How a Simple "Clicked" PEGylated 1,2,3-Triazole Ligand Stabilizes Gold Nanoparticles for Multiple Usages

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Materials and Methods General data.

All solvents and chemicals were used as received. 5-(Bromomethyl) -1,2,3-tris(prop-2-yn-1-yloxy)benzene, azidomethylferrocene and ethynyl-mPEG were synthesized as referenced.¹⁻³ NMR spectra were recorded at 25°C with a Bruker 300 (300 MHz) spectrometer. All the chemical shifts are reported in parts per million (δ , ppm) with reference to Me₄Si for the ¹H and ¹³C NMR spectra. The DLS measurements were made using a Malvern Zetasizer 3000 HSA instrument at 25°C at an angle of 90°. The infrared (IR) spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. UV-vis. absorption spectra were measured with Perkin-Elmer Lambda 19 UV-vis. spectrometer. Elemental analyses were recorded on a PAR 273 potentiostat under nitrogen atmosphere. Raman spectra were acquired from a Thermo Scientific DXR Raman microscope with a 532 nm wavelength excitation laser.

Synthesis of the 1,2,3-triazole-mPEG ligand

Trimethylsilyl azide (0.2 mL, 1.5 mmol) was added to a DMF and MeOH solution (3 mL, 9:1) of CuI (5.8 mg, 0.03 mmol) and ethynyl-mPEG³ (1000 mg, 1 mmol) under N₂. The reaction mixture was stirred at 90 °C overnight. After consumption of ethynyl-mPEG, the mixture was cooled to room temperature and filtered. The solvent of the filtrate was evaporated under vacuum. Then, the residue was dissolved in CH₂Cl₂, and washed three times with water. The organic phase was dried over anhydrous sodium sulfate. (yield 49%). ¹H NMR (CDCl₃, 200 MHz) 7.67 (1H, *H* in triazole ring), 4.66 (2H, *CH*₂-triazole), 3.58 (164H, -*CH*₂*CH*₂O-), 3.32 (3H, -O*CH*₃); ¹³C NMR (CDCl₃, 200 MHz) δ = 140.64, 127.97, 71.88, 58.97 ppm. MS (MALDI-TOF): calcd. for M: 1941.5, found 1942.1.

Synthesis of the 1,2,3-triazole-mPEG-capped AuNPs, 1

An aqueous solution (10 mL) of hydrogen tetra(chloro)aurate (0.025 mmol) and tiazole-mPEG ligands (0.05 mmol) solution was stirred for 10 min. Then, after 5 min, a freshly-prepared 1-mL solution of sodium borohydride (0.1 mmol) was added dropwise under vigorous stirring. After the solution became purple, dialysis was carried out for 24 h to remove the excess ligands and salts. UV-vis.: plasmon band at 535 nm. DLS: 12.6 ± 3 nm.

Thermal stability of triazole-mPEG stabilized AuNPs

5 mL aqueous solution (2.5 mM) of triazole-mPEG stabilized AuNPs in a tube was immerged and kept 20 min in turn in the oil baths with different temperatures: 25°C, 35°C, 45°C, 60°C, 80°C, 100°C and 120°C according to priority, then the tube was cooled down to room temperature. The solution was monitored by UV-vis., and the plasmon band was found unchanged.

4-Nitrophenol reduction by triazole-mPEG-capped AuNPs, 1

An aqueous solution (2.5 mL) containing 0.37 µmol 4-nitrophenol and 0.03 mmol

NaBH₄ was prepared in a 3 mL standard quartz cuvette (path length: 1 cm). Various amounts (0.5%, 1%, 2%, 5% and 10%) of AuNP catalysts were added into this solution, and the reaction times were detected by UV-vis. spectroscopy.

Selective Hg²⁺ detection by triazole-mPEG-capped AuNPs, 1

Metal salts including Mg^{2+} , Ca^{2+} , Ag^{2+} , K^+ , Fe^{3+} , Cu^{2+} , Na^+ , and Hg^{2+} (see Figure 3) were added to the Au colloid (0.4 mM, 2 mL), respectively. In each case, the concentration of metal salt was 0.05 mM. All the UV-vis. detection experiments were conducted in a standard quartz cuvette (path length: 1 cm).

Ligand-substitution reaction of the triazole ligands by thiol-mPEG (PEG₅₅₀)

A 5mL methanol solution of thiol-mPEG (60 mg, 0.1 mmol) was added into 5 mL of a solution (2.5 mM) of 1, and the mixture was stirred for 30 min. Then 20 mL of dichloromethane was added into this mixture, and the organic phase was separated and dried over Na_2SO_4 . After evaporation of the solvent under vacuum, the product was precipitated with dichloromethane/methanol.

Ligand-substitution reaction of the triazole ligands by thiol-mPEG (PEG₅₅₀) and 11-mercaptoundencanoic acid

A 5-mL methanol solution with thiol-mPEG (60 mg 0.1 mmol) and 11-mercaptoundencanoic acid (22 mg 0.1 mmol) was added into 5 mL of a solution (2.5 mM) of triazole-mPEG stabilized AuNPs 1, and stirred for 30 min. Then 20 mL dichloromethane was added into this mixture, and the organic phase was separated and dried over Na_2SO_4 . After evaporating the solvent, the product was precipitated with dichloromethane/methanol.

¹H NMR (CDCl₃, 300MHz): 3.68 (160H, $-OCH_2CH_2O$), 3.42 (3H, $-OCH_2CH_3$), 2.35 (2H, $-CH_2$ -COOH), 1.65, 1.38 (18H, $-CH_2$ -); UV-vis.: plasmon band at 535 nm. DLS: 16.3 ± 3 nm; TEM: 6.2 ± 0.5 nm.

Synthesis of the thiolate-nonaferrocenyl dendron 3.

Methyl 3,4,5-Tris[3',4',5'- tris(prop-2-yn-1-yloxy)benzyloxy]benzoate (dendron 5): A mixture of methyl 3,4,5-trihydroxy benzoate (1.2 mmol, 221 mg) and K₂CO₃(18 mmol, 3.48 g) was stirred for 10 min in degassed acetone, then a solution of 5-(bromomethyl)-1,2,3-tris(prop-2-yn-1-yloxy)benzene¹ (3.6mmol, 1.195g) in acetone was added, and the mixture was heated to reflux for 16h. After quenching with water, the product was extracted with CH₂Cl₂, and the organic solution was dried over anhydrous Na₂SO₄ and filtered. The solvent was removed by rotary evaporation. The dendron **5** was obtained as a brown oil (1.0 g, 89%). ¹H NMR (acetone-d6, 300 MHz) $\delta = 7.46(2H, H_{Ar}), 7.03$ (4H, H_{Ar}), 6.97 (2H, H_{Ar}), 5.20 (6H, ArO-CH₂-Ar), 4.79-4.67 (18H, O-CH₂-C≡CH), 3.87 (3H, CH₃O-), 3.02-2.95 ppm (9H, CH≡C-); ¹³C NMR (acetone-d6, 300 MHz) $\delta = 165.9(CH_3-CO), 152.4, 151.8, 151.6$ (*m*-C_{Ar}-O-), 142.3, 136.7 (*p*-C_{Ar}-O-), 134.1, 133.1(Ar-OCH₂-C_{Ar}), 125.5 (C_{Ar}-C=O), 109.2, 107.8 (CH in Ar) 79.4, 78.8 (Ar-O-CH₂-Ar), 76.5,75.7, 74.3 (-C≡CH), 70.8 (CH≡C-), 59.7, 56.6 (-OCH₂-C≡CH), 51.7 (O-CH₃). MS (ESI, *M* + Na⁺): calcd. for M: 963.26 m/z, found: 963.3 m/z.

3,4,5-Tris[**3**',**4**',**5**'-**tris**(**prop-2-yn-1-yloxy**)**benzyloxy**]**benzyl alcohol** (dendron 6): LiAlH₄ (3.188 mmol, 121 mg) was added to dry THF, and the suspension was cooled to 0°C; a solution of methyl 3,4,5-tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy] benzoate (1 g, 1.062 mmol) in dry THF was then added dropwise. The mixture was stirred at 0°C for 1 h and at r.t. for 5 h. When the reaction completed, excess LiAlH₄ was quenched with 10 mL water, the mixture was filtered and the solution was evaporated to remove THF, then the residue was dissolved in CH₂Cl₂ and washed with water. After drying over anhydrous Na₂SO₄ and filtering to remove the solvent under vacuum, the dendron **6** was obtained as a deep-red oil (678 mg, 70%). ¹H NMR (acetone-d6, 300 MHz) $\delta = 6.99$ (6H, H_{Ar}), 6.85 (2H, H_{Ar}), 5.12 (6H, ArO-CH₂-Ar), 4.77-4.67 (18H, O-CH₂-C=CH), 4.58 (2H, Ar-CH₂-OH), 3.00 -2.95 ppm (9 H, HC=C-); ¹³C NMR (acetone-d6, 300 MHz) $\delta = 152.64$, 151.79, 151.57 (*m*-C_{Ar}-O-), 138.4, 136.52 (*p*-C_{Ar}-O-), 133.6 (Ar-OCH₂-C_{Ar}), 107.5, 106.3 (CH in Ar), 79.5, 78.8 (Ar-O-CH₂-Ar), 76.6, 75.9 (-C=CH), 70.7, 69.4 (CH=C-), 63.9 (-CH₂-OH), 59.7, 56.7(-OCH₂-C=CH). MS (ESI, *M* + Na⁺): calcd. for M: 935.26 m/z, found: 935.3 m/z.

3.4.5-Tris[3',4',5'-tris(prop-2-vn-1-vloxy)benzvloxy|benzvlthioacetate (dendron 7): 1) Triethylamine (166 mg, 1.64 mmol) was added to a solution of dendron 5 (500 mg, 0.547 mmol) in 20 mL CH₂Cl₂, the solution was stirred at r.t. for 15 min, and methane sulfonyl chloride (75.6 mg, 0.657 mmol) was added dropwise; then, the solution was further stirred at r. t. overnight. After completion of the reaction, the organic solution was washed first with a saturated NaHCO₃ aqueous solution, and again with water. After drying over Na₂SO₄ and removing the solvent under vacuum, a light brown solid (504 mg, 93%) was obtained, and the next step was conducted in situ as follows. A mixture of the light brown solid (504 mg, 0.509 mmol) and potassium thioacetate (69.6 mg, 0.61 mmol) was refluxed in dry THF for 6 h under N₂, then quenched with water, and the product was extracted with CH₂Cl₂ and washed with water (3 \times 40 ml). After drying over anhydrous Na₂SO₄ and removing the solvent under vacuum, the dendron 6 was obtained as a brown gel (430 mg, 87%). ¹H NMR (acetone-d6, 300 MHz) $\delta = 6.8$ (6H, H_{Ar}), 6.80 (2H, H_{Ar}), 5.11 (6H, ArO-CH₂-Ar), 4.79-4.67 (18H, O-CH₂-C=CH), 4.08 (2H, Ar-CH₂-thioacetate), 3.01-2.95ppm (9H, *H*C=C-), 2.35 (3H, C*H*₃-C=O); ¹³C NMR (acetone-d6, 200 MHz) δ = 194.50 (-*C*=O), 152.63, 151.84, 151.58 (*m*-C_{Ar}-O-), 137.40, 136.65 (*p*-C_{Ar}-O-), 134.60, 133.95, 133.53 (-CH₂-C_{Ar}) 108.74, 107.64 (CH in Ar), 79.51, 78.82 (Ar-O-CH₂-Ar), 76.54, 75.83, 74.35 (-C=CH), 70.89, 70.74 (CH=C-), 59.72, 56.71 (-OCH₂-C=CH), 38.20 $(S-CH_2-Ar)$, 33.17 (CH₃-CO-S). MS (ESI, $M + Na^+$): calcd. for M: 933.2 m/z, found: 933.2 m/z.

"Click" CuAAC synthesis of thioacetate nonaferrocenyl dendron (dendron 8): 3,4,5-Tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl thioacetate (dendron 7) (200 mg, 0.206 mmol) and azidomethylferrocene² (500 mg, 2.06mmol) were dissolved

in THF(10 mL), copper(II) sulfate pentahydrate (515 mg, 2.06 mmol) dissolved in 5 mL water was then added, and the mixture was degassed and refilled with N₂. A freshly prepared sodium ascorbate (815 mg, 4.12 mmol) aqueous solution (5 mL) was then added dropwise into the mixture. The resulting mixture was stirred overnight at room temperature under a nitrogen atmosphere. It was then concentrated by rotary evaporation, and the residue was dissolved in CH₂Cl₂ and stirred with aqueous ammonia solution (3×15 mL). The organic layer was washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The residue was purified by reprecipitation from a minimum amount of CH₂Cl₂ into a large volume of pentane, resulting in a dark brown gel (530 mg, 82%). ¹H NMR (CDCl₃, 300 MHz) $\delta = 7.67, 7.61$ (9H, CH in triazole), 6.70 (6H, H_{Ar}), 6.59 (2H, H_{Ar}), 5.18-5.16 (24H, Ar-O-CH₂-), 4.92 (18H,- CH₂-Cp), 4..24-4.10 (81H, H in Cp; 2H, S-CH₂-Ar), 2.32 (3H, CH₃-CO-). ¹³C NMR (CDCl₃, 400 MHz) δ = 195.1 (-C=O), 152.68, 152.26 (m-CAr-O-), 152.0 (-CH₂-C_{triazole}), 144.4, 143.4, 143.2 (p-CAr-O-), 132.9 (CH₂-C_{Ar}), 123.5, 123.2 (CH in triazole), 106.8 (CH in Ar), 81.68, 81.3 (Ar-OCH₂-Ar), 71.19, 68.93, 66.50, 62.86 (CH₂ in Cp), 53.54 (O-CH₂-triazole), 49.98 (triazole-CH₂-Fc), 38.57 (S-CH₂-Ar), 33.78 (CH₃-CO-S). MS (MALDI, $M + Na^+$): calcd. For M: 3163.5 m/z, found: 3163.3 m/z.

Synthesis of the thiolate-nonaferrocenyl dendron, 3: The nona-ferrocene thioacetate dendron 8 (100 mg, 0.03 mmol) was dissolved in a solvent composed of CH_2Cl_2 : methanol (5mL: 5mL), KOH (8.9 mg, 0.15 mmol) was added, and the mixture was heated to 50°C and stirred under N₂ for 12 h. After quenching with water, the organic portion was extracted with CH_2Cl_2 and washed with water (3 × 30 mL). The organic solution was then dried over anhydrous NaSO₄, filtered, and dried under vacuum (90 mg, 91%)

¹H NMR (CDCl₃, 200 MHz) δ = 7.61 (9H, CH in triazole), 6.71 (8H, H_{Ar}), 5.16 (24H, Ar-O-CH₂-), 4.91 (18H, - CH₂-Cp), 4.24-4.11 (81H, CH in Cp), 3.70 (2H, HS-CH₂-Ar).

¹³C NMR (CDCl₃, 200 MHz) δ = 152.65 (*m*-*C*_{Ar}-O-), 152.28 (-CH₂-*C*_{triazole}), 144.46, 143.39 (*p*-*C*_{Ar}-O-), 136.88, 133.11 (CH₂-*C*_{Ar}), 123.58, 123.23 (CH in triazole), 106.90 (CH in Ar), 81.72,81.38 (Ar-OCH₂-Ar), 71.16, 68.93, 66.50, 62.89 (CH₂ in Cp), 53.53 (O-CH₂-triazole), 49.96 (triazole-CH₂-Fc), 29.66 (HS-CH₂-). MS (MALDI, *M* + H)⁺: calcd. 3102.5 m/z, found 3103.2.

Ligand-substitution reaction in 1 of the triazole ligands by a mixture of thiolate-nonaferrocenyl dendron 3 and dodecanethiol

3 mL of THF solution of the thiol-nonaferrocenyl dendron **3** (30 mg, 0.01mmol) and dodecanethiol (10mg, 0.05 mmol, 12 μ L) was added into 3 mL (1 mM) thiazole-mPEG stabilized AuNPs **1** and stirred for 10 min. Then 10 mL dichloromethane was added into the mixed solution, and the organic phase was separated and dried over Na₂SO₄. After evaporating the solvent, the product was washed with acetone and ethanol followed by precipitation with dichloromethane/methanol.

¹H NMR (CDCl₃, 200 MHz) δ = 7.61 (9H, CH in triazole), 6.71 (8H, H_{Ar}), 5.28, 5.16 (24H, Ar-O-CH₂-), 4.91 (18H,- CH₂-Cp), 4.24-4.12 (81H, CH in Cp), 1.83, 1.59. 1.24 (22H, CH₂- in alkyl chain), 0.86 (3H, CH₃-CH₂-). UV-vis.: plasmon band at 535 nm.

DLS: 16.3 ± 3 nm.

Characterization Triazole-mPEG ligand



Figure S1¹H NMR of triazole-mPEG ligand.









ISO:(C2H4O)41C3H4N3OCH3 + (Na)1

Figure S3 MS (MALDI-TOF) of triazole-mPEG ligand.

Triazole-mPEG-capped AuNPs, 1



Figure S4 UV-vis. spectrum of triazole-mPEG capped AuNPs, 1



Figure S5 DLS of triazole-mPEG-capped AuNPs, 1. The average size of AuNPs 1 is 12.6 ± 3 nm



Figure S6¹H NMR of triazole-mPEG capped AuNPs 1 after decomposition.



Thermal stability of the triazole-AuNPs, 1, upon gradual heating

Figure S7 UV-vis. spectrum of triazole-mPEG capped AuNPs **1** which was kept 1 h at various temperatures (25°C, 35°C, 45°C, 60°C, 80°C, 100°C, and 120°C, respectively)

Triazole-mPEG-capped AuNPs, 1, as catalyst for 4-nitrophenol reduction

UV-vis. spectrum detection of various amounts of AuNPs during 4-nitrophenol reduction at various reaction times.



Figure S8 UV-vis. spectrum detection with 1% Au catalyst (AuNPs).



Figure S9 UV-vis. spectrum detection with 2% Au catalyst 1 (AuNPs) at various reaction times.



Figure S10 UV-vis. spectrum detection with 5% Au catalyst 1 (AuNPs) at various reaction times.



Figure S11 UV-vis. spectrum detection with 10% Au catalyst 1 (AuNPs).

Amount of AuNP catalyst 1	<i>k</i> value
0.5%	$5.2 \times 10^{-3} \text{ s}^{-1}$
1%	$8.6 \times 10^{-3} \text{ s}^{-1}$
2%	$16.7 \times 10^{-3} \text{ s}^{-1}$
5%	$37.5 \times 10^{-3} \text{ s}^{-1}$
10%	$50.1 \times 10^{-3} \text{ s}^{-1}$

Table S1 Rate constant k values for the reduction of 4-nitrophenol using various amounts of AuNP catalyst 1.



Selective detection of Hg²⁺ by UV-vis. spectroscopy

Figure S12 UV-vis. spectrum of AuNPs 1 in the presence of various metal ions.



Figure S13 Photograph of AuNPs **1** (0.4 mM) without metal ions (left) compared to those also containing a metal salt: MgCl₂, CaCl₂, KCl, Fe(C₆H₅O₇), Ag₂CO₃, CuCl₂, Hg(O₂CCH₃)₂ or NaCl (all 0.05 mM).

Ligand-substitution reaction of triazole ligands by thiol-mPEG (Au: L = 2: 1)

Au:L Ratio	SPB (nm)		Diameter (nm)	
	Before ligand exchange	after	Before	After ligand exchange
0.5: 1	535	535	6	6.2
2:1	536	536	10.4	12.9
10:1	538	539	17.5	_

Table S2 Plasmon band and diameter of the triazole-AuNPs synthesized with various Au³⁺: ligand (L) ratio and of the mPEG-thiolate AuNPs generated by ligand exchange.^a

^a With the 10:1 ratio, the triazole-AuNPs withstand heating for 1 h at 100°C, but aggregation occurs upon ligand exchange with thiols (unlike with other Au:L stoichiometries used here).



Figure S14 UV-vis. spectrum of triazole-mPEG capped AuNPs, 1 synthesized with the Au^{3+} : L ratio 2:1, and mPEG-thiolate AuNPs obtained by ligand substitution from 1.



Figure S15 TEM image of triazole-mPEG capped AuNPs synthesized with the Au^{3+} : L ratio 0.5:1



Figure S16 TEM image of the ligand substitution product of the AuNPs 2:1



Figure S17 ¹H NMR of the ligand substitution product of the AuNPs 2:1





Figure S18 UV-vis. Spectrum of triazole-mPEG capped AuNPs synthesized with the Au^{3+} : L ratio 10:1, and the mPEG-thiolate AuNPs obtained by ligand substitution.



Figure S19 TEM image of triazole-mPEG capped AuNPs synthesized with the Au^{3+} : L ratio is 10:1.

Ligand-substitution reaction of triazole ligands by thiol-mPEG and 11-mercaptoundencaonic acid in 1 yielding 2 (Scheme 1)



Figure S20 ¹H NMR of mixed ligand-stabilized AuNPs **2** after the ligand-exchange reaction (ligands: thiol-mPEG + 11-mercaptoundencaonic acid). ¹H NMR (CDCl₃, 300MHz): 3.68 (160H, $-OCH_2CH_2O$), 3.42 (3H, $-OCH_2CH_3$), 2.35 (2H, $-CH_2$ -COOH), 1.65, 1.38 (18H, $-CH_2$ -)



Figure S21 IR spectrum of AuNPs **2** containing mixed ligands. The bands at 1730 cm⁻¹ indicate the presence of –COOH (ligands: thiol-mPEG + 11-mercaptoundencaonic acid).



Figure S22 DLS: Average size of AuNPs **2** (including the thiol-mPEG + 11-mercaptoundencaonic acid ligands): 16.3 ± 3 nm.



Figure S23 TEM. Average size of AuNP cores of 2 (without ligand): 6.2 ± 0.5 nm.



Figure S24 Plasmon band of mixed-ligand-capped AuNPs **2** (ligands: thiol-mPEG + 11-mercaptoundencaonic acid).

Ligand-substitution reaction of triazole ligands in 1 by a mixture of thiolate-nonaferrocenyl dendron, 3, and dodecanethiol yielding 4 (Scheme 1)



Figure S25 ¹H NMR of mixed-ligand stabilized AuNPs, **4**, after the ligand-exchange reaction (ligands: thiolate-nonaferrocenyl dendrons + dodecanethiolate). ¹H NMR (CDCl₃, 200 MHz) $\delta = 7.61(9H,CH$ in triazole), $6.71(8H, H_{Ar})$, $5.28, 5.16(24H, Ar-O-CH_2-)$, $4.91(18H, -CH_2-Cp)$, 4.24-4.12(81H, CH in Cp), 1.83, 1.59, 1.24 (22H, CH₂- in alkyl chain), $0.86(3H, CH_3-CH_2-)$.



Figure S26 DLS: Average size of AuNPs 4 (with thiolate-nonaferrocenyl dendrons + dodecanethiolate ligands): 13.1 ± 3 nm



Figure S27 Plasmon band of mixed ligand capped AuNPs **4** (ligands: thiolate-nonaferrocenyl dendrons + dodecanethiolate)



Figure S28 Cyclic voltammetry of dendrimer-shape AuNPs **4** containing approximately 1000 ferrocenyl groups around the core (Scheme 1). Note the significant adsorption on the cathodic side. The decamethyl ferrocene internal reference is shown at 0V (see ref. 15 for the reference aspect). Epa – Epc = 40 mV.

¹H NMR, ¹³C NMR and mass spectrometry of the thiolate-nonaferrocenyl dendron 3.

Methyl 3,4,5-tris[3',4',5'- tris(prop-2-yn-1-yloxy)benzyloxy]benzoate (dendron 5):



figure S29

¹H NMR of methyl 3,4,5-tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzoate, **5**



Figure S30

¹³C NMR of methyl 3,4,5-Tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzoate, **5.**



Figure S31

MS of methyl 3,4,5-tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzoate, 5.

3,4,5-Tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl alcohol (dendron-6):



Figure S32 ¹H NMR of 3,4,5-tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl alcohol, **6.**



Figure S33

¹³C NMR of 3,4,5-Tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl alcohol, **6.**



Figure S34

MS of 3,4,5-Tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl alcohol, 6.

3,4,5-Tris[3',4',5'- tris(prop-2-yn-1-yloxy)benzyloxy]benzyl thioacetate (Dendron7):







Figure S36

¹³C NMR of 3,4,5-tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl thioacetate, 7.





MS of 3,4,5-tris[3',4',5'-tris(prop-2-yn-1-yloxy)benzyloxy]benzyl thioacetate, 7.





Figure S39 ¹³C NMR of thioacetate nonaferrocenyl dendron 8.



Figure S40 Mass spectrum of the thioacetate nonaferrocenyl dendron 8.



Figure S42 ¹³C NMR of thiol-nonaferrocenyl dendron 3.



Figure S43 MS of the thiol-nonaferrocenyl dendron **3**. MS (MALDI, M + H)⁺: calcd. 3102.5 m/z, found 3103.2 (major peak).

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