conjugates.

General procedure for the surface functionalization of Si-NP (GP6)

Dye loaded, NH_2-terminated silica particles which were either synthetically prepared by Dr. Sandra Fibikar (0.5-1.0 µm) or commercially available (*micromod*, *sicastar*, 3.0-4.0 µm, loading 3.0-4.0 µmol/g) were suspended in DMF by ultrasonication (3 min). The corresponding active ester was added to the suspension and the reaction mixture was stirred for 17 h at rt. Purification was conducted according to **GP5** by centrifugation (3×15 min, 5300 r/min) and washing with Et_2O. The functionalized particles were dried *in vacuo*.

General procedure for the sample preparation for analysis (GP7)

If the reaction success was verified by fluorescence or confocal microscopy, a sample fraction (*ca.* 0.1 mg zeolite crystals) was suspended in the corresponding solvent (0.2 mL H_2O (mQ) or toluene) by ultrasonication (3 min). A droplet of this suspension was wept with a pipette onto a microscope cover slip and the solvent was vaporized at rt. The sample was analyzed by microscopy.

If the reaction success was verified by zetapotential measurements, the zeolite L crystals (*ca.* 0.1 mg) were suspended in NH_4HCO_2 buffer (pH 7.4) or in H_2O (mQ) and ultrasonicated for 1 min. This suspension was transferred into the measuring cell and the measurement was performed at rt.

General procedure for the self-assembly by nitroxide exchange reactions (GP8)

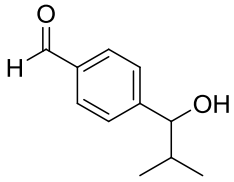
Nitroxide functionalized particles, as well as alkoxyamine functionalized particles were suspended in DCE in a small sealed tube (2 cm lenght, 0.5 cm diameter). A light argon stream was bubbled through the solvent (3 min), the gasous layer was saturated with inert gas and the tube was sealed. The reaction mixture was ultrasonicated (3 min) and the nitroxide exchange reaction was performed between 2 h to 24 h at temperature T (125 °C, 90 °C, 70 °C or at rt). After cooling to rt the reaction mixture was suspended in THF and transferred to a centrifuge tube. The purification was conducted by centrifugation (3×15 min, 5300 r/min). The supernatant solvent was removed and the particles were dried *in vacuo*.

General procedure for the self-assembly through a dinitroxide linker 1 (GP9)

Entrance functionalized alkoxyamine zeolite conjugates **2** (1 µm or 3 µm, dye loaded) were suspended in DCE (c = 1 mg/0.2 mL) by ultrasonication (3 min) in a sealed tube (2 cm length, 0.5 cm diameter). The nitroxide **1** was added to the suspension, a light argon stream was bubbled through the reaction mixture (3 min), the gasous layer was saturated with argon and the tube was sealed. The reaction mixture was ultrasonicated (3 min) and the suspension was stirred for 4 h at temperature T (125 °C, rt). The suspension was dissolved in THF and purified by centrifugation (3×15 min, 5300 r/min). The crystals were dried *in vacuo* and analyzed by fluorescence or confocal microscopy afterwards.

1.5 Syntheses of the alkoxyamines

4-(1-Hydroxy-2-methylpropyl)-benzaldehyde (6)

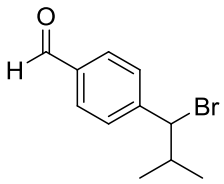


Magnesium turnings (3.04 g, 125 mmol, 1.0 eq) and isopropylchloride (11.4 mL, 125 mmol, 1.0 eq) were suspended in Et_2O (65 mL) and refluxed for 1.5 h. Terephthaldehyde monodiethylacetate (20.0 mL, 100 mmol, 0.8 eq) was dissolved in Et_2O (60 mL) and added dropwise over a period of 30 min to the reaction mixture which was refluxed subsequently for 3 h. After cooling to rt the reaction was stopped by the addition of H_2O (10 mL). HCl (aq. 6 M, 18 mL) was added and the reaction mixture was stirred at rt over night. The aqueous layer was extracted with Et_2O (3×50 mL) and the combined organic layers were washed with Na_2SO_4 (aq. sat., 50 mL), $NaHCO_3$ (aq. sat., 50 mL) and H_2O (50 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification of the crude product was carried out by FC (Pentan/MTBE 15:1) to give aldehyde **6** as a light yellow oil (12.3 g, 69.0 mmol, 55%).

^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.96 (*s*, 1H, CHO), 7.82 (*d*, *J* = 8.1 Hz, 2H, Ar-H), 7.46 (*d*, *J* = 8.1 Hz, 2H, Ar-H), 4.47 (*d*, *J* = 5.9 Hz, 1H, C*H*OH), 2.08 (*s*, 1H, OH), 2.02-1.87 (*m*, 1H, C*H*$(CH_3)_2$), 0.94 (*d*, *J* = 6.7 Hz, 3H, CH_3), 0.83 (*d*, *J* = 6.7 Hz, 3H, CH_3). **MS (ESI$^+$):** 201 ([M+Na]$^+$). **HRMS (ESI)** *m/z* = 201.0886 calculated for $C_{11}H_{14}O_2Na$ [M+Na]$^+$, found: 201.0890.

The analytical data is in agreement with the literature.[6]

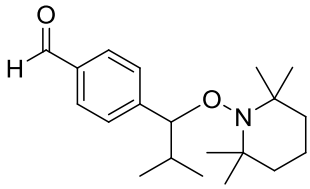
4-(1-Bromo-2-methylpropyl)-benzaldehyde (7)



To a solution of alcohol **6** (2.45 g, 13.8 mmol, 1.0 eq) in CH_2Cl_2 (17 mL) HBr (in acetic acid, 33wt%, 3.08 mL, 17.9 mmol, 1.3 eq) was added dropwise at 0 °C. The reaction mixture was allowed to warm to rt while stirring for 4.5 h. The reaction was stopped by the addition of H_2O (15 mL) and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with H_2O (15 mL), $NaHCO_3$ (aq. sat., 3×20 mL), NaCl (aq. sat., 15 mL), H_2O (15 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo*. Purification of the crude product was carried out by FC (Pentan/MTBE 40:1) to give bromide **7** as a light yellow oil (2.75 g, 11.4 mmol, 83%).

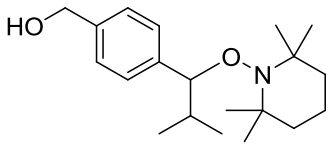
^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.98 (*s*, 1H, CHO), 7.85-7.80 (*m*, 2H, Ar-H), 7.51 (*d*, *J* = 8.2 Hz, 2H, Ar-H), 4.70 (*d*, *J* = 8.4 Hz, 1H, CHBr), 2.39-2.22 (*m*, 1H, C*H*$(CH_3)_2$), 1.17 (*d*, *J* = 6.5 Hz, 3H, CH_3), 0.85 (*d*, *J* = 6.6 Hz, 3H, CH_3).
The analytical data is in agreement with the literature.[6]

4-(2-Methyl-1-(2,2,6,6-tetramethylpiperidine-1-yloxy)-propyl)-benzaldehyde (8)



According to **GP1** with $Cu(OTf)_2$ (40.9 mg, 110 µmol, 0.01 eq), 4,4'-di-*t*-butyl-2,2'-bipyridine in benzene (1 mL) and TEMPO (2.14 g, 13.7 mmol, 1.21 eq) in benzene (1 mL), bromide **7** (2.73 g, 11.3 mmol, 1.0 eq) in benzene (3 mL) and copper powder (750 mg, 11.9 mmol, 1.05 eq) for 17 h at 75 °C. Purification of the crude product was carried out by FC (Pentan/MTBE 60:1) to give alkoxyamine **8** as a colourless oil (2.65 g, 8.36 mmol, 74%).
^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 9.97 (*s*, 1H, CHO), 7.89-7.74 (*m*, 2H, Ar-H), 7.37 (*d*, *J* = 8.1 Hz, 2H, Ar-H), 4.60 (*d*, *J* = 5.3 Hz, 1H, C*H*CH$(CH_3)_2$), 2.69-2.49 (*m*, 1H, C*H*$(CH_3)_2$), 1.65-0.88 (*m*, 18H, 3×CH_2, 2×C$(CH_3)_2$), 0.76 (*dd*, *J* = 6.9, 1.6 Hz, 6H, CH(C*H*$_3)_2$). **MS (ESI$^+$):** 340 ($[M+Na]^+$). **HRMS (ESI)** *m/z* = 340.2247 calculated for $C_{20}H_{31}NO_2Na$ $[M+Na]^+$, found: 340.2249.
The analytical data is in agreement with the literature.[6]

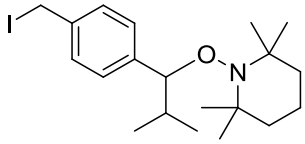
(4-(2-Methyl-1-(2,2,6,6-tetramethylpiperidine-1-yloxy)-propyl)-phenyl)-methanol (9)



To a solution of alkoxyamine **8** (1.00 g, 3.15 mmol, 1.0 eq) in THF (55 mL) $LiAlH_4$ (110 mg, 3.15 mmol, 1.0 eq) was added at 0 °C and the reaction mixture was stirred for 1.5 h at rt. The reaction was stopped by the addition of H_2O (148 µL). After stirring for 5 min at rt, NaOH (aq., 15%, 148 µL) and after stirring for further 5 min H_2O (148 µL) was added. After 20 min the precipitate was filtered off, washed with CH_2Cl_2 (200 mL) and the filtrate was dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by FC (Pentan/MTBE 2:1). Alkoxyamine **9** was isolated as a colourless solid (850 mg, 2.65 mmol, 84%).
^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.33-7.14 (*m*, 4H, Ar-H), 4.66 (*d*, *J* = 5.8 Hz, 2H, C*H*$_2$OH), 4.51 (*d*, *J* = 5.3 Hz, 1H, C*H*CH$(CH_3)_2$), 2.62-2.43 (*m*, 1H, C*H*$(CH_3)_2$), 1.67-1.63 (*m*, 1H, OH), 1.63-0.48 (*m*, 18H, 3×CH_2, 2×C$(CH_3)_2$), 0.77 (*d*, *J* = 6.8 Hz,

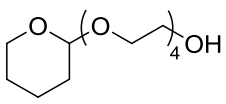
3H, CH(C*H*$_3$)$_2$); 0.74 (*d*, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). **MS (ESI):** 320 ([M+H]$^+$). **HRMS (ESI)** *m/z* = 320.2584 calculated for $C_{20}H_{33}NO_2H$ [M+H]$^+$, found: 320.2582.
The analytical data is in agreement with the literature.[6]

1-(1-(4-Iodomethylphenyl)-2-methylpropoxy)-2,2,6,6-tetramethylpiperidine (10)



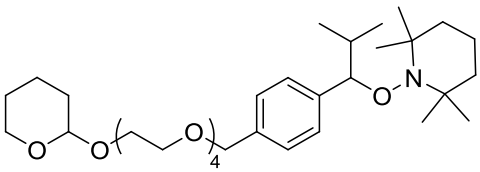
Alkoxyamine **9** (828 mg, 2.59 mmol, 1.0 eq) and sodium iodide (1.16 g, 7.76 mmol, 3.0 eq) were dissolved in acetonitrile (7 mL). TMSCl (843 mg, 7.76 mmol, 3.0 eq) was added dropwise at 0 °C and the reaction mixture was allowed to warm to rt during 5 h. The reaction was stopped by the addition of H_2O (5 mL) and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were washed with Na_2SO_4 (aq. sat., 10 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and iodide **10** was obtained as a yellow oil (1.05 g, 2.45 mmol, 95%) which was used without further purification.
^{1}H-NMR (300 MHz, $CDCl_3$, 298 K): δ = 7.27 (*d*, *J* = 8.1 Hz, 2H, Ar-H), 7.11 (*d*, *J* = 8.1 Hz, 2H, Ar-H), 4.48 (*d*, *J* = 5.5 Hz, 1H, C*H*CH(CH$_3$)$_2$), 4.45 (*s*, 2H, CH_2I), 2.60-2.44 (*m*, 1H, C*H*(CH$_3$)$_2$), 1.74-0.31 (*m*, 18H, 3×CH$_2$, 2×C(CH$_3$)$_2$), 0.77 (*d*, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$), 0.75 (*d*, *J* = 6.8 Hz, 3H, CH(C*H*$_3$)$_2$). **MS (ESI):** 452 ([M+Na]$^+$). **HRMS (ESI)** *m/z* = 452.1421 calculated for $C_{20}H_{32}INONa$ [M+Na]$^+$, found: 452.1443.
The analytical data is in agreement with the literature.[6]

2-(2-(2-(2-(Tetrahydropyrane-2-yloxy)-ethoxy)-ethoxy)-ethoxy)-ethanol (11)



Tetraethylene glycol (8.0 mL, 46 mmol, 5.0 eq) was dissolved in CH_2Cl_2 (50 mL). 3,4-Dihydro-2*H*-pyrane (0.84 mL, 9.2 mmol, 1.0 eq) and *p*-toluene sulfonic acid monohydrate (0.16 g, 0.92 mmol, 0.1 eq) were added and the reaction mixture was stirred for 30 min at rt and hydrolysed by subsequent addition of H_2O. After phase separation the organic layer was washed with H_2O and dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by FC (EtOAc/Aceton 10:1). The protected glycol derivate **11** was obtained as a colourless oil (1.07 g, 3.85 mmol, 42%).
^{1}H-NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.52-4.46 (*m*, 1H, OCHO), 3.76-3.66 (*m*, 2H, OCH$_2$), 3.63-3.30 (*m*, 16H, 4×O(CH$_2$)$_2$O), 3.24 (*br s*, 1H, OH), 1.75-1.26 (*m*, 6H, 3×CH$_2$).
The analytical data is in agreement with the literature.[7]

1-(2-Methyl-(1-ethoxy]-ethoxy))-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (12)

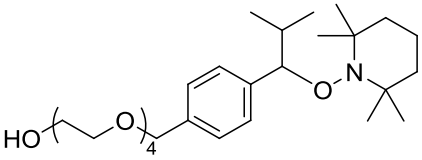


Glycol **11** (418 mg, 1.50 mmol, 4.0 eq) was dissolved in THF (5 mL) and NaH (60% in mineral oil, 58 mg, 1.5 mmol, 4.0 eq) was added portionwise. The suspension was stirred for 20 min at rt and afterwards for further 2 h at 40 °C. 1-[1-(4-iodomethylphenyl)-2-methylpropoxy]-2,2,6,6-tetramethylpiperidine (**10**) (161 mg, 0.375 mmol, 1.0 eq), dissolved in THF (1 mL), was added and the reaction mixture was stirred for further 4.5 h at 40 °C. Afterwards, the reaction mixture was acidified to pH 4 at rt by the addition of HCl (aq. 2 M, 1 mL) and diluted with H_2O. The aqueous layer was extracted with CH_2Cl_2 (3×6 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by FC (Pentan/EtOAc 10:1→ 2:1). Alkoxyamine **12** was obtained as a colourless oil (153 mg, 0.264 mmol, 70%).

IR (neat): 3001*m*, 2932*s*, 2870*s*, 1458*m*, 1375*m*, 1360*m*, 1351*m*, 1258*w*, 1242*w*, 1202*w*, 1124*s*, 1078*m*, 1035*m*, 1020*m*, 988*m* cm^{-1}. **^{1}H-NMR** (300 MHz, $CDCl_3$, 298 K): δ = 7.22 (*d*, *J* = 7.9 Hz, 2H, Ar-H), 7.17 (*d*, *J* = 7.9 Hz, 2H, Ar-H), 4.64-4.58 (*m*, 1H, OCHO), 4.53 (*s*, 2H, CH_2-Ar), 4.50 (*d*, *J* = 5.3 Hz, 1H, C*H*CH$(CH_3)_2$), 3.93-3.77 (*m*, 2H, OC*H*$_2(CH_2)_3$), 3.71-3.55 (*m*, 16H, 4×O$(CH_2)_2$O), 2.60-2.40 (*m*, 1H, C*H*$(CH_3)_2$), 1.86-0.42 (*m*, 30H, 6×CH_2, 2×C$(CH_3)_2$, CH(C*H*$_3)_2$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 298 K): δ = 139.6 (C), 136.3 (C), 128.7 (CH), 126.4 (CH), 98.8 (CH), 90.9 (CH), 73.2 (CH_2), 70.6 (CH_2), 70.4 (CH_2), 69.4 (CH_2), 66.6 (CH_2), 62.1 (CH_2), 59.7 (C), 40.5 (CH_2), 34.7 (CH_3), 33.9 (CH_3), 31.0 (CH), 30.5 (CH_2), 25.4 (CH_2), 20.5 (CH_3), 20.1 (CH_3), 19.4 (CH_2), 17.1 (CH_2), 16.0 (CH_3). **MS (ESI)**: 580 ($[M+H]^+$). **HRMS (ESI)**: *m/z* = 580.4208 calculated for $C_{33}H_{57}NO_7H$ $[M+H]^+$, found: 580.4210. **Element. Anal.** calculated for $C_{33}H_{57}NO_7$: C: 68.36, H: 9.91, N: 2.42; found: C: 68.31, H: 9.89, N: 2.31.

The analytical data is in agreement with the literature.[13]

1-(2-Methyl-1-(4-(2,5,8,11-tetraoxatridecan-13-ol))-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (13)



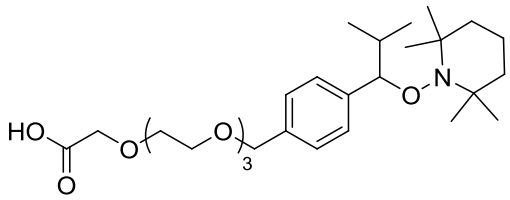
Alkoxyamine **12** (150 mg, 0.260 mmol, 1.0 eq) was dissolved in methanol (7 mL), HCl (aq. 1 M, 0.13 mL)

was added and the reaction mixture was stirred for 20 h at rt. The solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2 (10 mL) and washed with H_2O (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3×15 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude product was purified by FC (Pentan/EtOAc 1:1). Alcohol **13** was isolated as a light yellow oil (78.4 mg, 0.160 mmol, 79%).

IR (neat): 3477*w*, 2963*m*, 2929*m*, 2870*m*, 1462*m*, 1375*m*, 1360*m*, 1351*m*, 1242*m*, 1209*m*, 1098*s*, 1013*m*, 988*m*, 953*m* cm^{-1}. **^{1}H-NMR** (300 MHz, $CDCl_3$, 298 K): δ = 7.22 (*d*, *J* = 8.0 Hz, 2H, Ar-H), 7.15 (*d*, *J* = 8.0 Hz, 2H, Ar-H), 4.53 (*s*, 2H, CH_2-Ar), 4.50 (*d*, *J* = 5.3 Hz, 1H, C*H*CH$(CH_3)_2$), 3.76-3.52 (*m*, 16H, 4×O$(CH_2)_2$O), 2.66 (*br s*, 1H, OH), 2.57-2.44 (*m*, 1H, C*H*$(CH_3)_2$), 1.71-0.33 (*m*, 24H, 3×CH_2, 2×C$(CH_3)_2$, CH(C*H*$_3)_2$). **^{13}C-NMR** (75 MHz, $CDCl_3$, 298 K): δ = 139.6 (C), 136.3 (C), 128.7 (CH), 126.4 (CH), 90.9 (CH), 73.2 (CH_2), 72.4 (CH_2), 70.6 (CH_2), 70.5 (CH_2), 70.3 (CH_2), 69.4 (CH_2), 61.6 (CH_2), 59.7 (C), 40.5 (CH_2), 34.7 (CH_3), 33.8 (CH_3), 31.0 (CH), 20.5 (CH_3), 20.1 (CH_3), 17.1 (CH_2), 16.0 (CH_3). **MS (ESI)**: 496 ($[M+H]^+$). **HRMS (ESI)**: *m/z* = 496.3633 calculated for $C_{28}H_{49}NO_6H$ $[M+H]^+$, found: 496.3627. **Element. Anal.** calculated for $C_{28}H_{49}NO_6$: C: 67.84, H: 9.96, N: 2.83; found: C: 67.47, H: 10.14, N: 2.71.

The analytical data is in agreement with the literature.[13]

1-(2-Methyl-1-(4-(13-(2,5,8,11-tetraoxa)-tridecanic acid))-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (14)



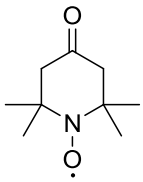
According to **GP2** with alkoxyamine **13** (72.7 mg, 147 µmol, 1.0 eq) in acetone (1.6 mL) and *Jones* reagent (2.6 M CrO_3 in H_2SO_4/H_2O, 0.17 mL, 0.44 mmol, 3.0 eq). Alkoxyamine **14** was obtained as a colourless oil (71.8 mg, 141 µmol, 96%) and directly used without further purification.

IR (neat): 3487*w*, 2931*s*, 2872*s*, 2247*w*, 1736*s*, 1611*m*, 1512*m*, 1463*m*, 1375*m*, 1360*m*, 1242*m*, 1210*m*, 1132*m*, 1013*m*, 988*m*, 952*m* cm^{-1}. **^{1}H-NMR** (300 MHz, $CDCl_3$, 298 K): δ = 9.93 (*br s*, 1H, CO_2H), 7.23 (*d*, *J* = 8.0 Hz, 2H, Ar-H), 7.16 (*d*, *J* = 8.1 Hz, 2H, Ar-H), 4.63 (*d*, *J* = 4.8 Hz, 1H, C*H*CH$(CH_3)_2$), 4.54 (*s*, 2H, CH_2-Ar), 4.12 (*s*, 2H, C(O)CH_2), 3.80-3.53 (*m*, 12H, 3×O$(CH_2)_2$O), 2.60-2.45 (*m*, 1H, C*H*$(CH_3)_2$), 1.71-0.33 (*m*, 24H, 3×CH_2, 2×C$(CH_3)_2$, CH(C*H*$_3)_2$). **^{13}C-NMR** (75 MHz, $CDCl_3$,

298 K): δ = 172.9 (C), 139.3 (C), 136.2 (C), 128.7 (CH), 126.5 (CH), 90.8 (CH), 73.1 (CH_2), 71.1 (CH_2), 70.6 (CH_2), 70.5 (CH_2), 70.4 (2 · CH_2), 69.4 (CH_2), 68.8 (CH_2), 60.5 (C), 40.2 (CH_2), 34.2 (CH_3), 33.5 (CH_3), 31.1 (CH), 20.5 (CH_3), 20.0 (CH_3), 17.0 (CH_2), 15.9 (CH_3). **MS (ESI)**: 508 ($[M-H]^+$). **HRMS (ESI)**: *m/z* = 508.3280 calculated for $C_{27}H_{47}NO_7$ $[M-H]^-$, found: 508.3285. **Element. Anal.** calculated for $C_{28}H_{47}NO_7$: C: 65.98, H: 9.29, N: 2.75; found: C: 65.94, H: 9.18, N: 2.77.

The analytical data is in agreement with the literature.[13]

2,2,6,6-Tetramethylpiperidin-*N*-oxy-4-one (15)

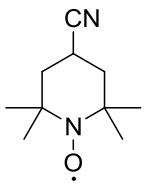


According to a literature procedure by *Couet*[8], 2,2,6,6-tetramethyl-4-piperidone (**16**) (1.00 g, 6.44 mmol, 1.0 eq) was dissolved in methanol (12 mL) and H_2O (8 mL). $Na_2WO_4{\times}2H_2O$ (350 mg, 1.09 mmol, 0.17 eq) and H_2O_2 (4.40 mL, 38.7 mmol, 6.0 eq) were added and the reaction mixture was stirred for 5 d at rt. A catalytic amount of $Na_2WO_4{\times}2H_2O$ was added daily. The reaction completion was verified by TLC. The layers were separated, the aqueous layer was saturated with K_2CO_3 and extracted with Et_2O (3×20 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by FC (Pentan/Et_2O 10:1 → 5:1) and nitroxide **15** was obtained as a red solid (920 mg, 5.43 mmol, 84%).

MS (ESI): 171 ($[M+H]^+$). **HRMS (ESI)** *m/z* = 171.1254 calculated for $C_9H_{16}NO_2H$ $[M+H]^+$, found: 171.1244.

The analytical data is in agreement with the literature.[9]

4-Carbonitrile-2,2,6,6-tetramethyl-4-piperidin-*N*-oxyl radical (16)

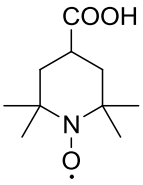


Nitroxide **15** (500 mg, 2.94 mmol, 1.0 eq) was dissolved in DME (40 mL) and tosylmethylisocyanide (603 mg, 3.09 mmol, 1.05 eq) was added. At 0 °C, a solution of *t*-BuOK (660 mg, 5.87 mmol, 2.0 eq) in DME (5 mL) and *t*-butanol (5 mL) was added to the reaction mixture. The reaction mixture was stirred for 45 min at 0 °C and for further 1 h at rt. The reaction was stopped by the addition of H_2O (50 mL) and the solution was extracted with Et_2O (3×25 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. Nitroxide **16** was obtained as a red solid (532 mg, 2.93 mmol, quant.) and used without further purification.

MS (ESI): 204 ([M+Na]$^+$). **HRMS (ESI)**: *m/z* = 204.1233 calculated for $C_{10}H_{17}N_2ONa$ [M+Na]$^+$, found: 204.1233.

The analytical data is in agreement with the literature.[10]

4-Carboxy-2,2,6,6-tetramethyl-4-piperidin-*N*-oxyl radical (17)

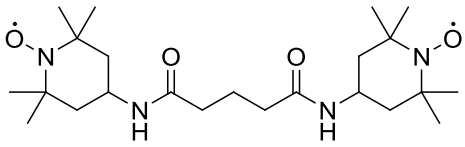


Nitroxide **16** (532 mg, 2.93 mmol, 1.0 eq) was dissolved in methanol (7.75 mL) and a solution of $Ba(OH)_2{\times}8H_2O$ (3.28 g, 10.4 mmol, 3.5 eq) and NaOH (174 mg, 4.35 mmol, 1.5 eq) in H_2O (27 mL) was added. The reaction mixture was refluxed for 24 h. After cooling to rt, the mixture was extracted with $CHCl_3$ (3×30 mL). The aqueous layer was acidified with HCl (aq. 10%) to pH 2 and extracted with $CHCl_3$ (3×30 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed *in vacuo*. Nitroxide **17** was isolated as a red solid (511 mg, 2.55 mmol, 87%) and used without further purification.

IR (neat): 3477*w*, 2978*m*, 2937*m*, 1720*s*, 1467*m*, 1446*m*, 1406*m*, 1365*m*, 1316*m*, 1223*s*, 1125*m* cm^{-1}. **MS (ESI)**: 223 ([M+Na]$^+$). **HRMS (ESI)**: *m/z* = 223.1179 calculated for $C_{10}H_{18}NO_3Na$ [M+Na]$^+$, found: 223.1138.

The analytical data is in agreement with the literature.[10]

N^1,N^5-Bis-(2,2,6,6-tetramethylpiperidin-*N*-oxyl)-glutaramide radical (1)

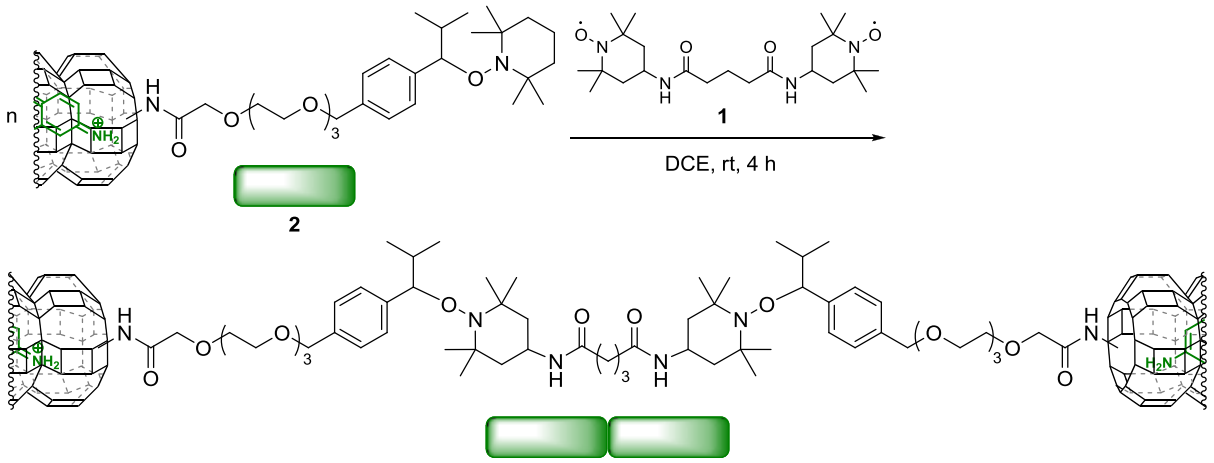


According to **GP3** with 4-amino-TEMPO (**18**)[12] (500 mg, 2.92 mmol, 2.0 eq), glutaric acid (**19**) (193 mg, 1.46 mmol, 1.0 eq) in CH_2Cl_2 (15 mL) and EDCI×HCl (544 mg, 3.50 mmol, 2.4 eq), HOBt (473 mg, 3.50 mmol, 2.4 eq) as well as NMM (295 mg, 2.92 mmol, 2.0 eq) for 72 h at rt. The crude product was purified by FC (CH_2Cl_2/Methanol 20:1) to give dinitroxide **1** as a red solid (386 mg, 0.886 mmol, 61%).

MS (ESI): 461 ([M+Na]$^+$). **HRMS (ESI)** *m/z* = 461.3098 calculated for $C_{23}H_{42}N_4O_4Na$ [M+Na]$^+$, found: 461.3100.

The analytical data is in agreement with the literature.[11]

Self-assembly by nitroxide exchange reaction with dinitroxide 1



Self-assemly by nitroxide exchange reaction with dinitroxide 1 at rt

According to **GP9** alkoxyamine zeolite conjugates **2** (1 µm, 1.0 mg, pyronine loaded) were suspended in DCE (0.2 mL) for 3 min by ultrasonication. After addition of diradical **1** (2.0 mg, 4.6 mmol, large excess) the suspension was stirred for 4 h at rt. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

Self-assembly by nitroxide exchange reaction with dinitroxide 1 at rt

According to **GP9** alkoxyamine zeolite conjugates **2** (1 µm, 1.0 mg, 0.52 nmol, 1.0 eq, pyronine loaded) were suspended in DCE (0.2 mL) for 3 min by ultrasonication. After addition of diradical **1** (1.0 µL of a 2.28 mM solution in DCE, 2.28 nmol, 4.4 eq) the suspension was stirred for 4 h at rt. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

Self-assembly by nitroxide exchange reaction with dinitroxide 1 at 125 °C

According to **GP9** alkoxyamine zeolite conjugates **2** (1 µm, 1.0 mg, 0.52 nmol, 1.0 eq, pyronine loaded) were suspended in DCE (0.2 mL) for 3 min by ultrasonication. After addition of diradical **1** (1.0 µL of a 2.28 mM solution in DCE, 2.28 nmol, 4.4 eq) the suspension was stirred for 4 h at 125 °C. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

Self-assembly by nitroxide exchange reaction with dinitroxide 1 at rt

According to **GP9** alkoxyamine zeolite conjugates **2** (3 µm, 1.0 mg, 0.17 nmol, 1.0 eq, oxonine loaded) were suspended in DCE (0.2 mL) for 3 min by ultrasonication. After addition of diradical **1** (1.0 µL of a 2.28 mM solution in DCE, 2.28 nmol, 13.4 eq) the suspension was stirred for 4 h at rt. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

Self-assembly by nitroxide exchange reaction with dinitroxide 1 at 125 °C

According to **GP9** alkoxyamine zeolite conjugates **2** (3 µm, 1.0 mg, 0.17 nmol, 1.0 eq, oxonine loaded) were suspended in DCE (0.2 mL) for 3 min by ultrasonication. After addition of diradical **1** (1.0 µL of a 2.28 mM solution in DCE, 2.28 nmol, 13.4 eq) the suspension was stirred for 4 h at 125 °C. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

Self-assembly by nitroxide exchange reaction with dinitroxide 1 at rt

According to **GP9** alkoxyamine zeolite conjugates **2** (1 µm, 3.0 mg, 1.56 nmol, 1.0 eq, pyronine loaded) were suspended in DCE (0.56 mL) for 3 min by ultrasonication. After addition of diradical **1** (1.0 µL of a 78.2 mM solution in DCE, 0.78 nmol, 0.5 eq) the suspension was stirred for 4 h at rt. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

Self-assembly by nitroxide exchange reaction with dinitroxide 1 at 125 °C

According to **GP9** alkoxyamine zeolite conjugates **2** (1 µm, 3.0 mg, 1.56 nmol, 1.0 eq, pyronine loaded) were suspended in DCE (0.56 mL) for 3 min by ultrasonication. After addition of diradical **1** (1.0 µL of a 78.2 mM solution in DCE, 0.78 nmol, 0.5 eq) the suspension was stirred for 4 h at 125 °C. The reaction success was qualitatively verified by fluorescence microscopy after ultrasonication (15 s).

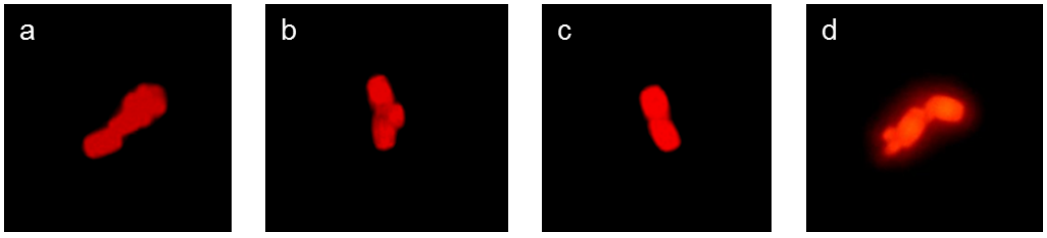
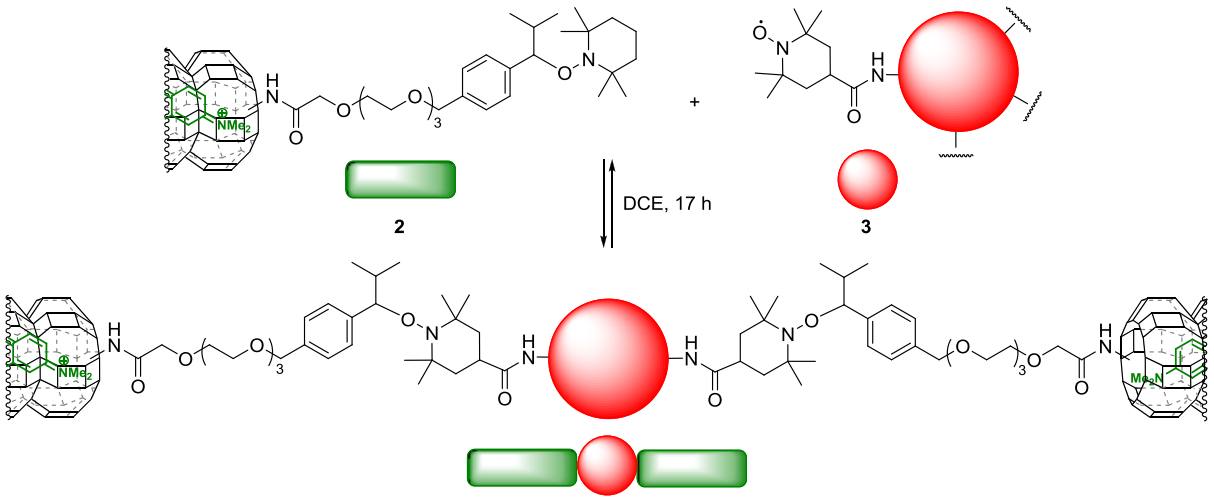


*Fig. 1: Fluorescence microscopy images after the linear assembly of zeolite L crystals (3 µm) with dinitroxide **1** (5.0 eq). a, b) self-assembly at rt and c, d) self-assembly at 125 °C.*

Self-assembly of Si-zeolite hybridmaterials by nitroxide exchange reactions

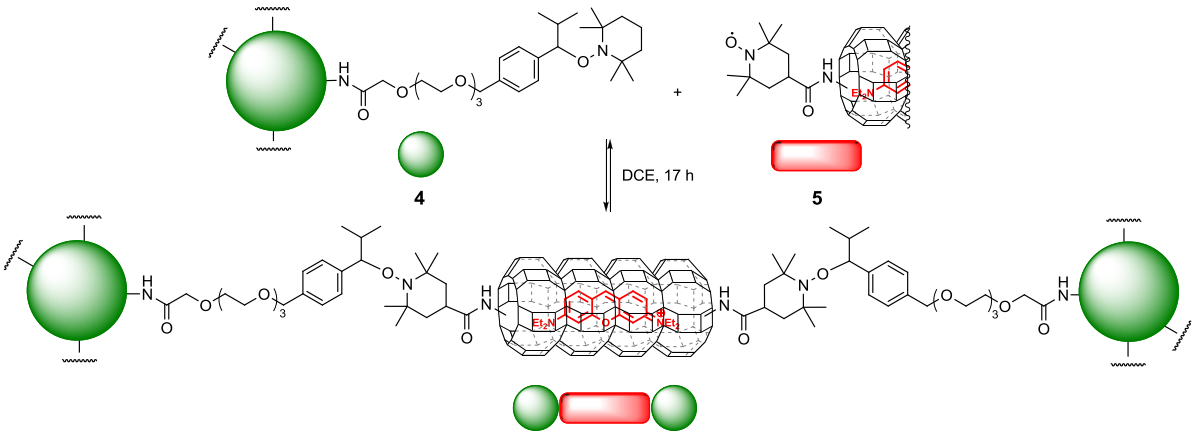


Nitroxide exchange at 100 °C

Green entrance functionalized alkoxyamine zeolite conjugates **2** (1 µm, 1.2 mg, pyronine loaded) and red nitroxide functionalized silica particles **3** (0.5-1.0 µm, 1.2 mg) were suspended in DCE (0.2 mL). A light argon stream was bubbled through the suspension (3 min), the gaseous layer was saturated with argon and the tube was sealed. The particles were suspended in the solvent by ultrasonication (3 min) and the suspension was stirred for 17 h at 100 °C. Purification was conducted by centrifugation (3×15 min, 5300 r/min) and the reaction success was qualitatively verified according to **GP7** by fluorescence microscopy.

Nitroxide exchange at rt

Green entrance functionalized alkoxyamine zeolite conjugates **2** (1 µm, 1.2 mg, pyronine loaded) and red nitroxide functionalized silica particles **3** (0.5-1.0 µm, 1.2 mg) were suspended in DCE (0.2 mL). A light argon stream was bubbled through the suspension (3 min), the gaseous layer was saturated with argon and the tube was sealed. The particles were suspended in the solvent by ultrasonication (3 min) and the suspension was stirred for 17 h at rt. Purification was conducted by centrifugation (3×15 min, 5300 r/min) and the reaction success was qualitatively verified according to **GP7** by fluorescence microscopy.



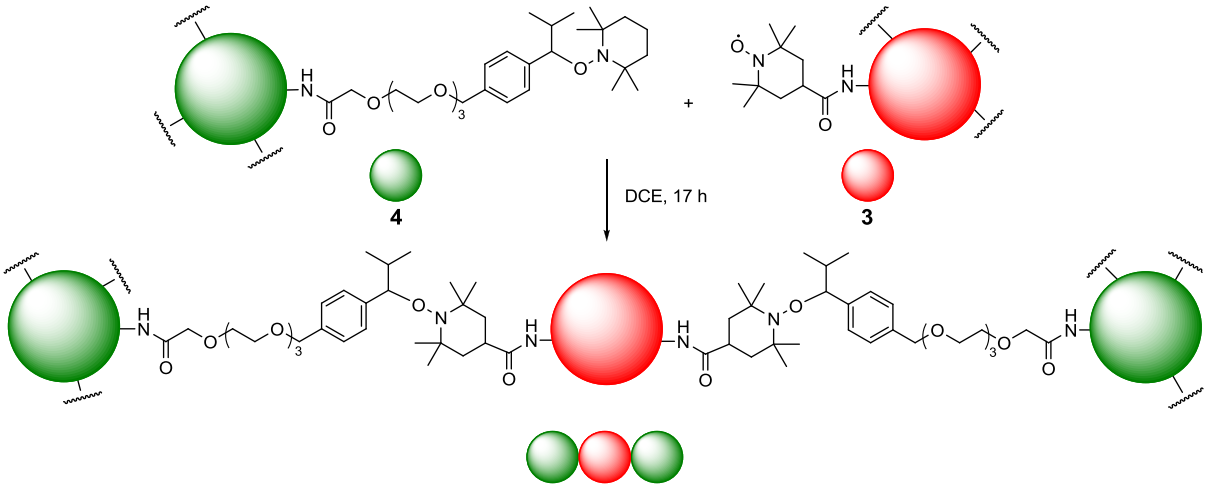
Nitroxide exchange at 100 °C

Green alkoxyamine functionalized silica particles **4** (0.5-1.0 µm, 1.2 mg) and red entrance functionalized nitroxide zeolite conjugates **5** (1 µm, 1.2 mg, oxonine loaded) were suspended in DCE (0.2 mL). A light argon stream was bubbled through the suspension (3 min), the gaseous layer was saturated with argon and the tube was sealed. The particles were suspended in the solvent by ultrasonication (3 min) and the suspension was stirred for 17 h at 100 °C. Purification was conducted by centrifugation (3×15 min, 5300 r/min) and the reaction success was qualitatively verified according to **GP7** by fluorescence microscopy.

Nitroxide exchange at rt

Green alkoxyamine functionalized silica particles **4** (0.5-1.0 µm, 1.1 mg) and red entrance functionalized nitroxide zeolite conjugates **5** (1 µm, 1.1 mg, oxonine loaded) were suspended in DCE (0.2 mL). A light argon stream was bubbled through the suspension (3 min), the gaseous layer was saturated with argon and the tube was sealed. The particles were suspended in the solvent by ultrasonication (3 min) and the suspension was stirred for 17 h at rt. Purification was conducted by centrifugation (3×15 min, 5300 r/min) and the reaction success was qualitatively verified according to **GP7** by fluorescence microscopy.

Self-assembly of silica particles by nitroxide exchange reactions



According to **GP5c**, commercially available NH_2-functionalized red or green dye loaded silica beads *(micromod*, *sicastar*) were either modified with nitroxide **17** or with alkoxyamine **14**. For the self-assembly by nitroxide exchange reactions, spherical all over modified silica particles **4** (*sicastar@red*, 3 µm, 2.0 mg) and silica particles **3** (*sicastar@green*, 4 µm, 2.0 mg) were suspended in DCE (0.2 mL) according to **GP9**. A light argon stream was bubbled through the suspension (3 min), the gaseous layer was saturated with argon and the tube was sealed. The particles were suspended in the solvent by ultrasonication (3 min) and the suspension was stirred for 17 h at rt. Purification was conducted by centrifugation (3×15 min, 5300 r/min) and the reaction success was qualitatively verified according to **GP7** by fluorescence microscopy.

Literature

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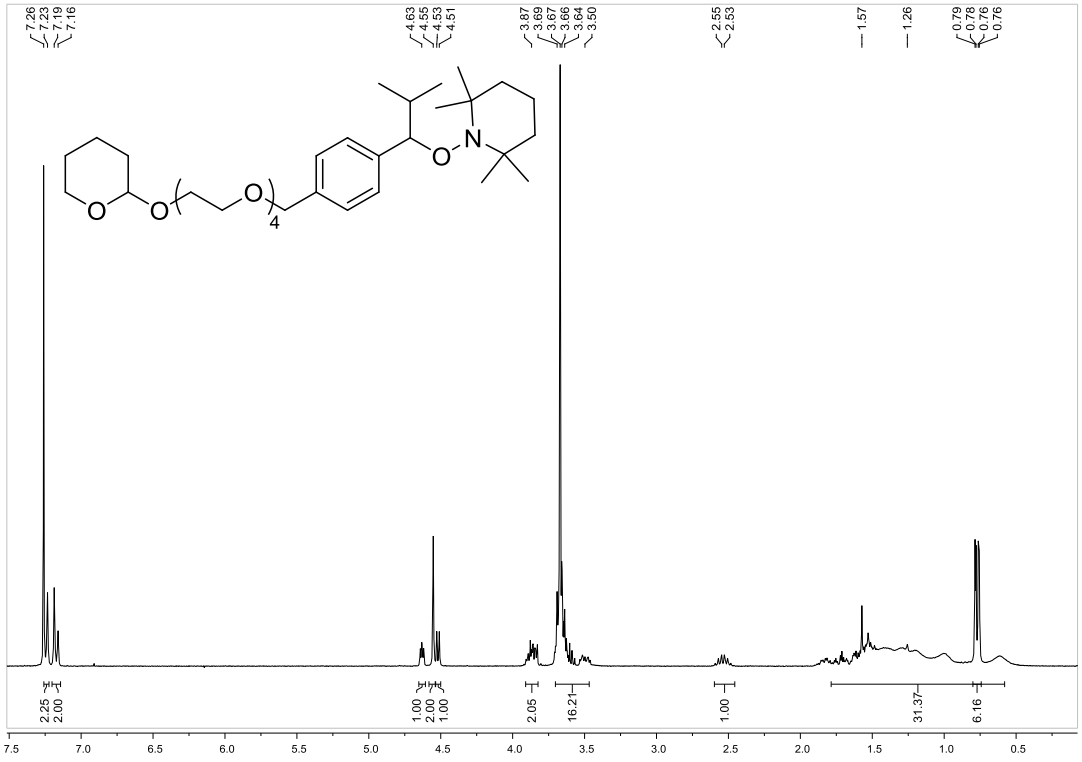
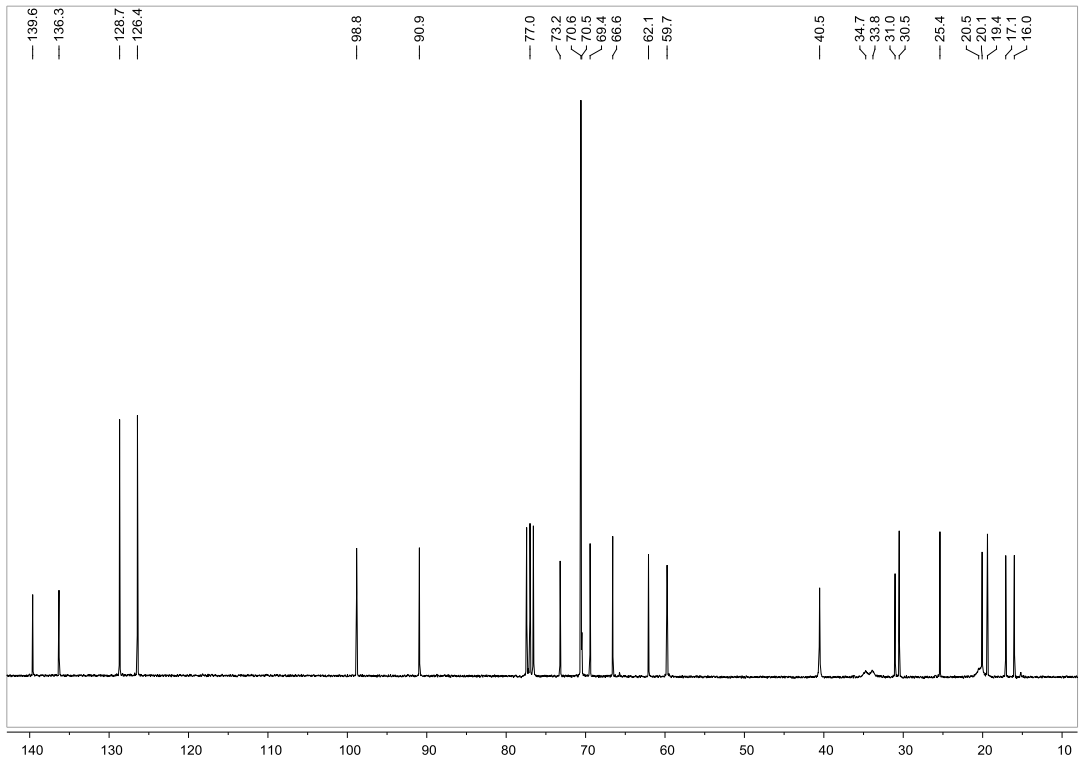
Appendix

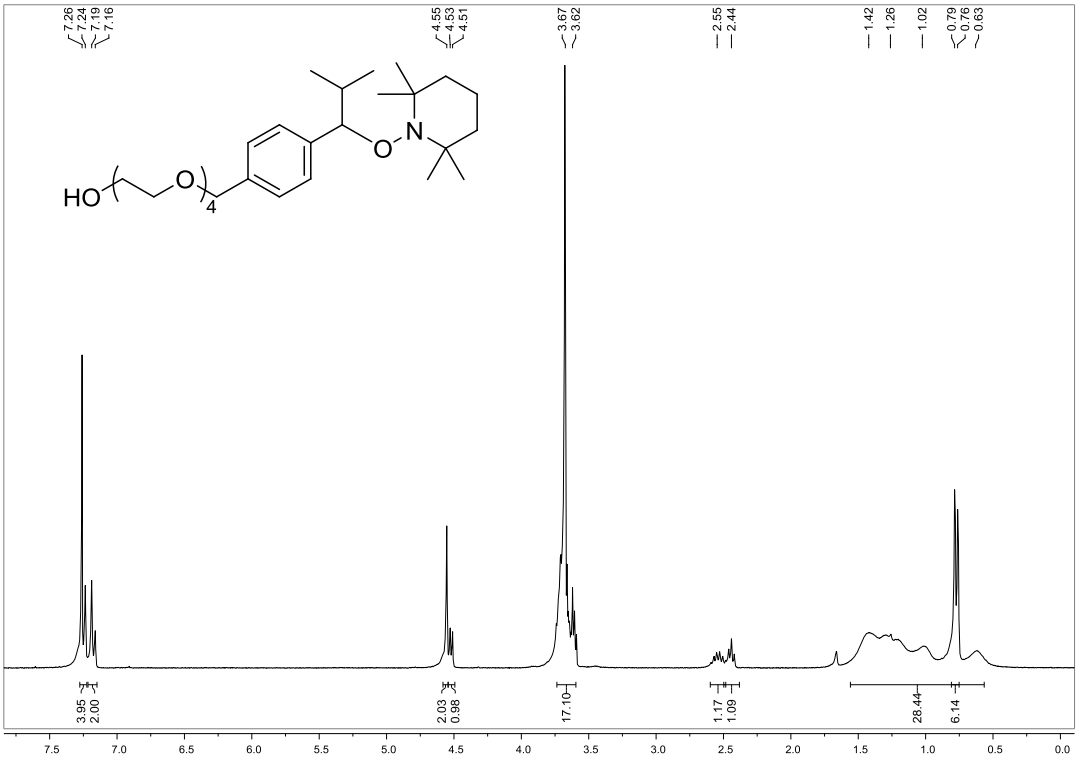
^{1}H- und ^{13}C-NMR spectra of new compounds

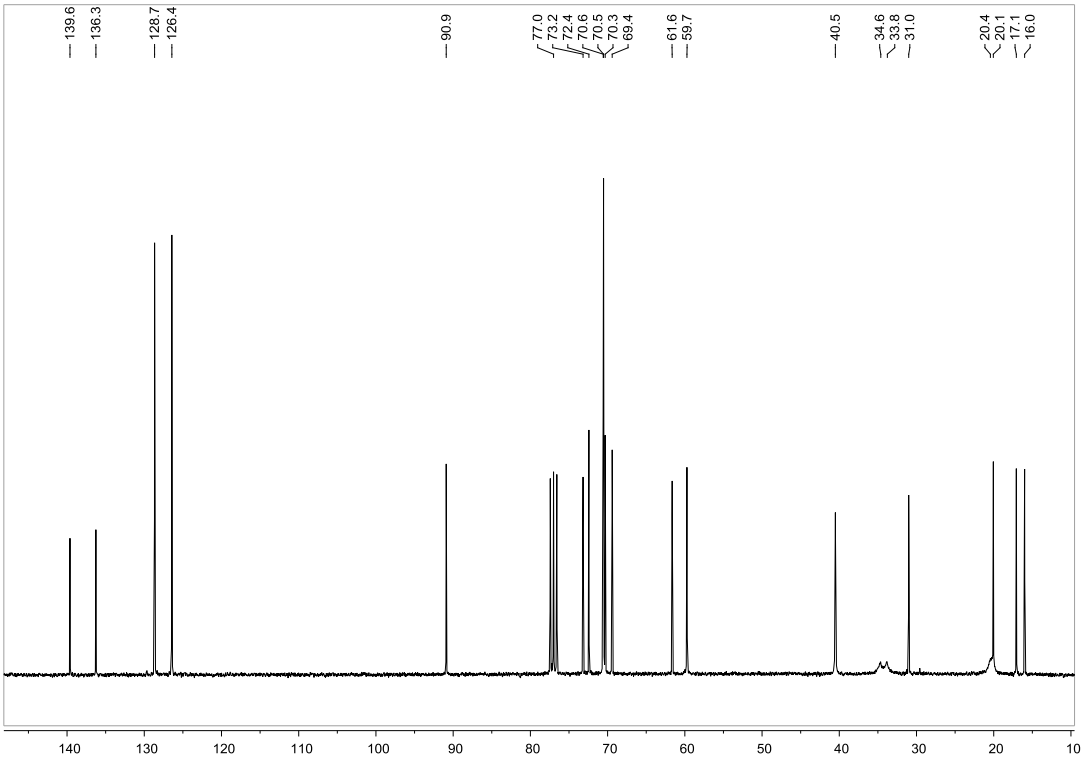
1-(2-Methyl-(1-ethoxy]-ethoxy))-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (**12**)





1-(2-Methyl-1-(4-(2,5,8,11-tetraoxatridecan-13-ol))-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (**13**)





1-(2-Methyl-1-(4-(13-(2,5,8,11-tetraoxa)-tridecanic acid))-phenylpropoxy)-2,2,6,6-tetramethylpiperidine (**14**)