

Synthesis, H_2PO_4^- and Pd^{2+} ions sensing and Gold nanoparticles encapsulation of ferrocenyldendrimers by Green chemistry approach.

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S1: General Experimental procedure

General Information

Analytical TLC was performed on commercial Merk plates coated with Silica Gel GF254. Analytical samples were obtained from flash silica gel chromatography, using silica gel of 100-200 mesh and elution with solvent system as mentioned order each experiment. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz BRUKER AVANCE (75 MHz for ^{13}C NMR) spectrometer. All chemical shifts values are reported in δ ppm relative to internal standard tetramethylsilane (TMS, δ 0.00). ^{13}C chemical shifts are reported relative to CDCl_3 (center of triplet, δ 77.23) or relative to $\text{DMSO}-d_6$ (center of septet, δ 39.51). The spin multiplicities are indicated by the symbols s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad), dd (doublet of doublets). The coupling constants J, are reported in Hertz (Hz). Elemental analysis data was recorded on Vario EL III (CDRI, Lucknow) instrument. Mass spectra (M.S) were recorded obtained using Fast Atom Bombardment and MALDI-TOF. All other chemicals used were of reagent grade (SRL-Mumbai).

General procedure for the synthesis of Cu (I) catalyzed click reaction (Procedure A)

To a mixture of alkyne (1.0 equiv., 1.0 mmol) and *N*-methylmorpholine (1.5 equiv., 1.5 mmol) in water (3 mL) added the azide (2.1 equiv., 2.1 mmol) in the presence of CuSO₄·5H₂O (5 mol %) and NaAsc (10 mol %) and kept under microwave irradiation (80 W) for 1 min. The reaction mixture was kept aside for 5 min and subsequently added NaN₃ (1.5 equiv., 1.5 mmol) in Na₂SO₄ (0.5 g) kept again under microwave irradiation (80 W) for 1 min. water (100 mL) was added to the reaction mixture and stirred for 10 min in order to resume all the Cu (I) trapped in the dendrimer as Cu(NH₃)₆⁺ and then extracted with CHCl₃ (2 X 100 mL). The organic phase was separated and then washed twice with water (2 X 150 mL), dried over Na₂SO₄ and the solvent was removed under vacuum to give the crude triazole, which was purified by column chromatography (SiO₂), using the eluent as mentioned under each compound.

General procedure for solid support click chemistry (Procedure B):

A mixture of azide (1 equiv., 1.0 mmol), alkyne (1 equiv., 1.0 mmol) in Na₂SO₄ (0.5 g) and in the presence of CuSO₄·5H₂O (5 mol %) and NaAsc (10 mol %) was kept under microwave irradiation (80 W) for 1 min. The crude residue was treated with water (150 mL) for 10 min in order to resume all the Cu (I) trapped in the dendrimer as Cu(NH₃)₆⁺ and then extracted with CHCl₃ (2 X 150 mL). The organic layer was separated, washed with brine (1 × 150 mL), dried over Na₂SO₄ and evaporated to give the crude triazole, which was purified by column chromatography (SiO₂), using the eluent as mentioned under each compound.

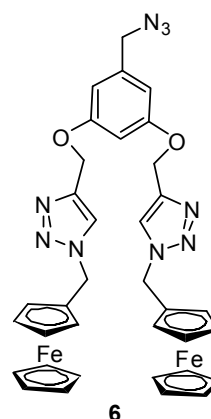
Ferrocenyl dendritic azide **6**:

Following the general procedure A, the dendritic azide **6** was obtained as white solid from 3,5-bis (propargyloxy) benzyl chloride **5** (0.16 g, 0.68 mmol) and azidomethyl ferrocene **4** (0.35 g, 1.4 mmol). $R_f = 0.5$ (CHCl_3 :MeOH, 25:1); M.p.: 134-136 °C;

^1H NMR: (300 MHz, CDCl_3) $\delta = 4.18$ (s, 10H), 4.22 (s, 6H), 4.28 (s, 4H), 5.12 (s, 4H), 5.29 (s, 4H), 6.53 (s, 1H), 6.56 (s, 2H), 7.51 (s, 2H).

^{13}C NMR: (75 MHz, CDCl_3) $\delta = 50.2, 62.2, (68.7, 68.9, 69.1, \text{Cp}) 80.6, 101.8, 107.5, 122.2, 137.8, 143.6, 159.7$. MS (ESI): $m/z = 723$ [M^+].

Elemental Anal. Calcd for $\text{C}_{35}\text{H}_{33}\text{Fe}_2\text{N}_9\text{O}_2$: C, 50.11; H, 4.60; N, 17.43 %. Found: C, 58.00; H, 4.47; N, 17.36 %.

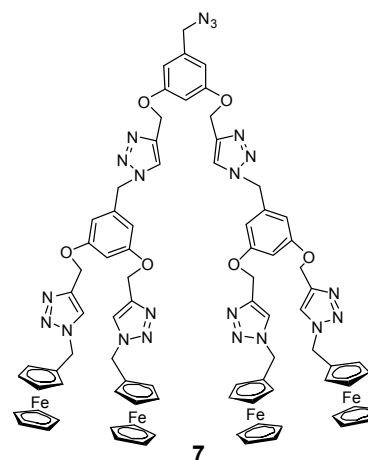


Second generation ferrocenyl dendritic azide **7**:

Following the general procedure A, the ferrocenyl dendritic azide **7** was obtained as white solid from 3,5-bis (propargyloxy) benzyl chloride **5** (0.13 g, 0.55 mmol) and dendritic azide **6** (0.86 g, 1.16 mmol). $R_f = 0.6$ (CHCl_3 : MeOH, 20:1); M.p.: 134-136 °C; ^1H NMR: (300 MHz, CDCl_3) $\delta = 4.12$ (s, 2H), 4.16, 4.21, 4.27 (s, 36H; Cp), 5.06 (s, 8H), 5.14 (s, 4H), 5.28 (s, 8H), 5.39 (s, 4H), 6.46 (s, 4H),

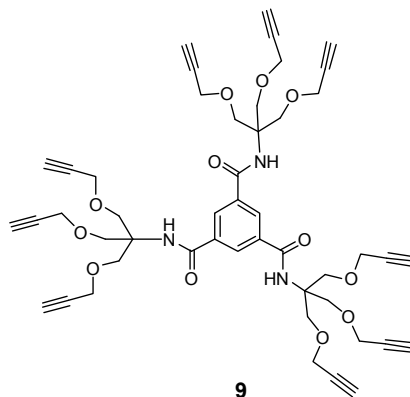
6.53 (s, 3H), 6.56 (s, 2H), 7.51 (s, 4H), 7.59 (s, 2H). ^{13}C NMR: (75 MHz, CDCl_3) $\delta = 50.1, 54.1, 54.6, 62.0, (68.6, 68.8, 68.9, 69.1, \text{Cp}), 80.7, 101.7, 102.0, 107.5, 122.4, 123.1, 133.5, 136.8, 137.8, 143.3, 144.1, 159.6, 159.8$. MS (EI): $m/z = 1687$ [MALDI-TOF].

Elemental Anal. Calcd for $\text{C}_{83}\text{H}_{77}\text{Fe}_4\text{N}_{21}\text{O}_6$: C, 50.06; H, 4.60; N, 17.43%. Found: C, 49.99; H, 4.44; N, 17.37 %.



TRIS acetylene terminated dendron **9**:

To a solution of *N*-(*t*-Butyloxycarbonyl)tris[(propargyloxy)methyl]aminomethane **8** (3g, 8.94 mmol) in dry CH₂Cl₂ (50 mL), cooled to 0 °C was added dropwise trifluoroacetic acid (15 mL, 197 mmol) over a period of 30 min. and the brown mixture was stirred at room temperature for 2 h. The mixture was then concentrated to dryness *in vacuo* with rotary evaporator using toluene as a co-solvent (2 X 3 mL).

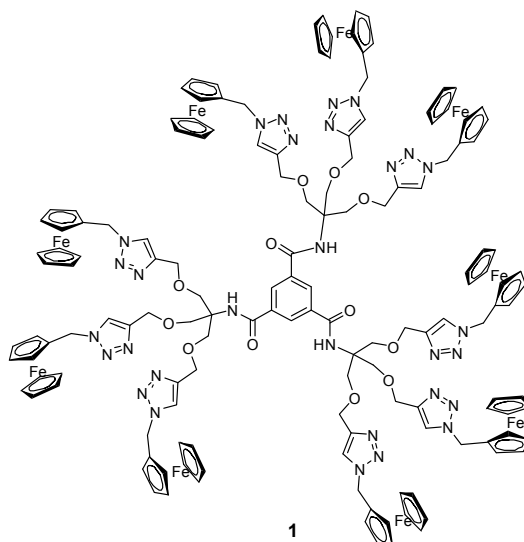


The solid obtained without further purification was dissolved in dry CH₂Cl₂ (50 mL) and the solution was cooled to 0 °C. Et₃N (1.3 mL, 18.6 mmol) and a solution of 1,3,5-benzenetricarboxylic acid chloride (0.55 g, 2.55 mmol) in dry CH₂Cl₂ (30 mL) were added. The mixture was allowed to warm up to room temperature and stirred under a nitrogen atmosphere for 15 h. The dark solution was washed with 0.5 M HCl (100 mL) and water (3 X 100 mL) and the organic layer was then collected, dried over Na₂SO₄ and concentrated to dryness. Purification by column chromatography (SiO₂) afforded **9** as a light brown solid. (CHCl₃/MeOH 99.3:0.7). Yield: 58%; M.p.: 96 °C; ¹H NMR: (300 MHz, CDCl₃) δ = 2.54 (t, 9H, *J* = 2.1), 4.00 (s, 18H), 4.19 (d, 18H, *J* = 2.4), 6.64 (s, 3H), 8.58 (s, 3H). ¹³C NMR: (75 MHz, CDCl₃) δ = 58.7, 60.1, 68.4, 75.1, 79.6, 131.3, 135.9, 165.9. MS (EI): *m/z* = 861 [M⁺]. Elemental Anal. Calcd for C₄₈H₅₁N₃O₁₂: C, 66.89; H, 5.96; N, 4.88 %. Found: C, 66.75; H, 5.84; N, 4.82 %.

S2: Spectral data for dendrimers

Ferrocenyldendrimer 1:

Following the general procedure B, the ferrocenyldendrimer **1** was obtained as white from TRIS acetylene terminated dendron **9** (0.07 g, 0.08 mmol) and azidomethyl

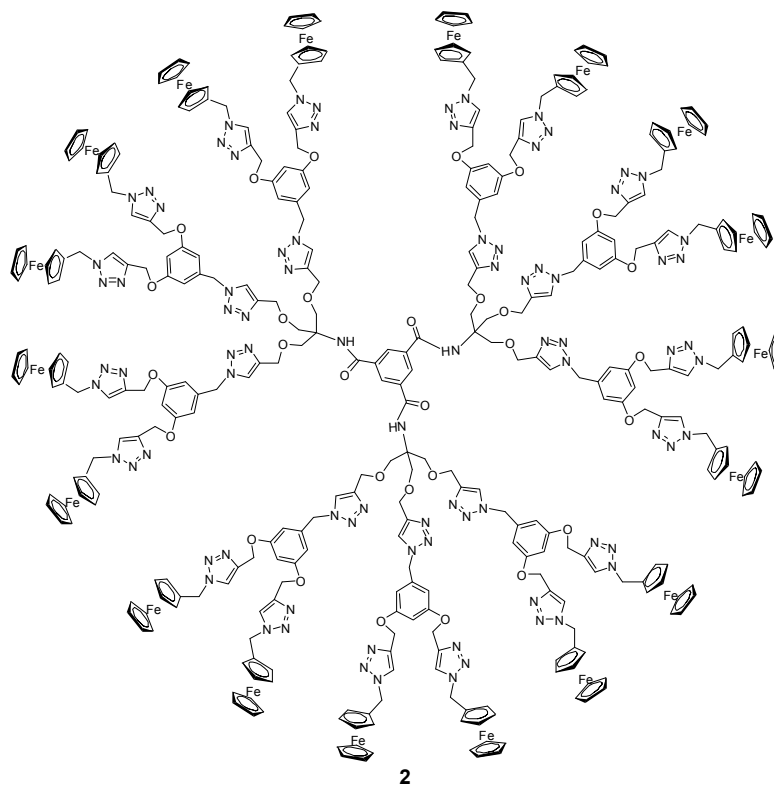


ferrocene **4** (0.19 g, 0.79 mmol). Yield: 94%; R_f = 0.55 (CHCl_3 : MeOH, 20:3); M.p.: 110-112 °C; ^1H NMR: (300 MHz, CDCl_3) δ = 3.89 (s, 18H), 4.14-4.15 (m, 63H), 4.26 (t, 18H, J 1.5), 4.54 (s, 18H), 5.22 (s, 18H), 7.14 (s, 3H), 7.05 (s, 9H), 8.42 (s, 3H). ^{13}C NMR: (75 MHz, CDCl_3) δ = 49.9, 60.5, 64.7, 68.9, 69.0, 81.19, 122.33, 131.0, 135.9, 144.6, 166.2. MS (MALDI-TOF): m/z = 3054 [$\text{M}^+ + \text{Na}$]. Elemental Anal. Calcd for $\text{C}_{147}\text{H}_{150}\text{Fe}_9\text{N}_{30}\text{O}_{12}$: C, 58.24; H, 4.99; N, 13.86 %. Found: C, 58.09; H, 4.88; N, 13.73 %.

Ferrocenyldendrimer 2:

Following the general procedure B, the ferrocenyldendrimer **2** was obtained as white solid from TRIS acetylene terminated dendron **9** (0.03 g, 0.03 mmol) and dendritic azide **6** (0.26 g, 0.03 mmol). Yield: 89%; R_f = 0.6 (CHCl_3 : MeOH, (25:3); M.p.: 126-

128°C; ^1H NMR: (300 MHz, CDCl_3) δ = 3.85 (s, 18H), 4.14, 4.17, 4.25 (s, 162H, Cp), 4.49 (s, 18H), 4.83-4.97 (m, 36H), 5.23 (s, 36H), 5.29 (s, 18H), 6.45 (s, 27H),

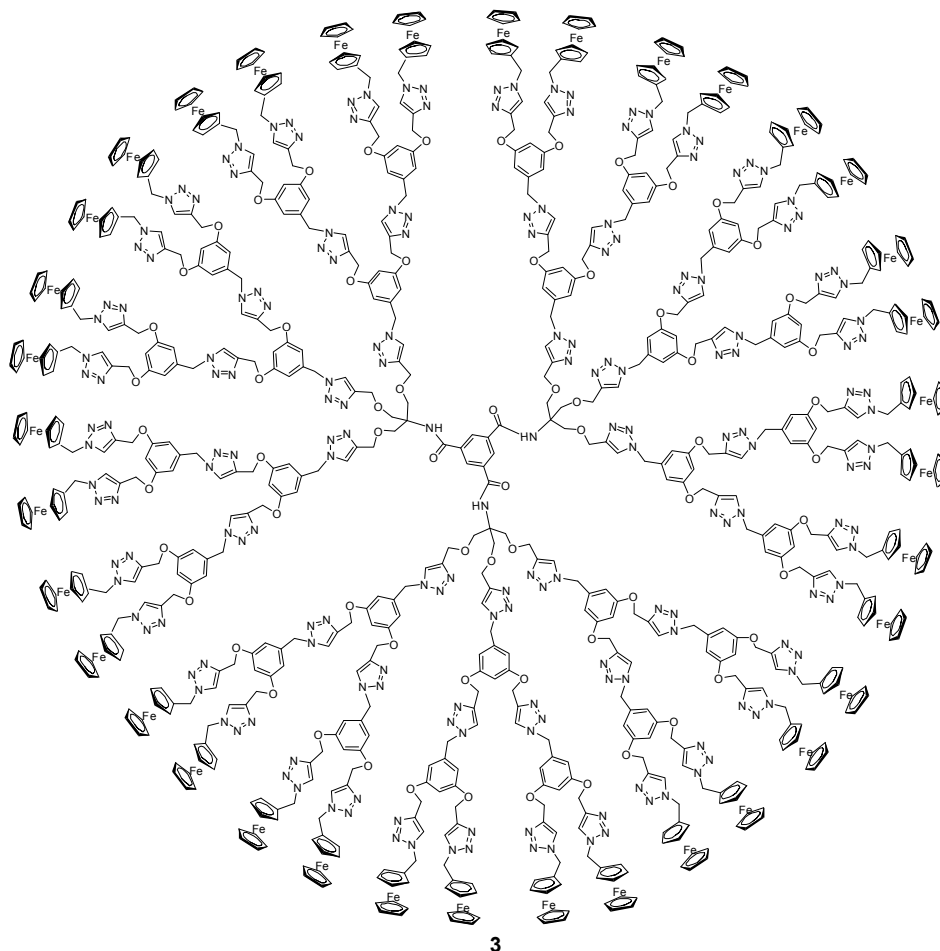


7.19 (m, 3H), 7.53 (s, 18H), 7.61 (s, 9H), 8.40 (s, 3H). ^{13}C NMR: (75 MHz, CDCl_3) δ = 48.7, 50.1, 53.8, 61.8, 64.7, (68.9, 69.0, 69.1, Cp), 80.8, 101.9, 107.3, 122.7, 123.2, 137.3, 143.1, 143.2, 145.1, 159.0, 159.6. MS (MALDI): m/z = 7394 [$\text{M}^+ + \text{Na}$] Elemental Anal. Calcd for $\text{C}_{363}\text{H}_{348}\text{Fe}_{18}\text{N}_{84}\text{O}_{30}$: C, 59.14; H, 4.76; N, 15.96 %. Found: C, 59.00; H, 4.57; N, 15.84 %.

Ferrocenyldendrimer 3:

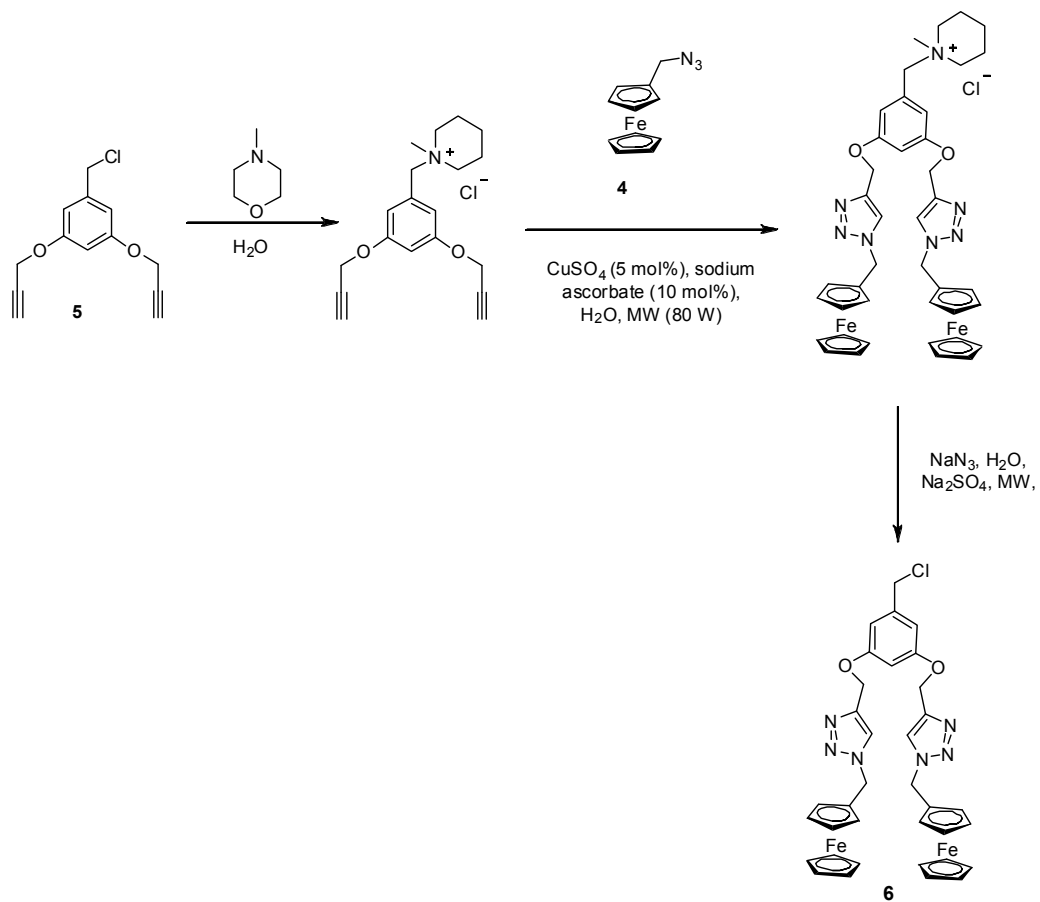
Following the general procedure B, the ferrocenyldendrimer **3** was obtained as white solid from TRIS acetylene terminated dendron **9** (0.007 g, 0.008 mmol) and dendritic azide **7** (0.14 g, 0.08 mmol). Yield: 80%; R_f = 0.59 (CHCl_3 : MeOH, 25:4); M.p.:

147-149°C; ^1H NMR: (300 MHz, CDCl_3) δ = 3.81 (s, 18H), 4.12, 4.23, 4.28 (s, 324H; Cp), 4.39 (s, 18H), 4.91-4.95 (m, 108H), 5.22-5.26 (m, 126H), 6.39-6.44 (m, 81H),



7.05 (s, 3H), 7.56 (s, 36H), 7.61 (s, 27H), 8.30 (s, 3H). ^{13}C NMR: (75 MHz, CDCl_3) δ = 50.1, 53.8, 54.6, 61.8, (68.9, 69.0, 69.1, Cp), 69.7, 73.2, 80.9, 81.8, 101.9, 107.4, 107.5, 114.1, 122.72, 123.5, 128.9, 133.6, 137.1, 137.3, 139.3, 143.2, 143.4, 143.6, 159.5, 159.7. MS (MALDI): m/z = 16077 [$\text{M}^+ + \text{Na}$]. Elemental Anal. Calcd for $\text{C}_{795}\text{H}_{744}\text{Fe}_{36}\text{N}_{192}\text{O}_{66}$: C, 59.14; H, 4.76; N, 15.96 %. Found: C, 59.00; H, 4.57; N, 15.84 %.

S3: Role of N-methylmorpholine as IL in the synthesis of dendritic arm.



S4: Cyclic voltammetry experiments

All the cyclic voltammetry experiments were carried out with the CHI model 1100A series electro chemical analyzer (CH instrument, USA) controlled by an Intel Pentium 4 personal computer with standard three-electrode configuration.

Electro chemical cells

The electrochemical cell was a conventional three-compartment glass cell. A fritted disk of maximum porosity separated the working electrode compartment and the counter electrode compartment. The top lid of the working electrode compartment was provided with entry ports for the working electrode, nitrogen gas inlet, nitrogen gas outlet and the reference electrode. The reference electrode compartment was connected to the working electrode compartment by means of a tightly fitting glass tube ending with a luggin capillary. A three-way glass stopper fused at the middle of the glass tube arrangement prevented the solution leaking into the test solution. Glassy carbon disc of 3 mm diameter with geometric area of 0.0707 cm^2 was used as a support for the working electrode. Glassy carbon electrode (GCE) surface was conditioned by polishing with increasingly finer grade alumina powders (1, 0.3 and 0.5 micron) down to mirror polish, sonicated about 1 to 2 minutes in double distilled (DD) water, degreased with acetone, washed with copious amount of DD water. This is followed by potential cycling for five times in the deaerated base electrolyte in the potential region -200 to 1000 mV (SCE) at a potential scan (v)= 100 mVs^{-1} . In all the electrochemical experiments the potentials were measured with respect to a dip type (ELICO, India) saturated calomel electrode (SCE). Saturated KCl solution of the SCE was changed periodically. A Pt wire in the form of a spiral with high geometrical surface area ($\sim 20\text{ cm}^2$) was used as a counter electrode. The electrode was cleaned in

conc.HNO₃ and then heated to red hotness in a blue flame. This treatment was given occasionally. The redox potentials and the value of internal standard [FeCp₂]/[FeCp₂]⁺ was measured in CH₂Cl₂ containing the supporting electrolyte [n-Bu₄N][PF₆].

S5: Synthesis of Au nanoparticles with dendrimers 1,2 and 3

The general procedure adopted for the synthesis of Au nanoparticles using dendrimer **1**: In a typical synthesis, 3.298x10⁻⁴ mmol (1 mg) of dendrimer **1** was dissolved in mixture of CHCl₃ and methanol (MeOH) with a ratio of 2:1 (2 mL), and the reaction mixture was allowed to stirring at room temperature under nitrogen atmosphere. After complete solubilization, Auric acetate (4.429x10⁻³ mmol) dissolved in methanol (2 mL) was added slowly into the reaction mixture in order to anchor Au (III) ions within the cores of the dendrimer. The stoichiometric amount of Au atoms was optimized (9, 27 and 63 equiv of Au per dendrimer for **1,2** and **3**) while excess equivalents number of Au atoms per triazole exceeds number of Au⁰ get precipitated. It is earlier reported that, Au nanoparticles formed would contain the number of atoms equal to the number of triazole rings present in the dendrimer. Then NaBH₄ (1.16 mg, 4.429x10⁻² mmol) was added drop wise and the yellow color of the reaction solution turned to wine red indicating the formation of Au nanoparticles.

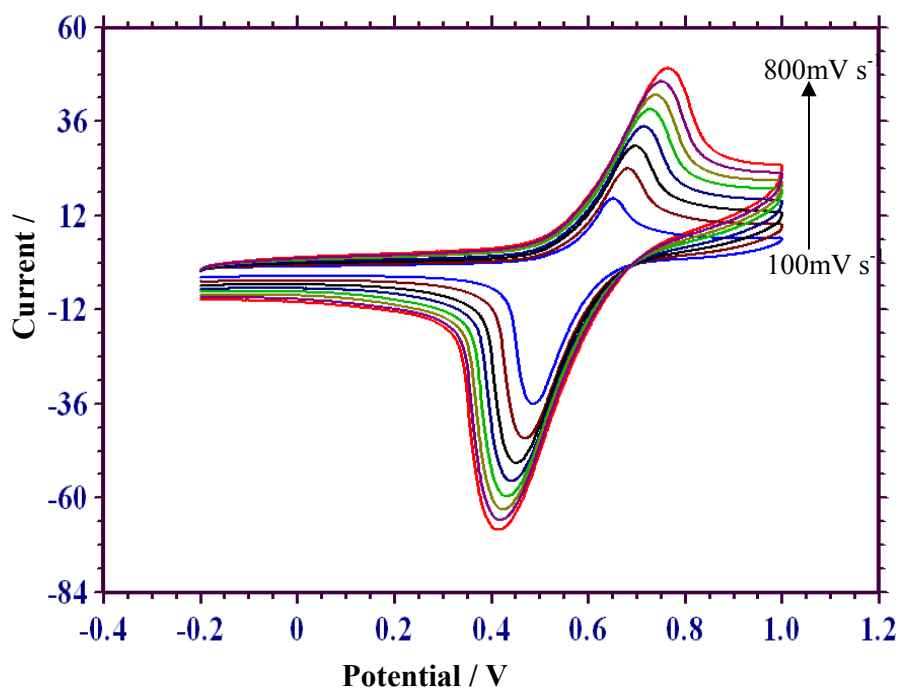


Figure S1: Ferrocenyldendrimer **1** for various scan rates (From inner to outer at 100 mV/s, 200 mV/s, 300 mV/s, 400 mV/s, 500 mV/s, 600 mV/s 700 mV/s and 800 mV/s)

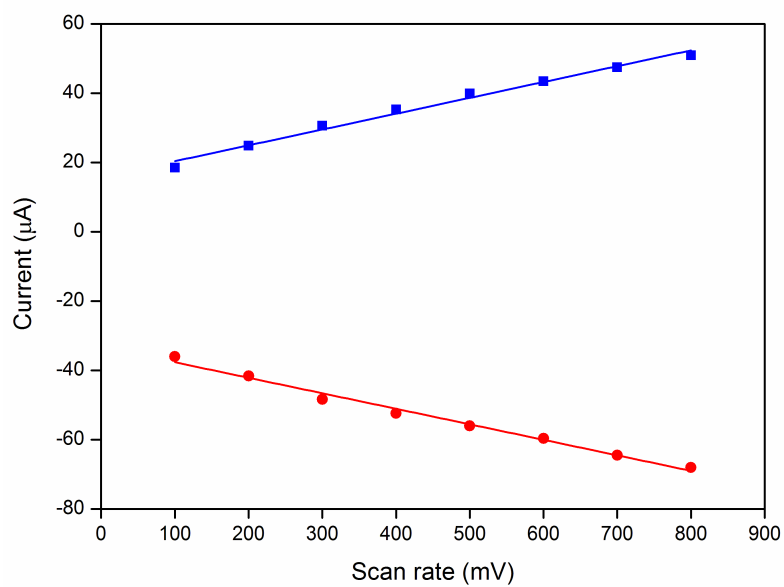


Figure S2: Intensity vs. scan rate of the effect with ferrocenyldendrimer **1**

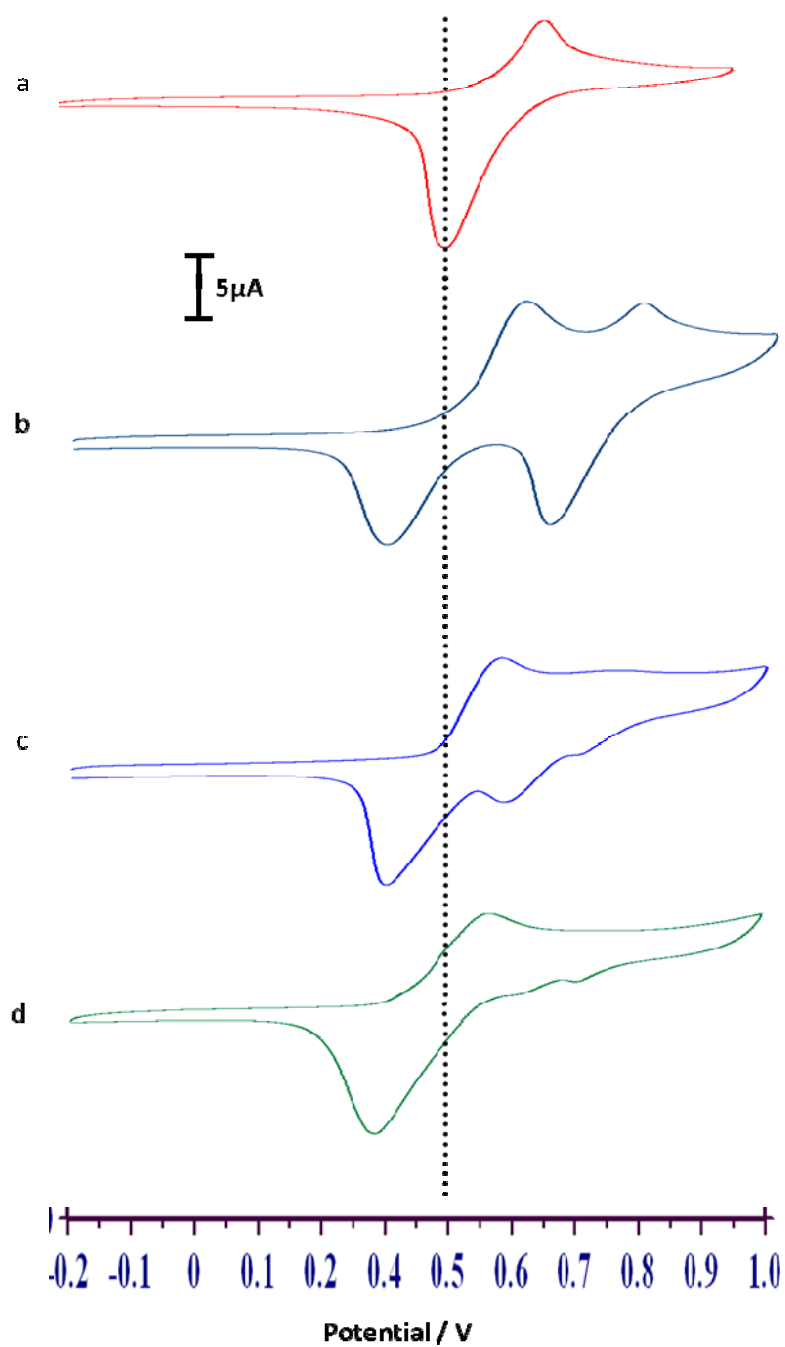


Figure S3a: Cyclic voltammetric redox sensing of anion on dendrimer **1** ($C = 9.82 \times 10^{-4}$ M): (a) before addition of $\text{H}_2\text{PO}_4^{2-}$; (b & c) during addition and of $\text{H}_2\text{PO}_4^{2-}$ and (d) at the end of addition of $\text{H}_2\text{PO}_4^{2-}$.

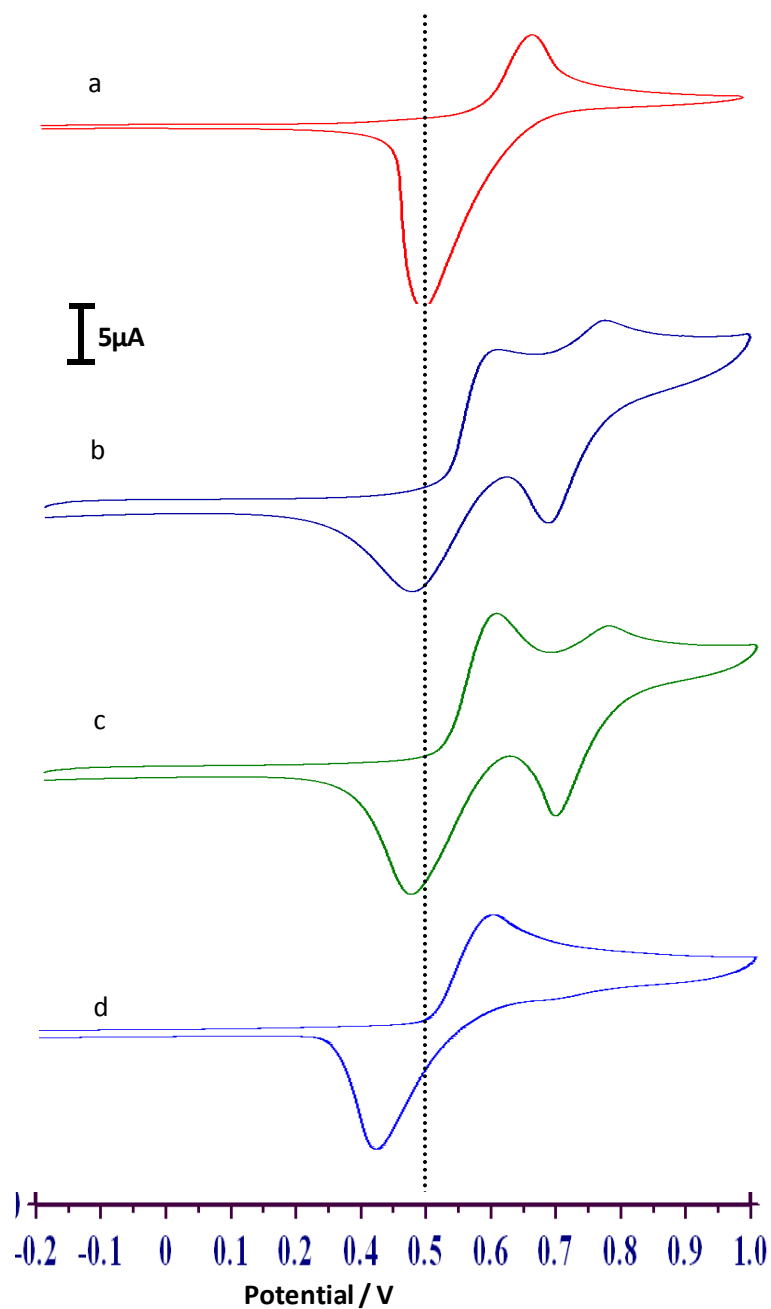


Figure S3b: Cyclic voltammetric redox sensing of anion on dendrimer **2** ($C = 1.00 \times 10^{-3}$ M): (a) before addition of H_2PO_4^- ; (b & c) during addition and of H_2PO_4^- and (d) at the end of addition of H_2PO_4^- .

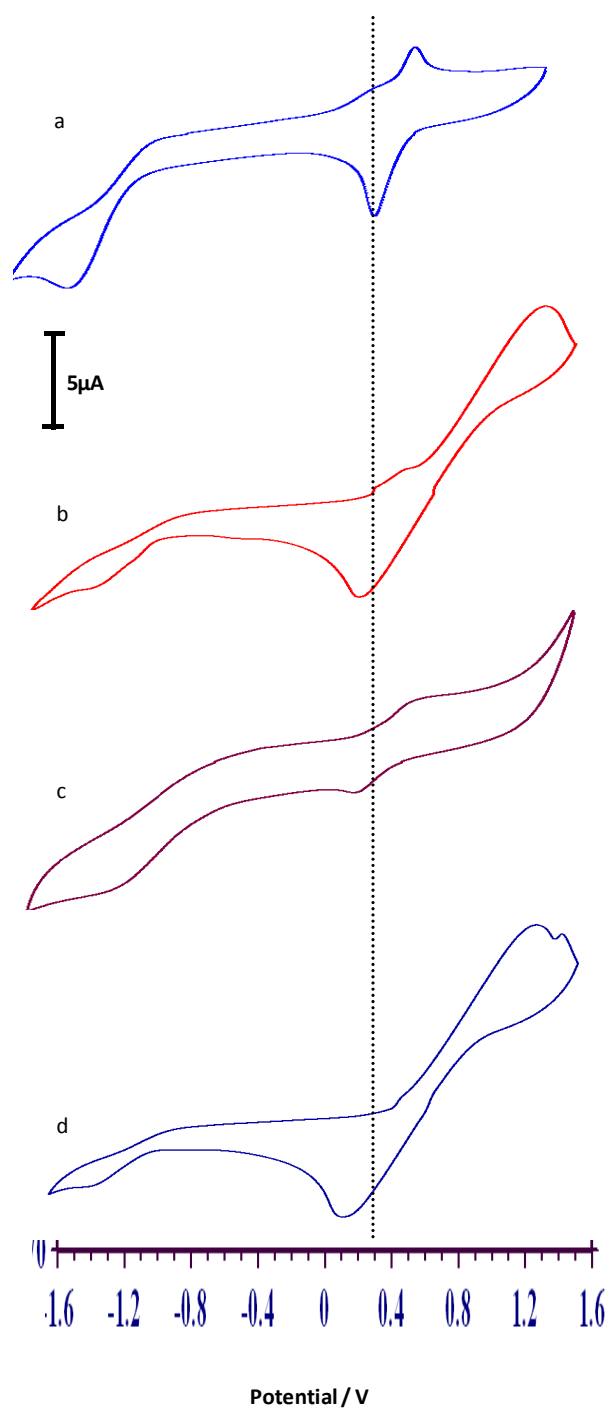


Figure S3c: Cyclic voltammetric redox sensing of anions on dendrimer **3** ($C = 4.97 \times 10^{-4}$ M): (a) before addition of H_2PO_4^- ; (b & c) during addition and of H_2PO_4^- and (d) at the end of addition of H_2PO_4^- .

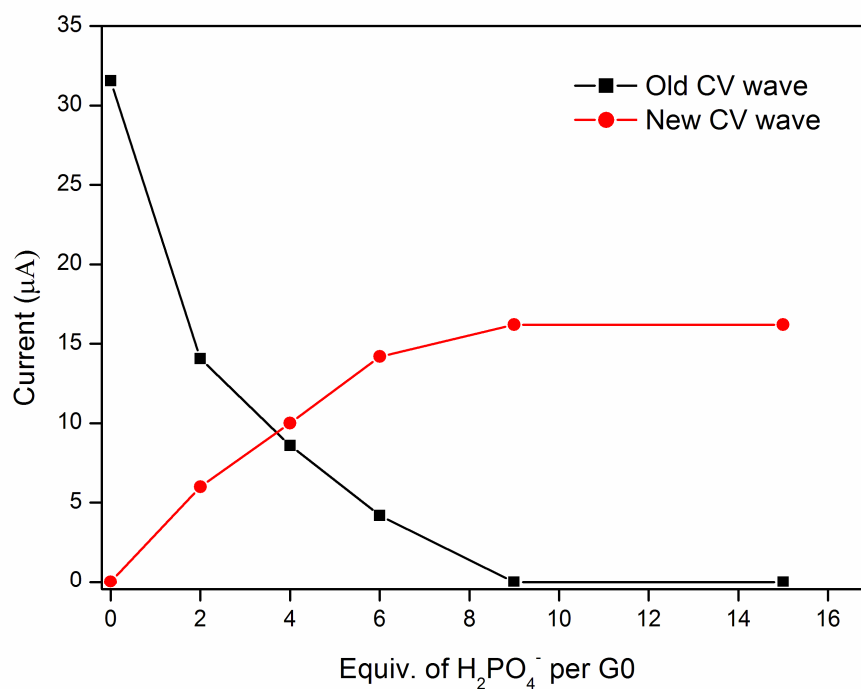


Figure S4a: Titration of $[n\text{-Bu}_4\text{N}]_2[\text{ATP}]$ with the 9-ferrocenyl dendrimer **1** by cyclic voltammetry

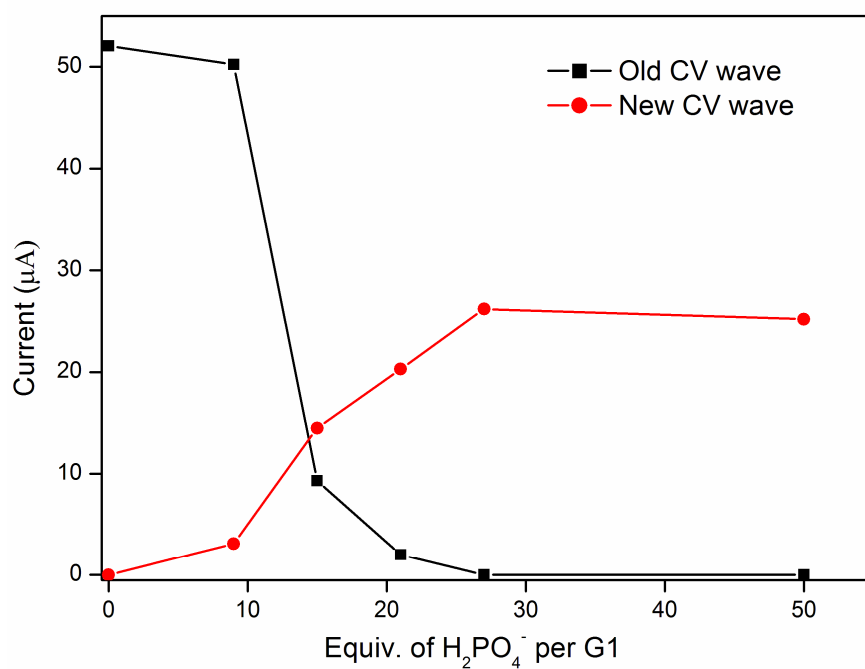


Figure S4b: Titration of $[n\text{-Bu}_4\text{N}]_2[\text{ATP}]$ with the 27-ferrocenyl dendrimer **2** by cyclic voltammetry

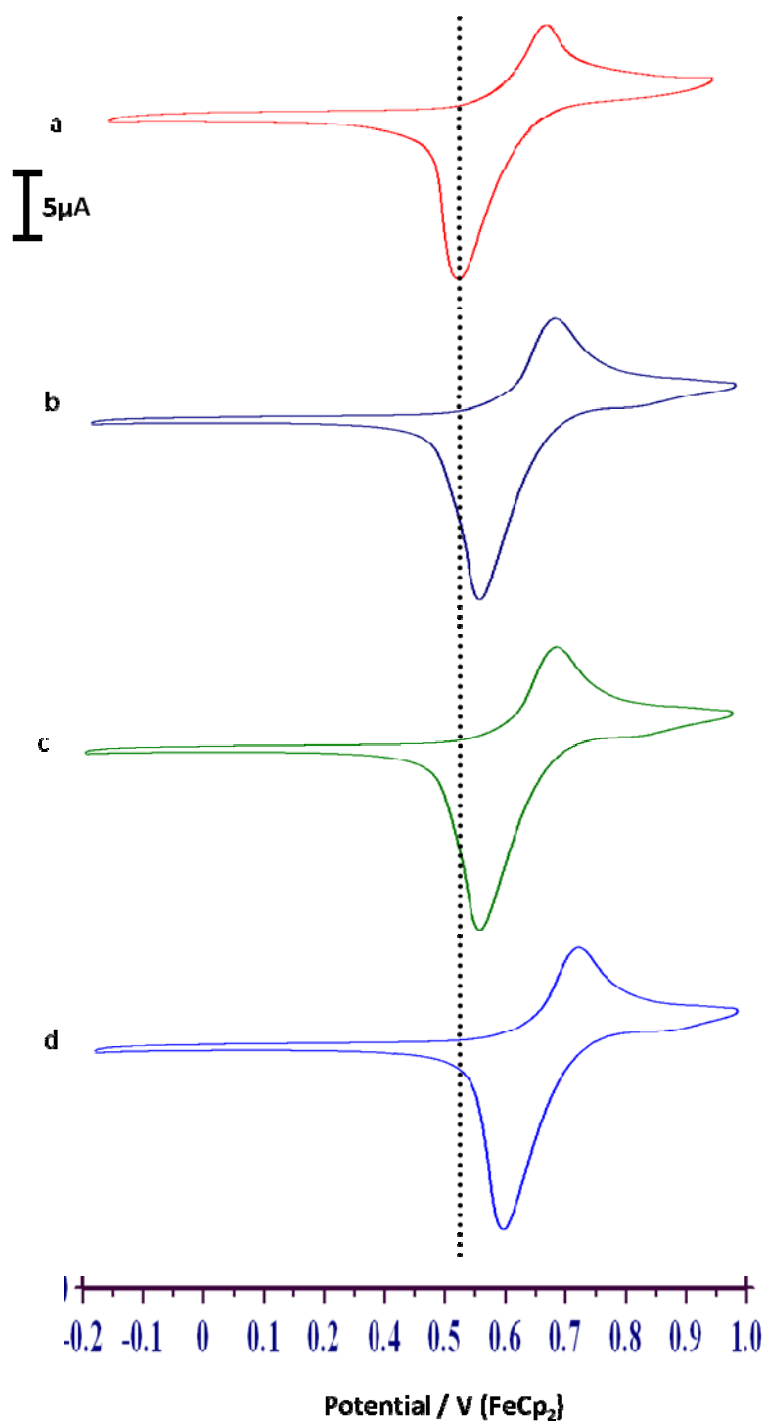


Figure S5a: Cyclic voltammetric redox sensing of cation on dendrimer **1** ($C = 9.82 \times 10^{-4}$ M): (a) before addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$; (b & c) during addition and of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and (d) at the end of addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$.

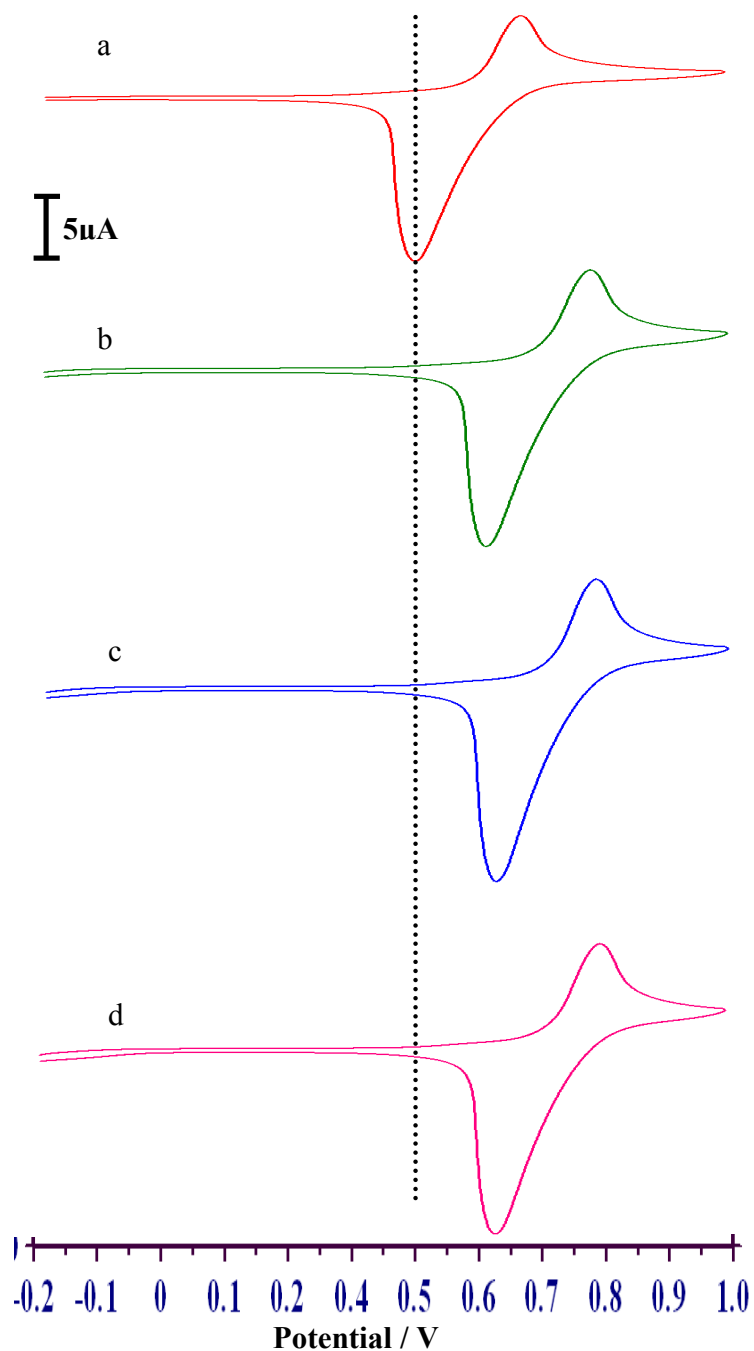


Figure S5b: Cyclic voltammetric redox sensing of cation on dendrimer **2** ($C = 1.00 \times 10^{-3}$ M): (a) before addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$; (b & c) during addition and of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and (d) at the end of addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$.

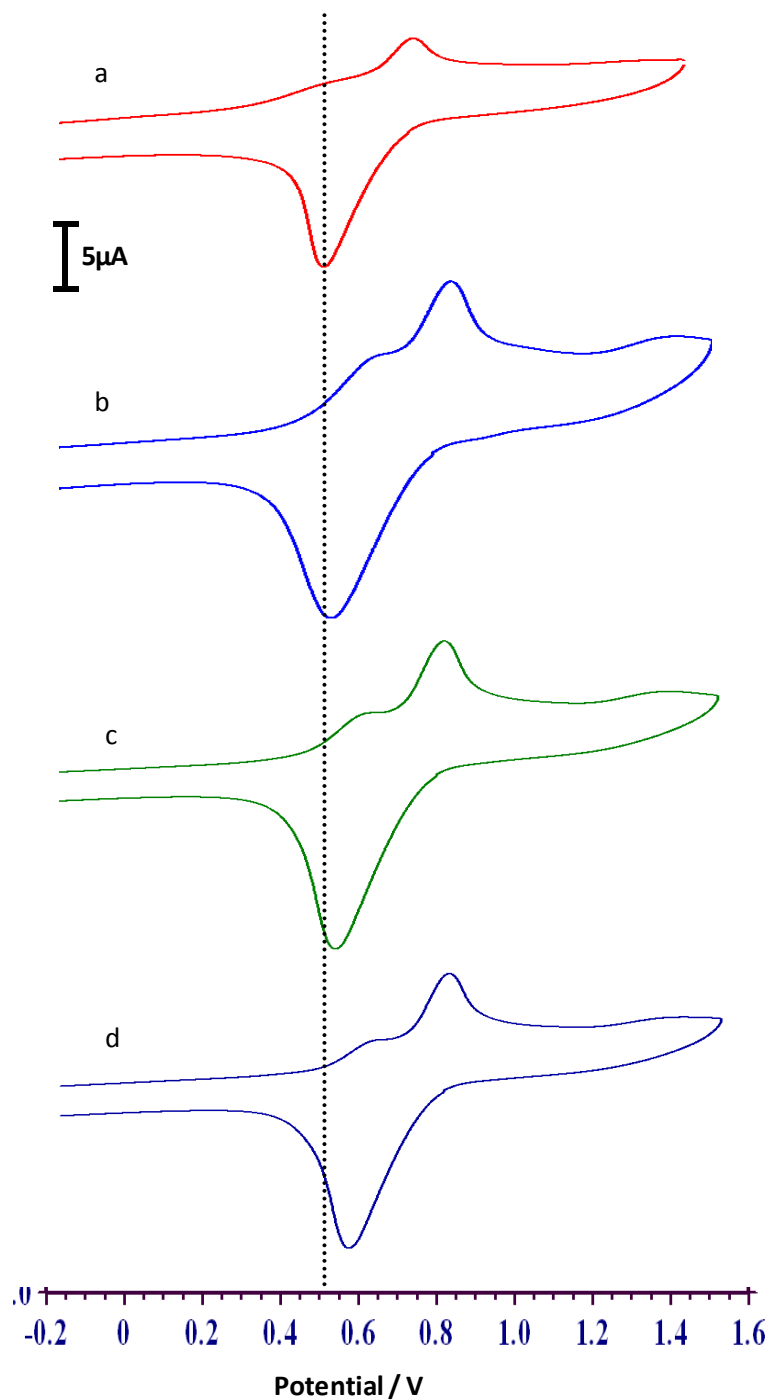


Figure S5c: Cyclic voltammetric redox sensing of cation of dendrimer **3** ($C = 4.97 \times 10^{-4}$ M): (a) before addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$; (b & c) during addition and of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and (d) at the end of addition of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$.

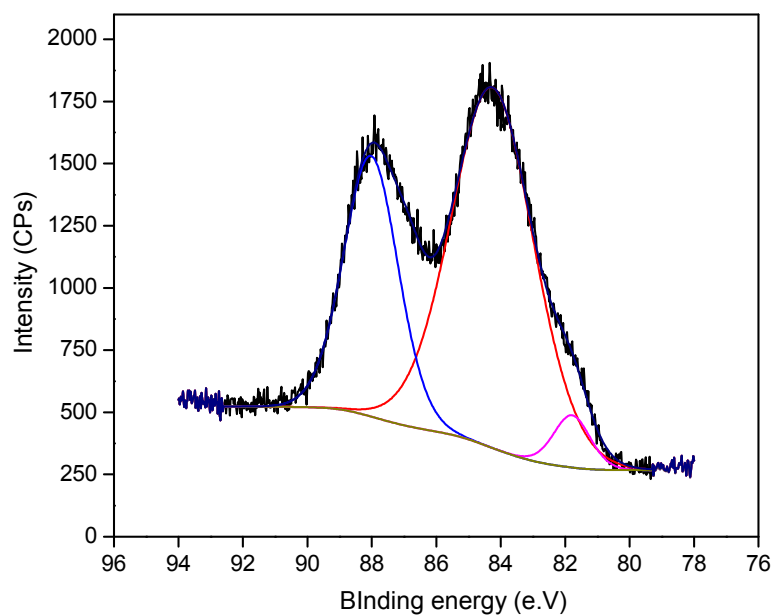
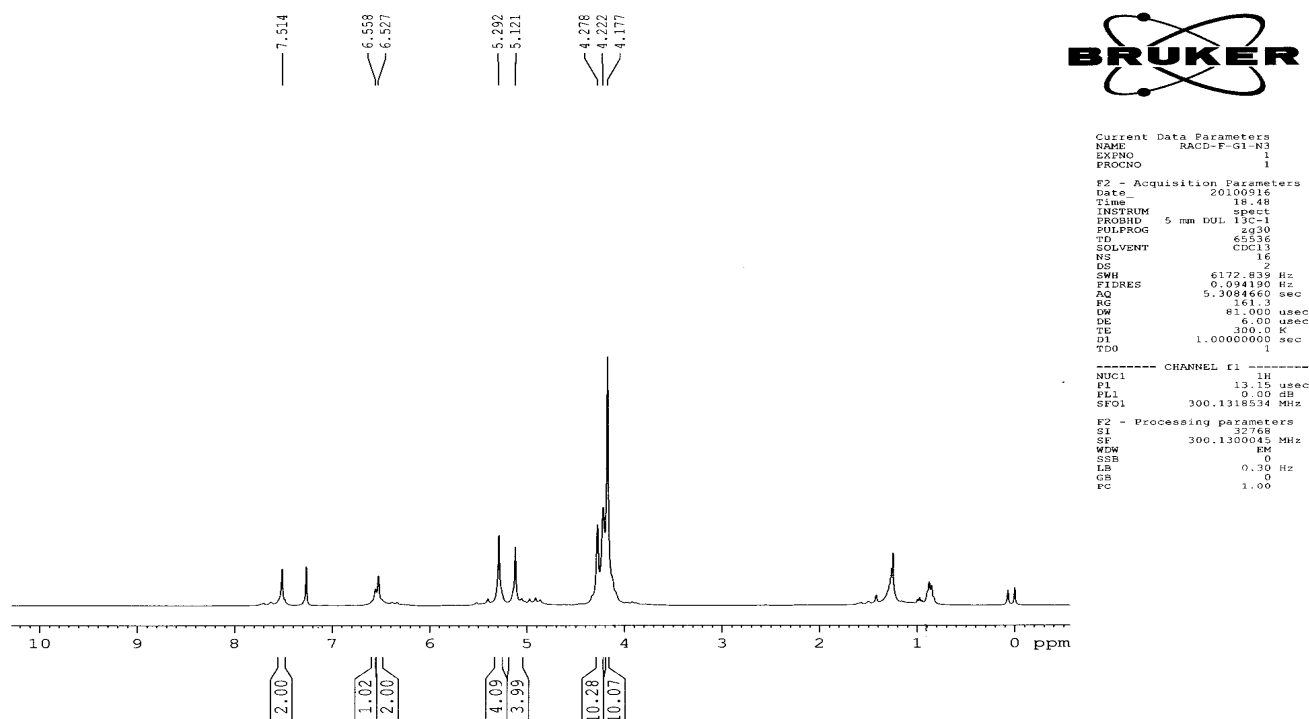
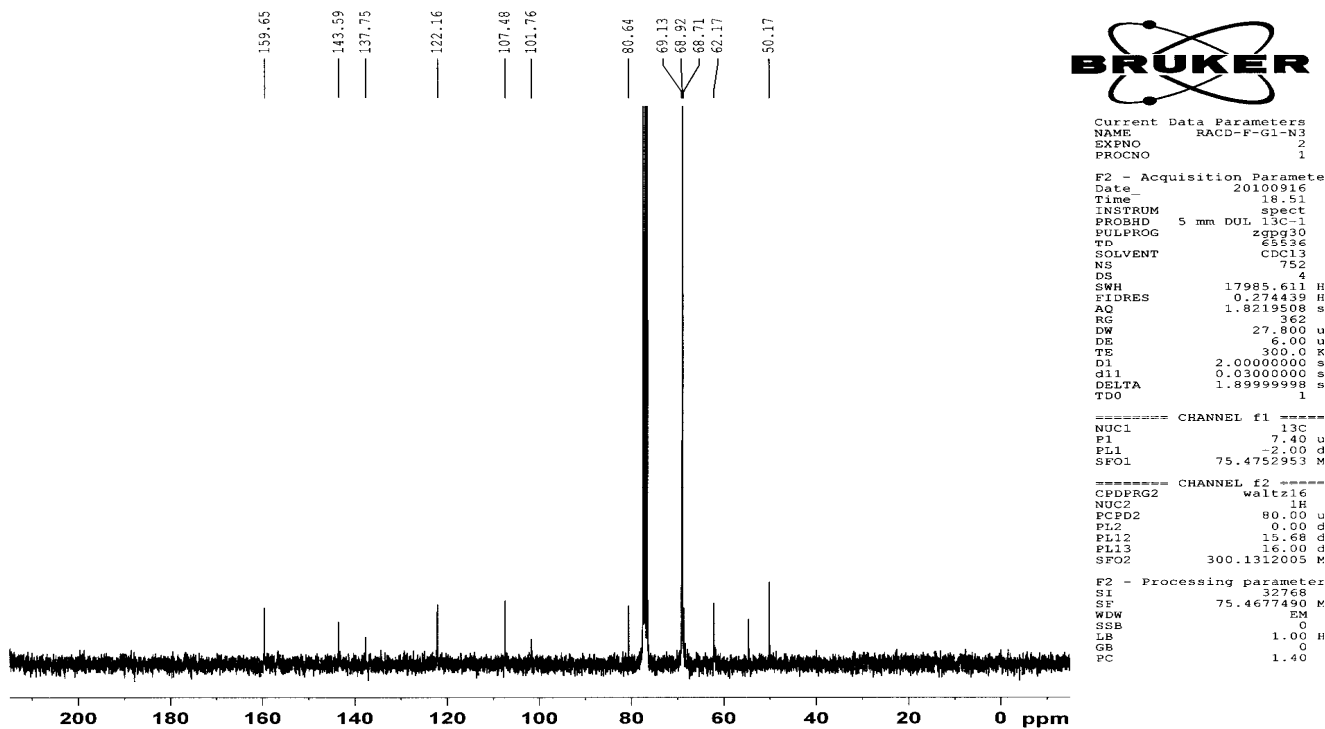


Figure S6: XPS spectrum of Au nanoparticles encapsulated by dendrimer **1**

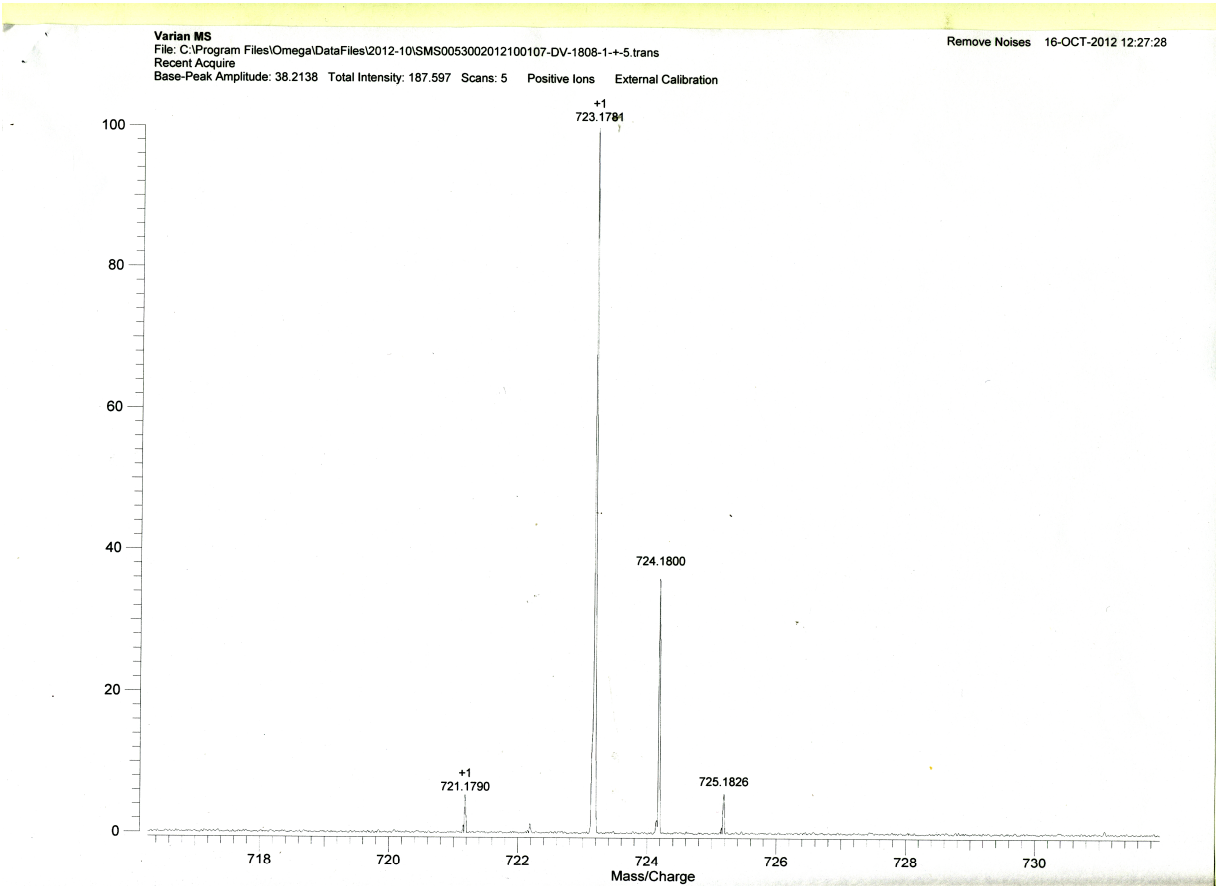
S7: ^1H , ^{13}C NMR and Mass Spectral data of Synthesized Compounds



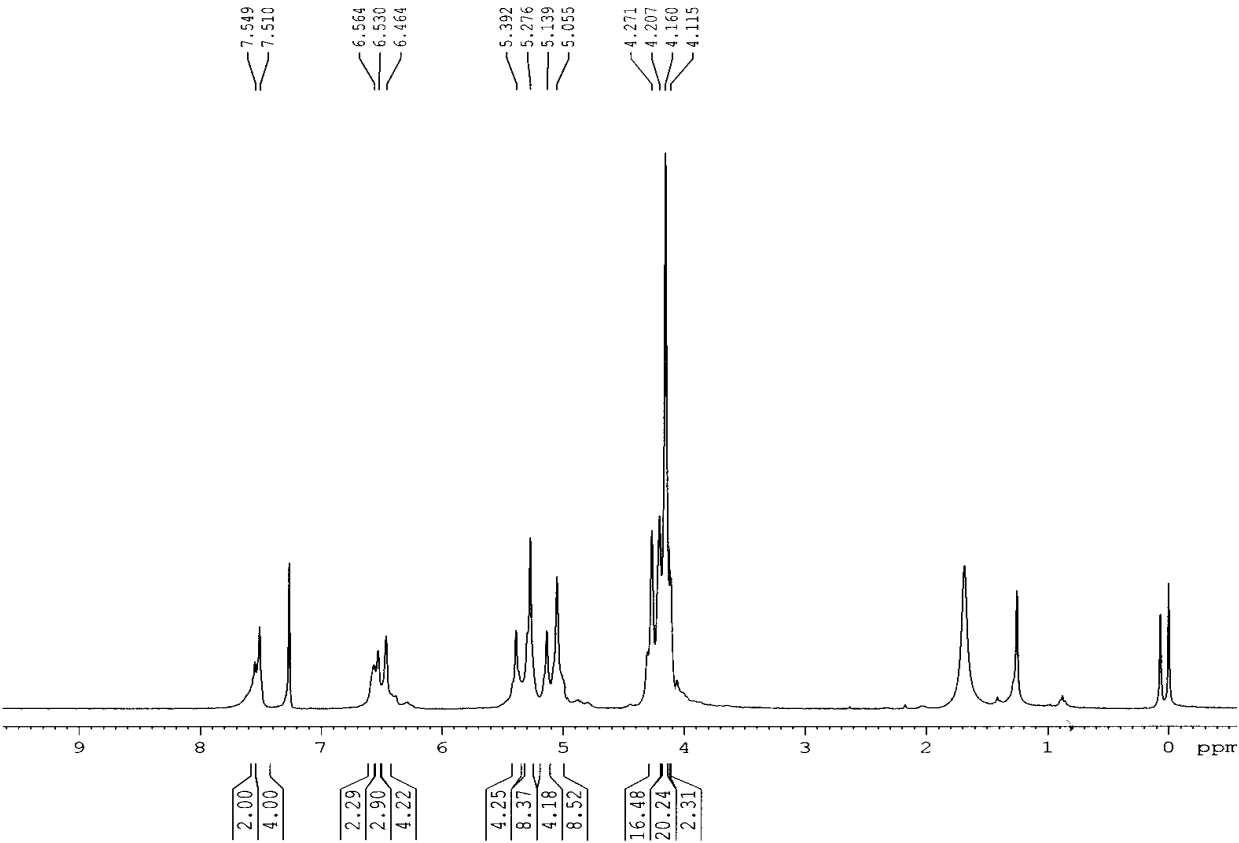
^1H NMR spectrum (300 MHz, CDCl_3) of dendritic azide 6



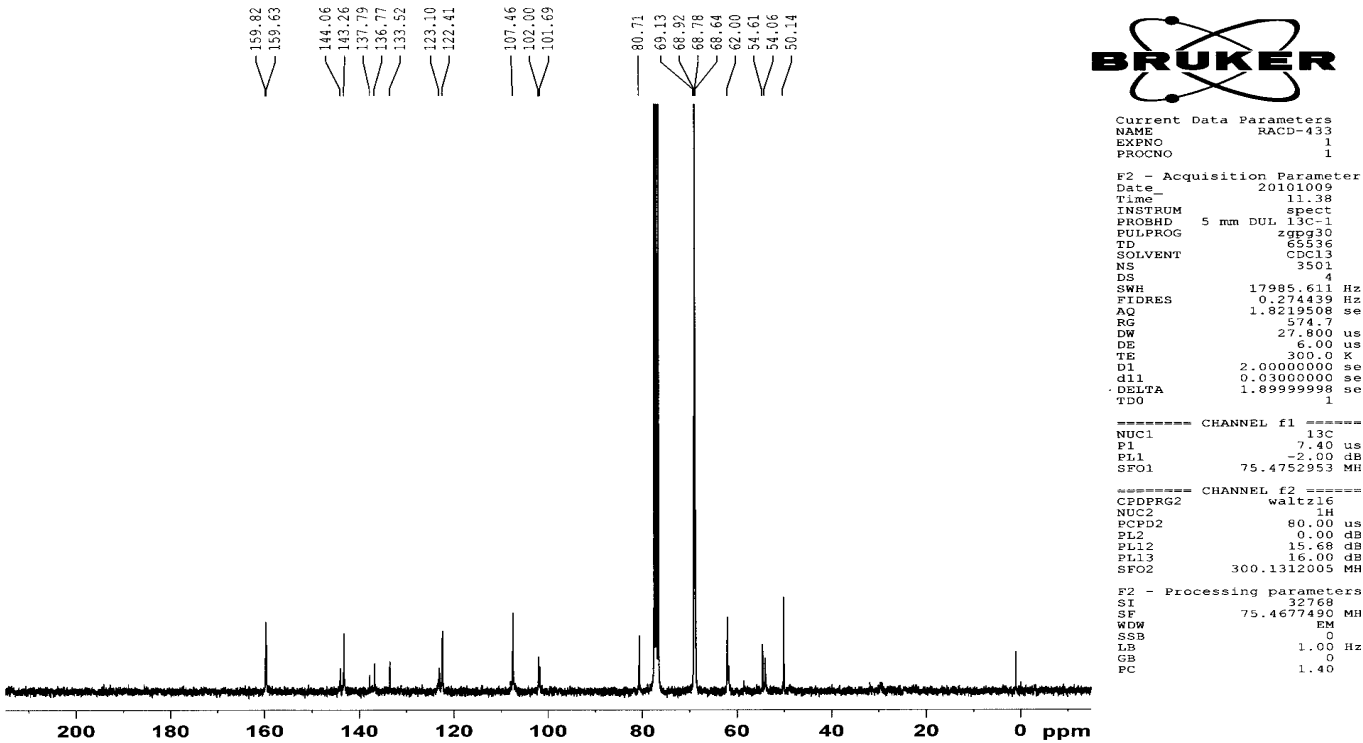
¹³C NMR spectrum (75 MHz, CDCl₃) of dendritic azide 6



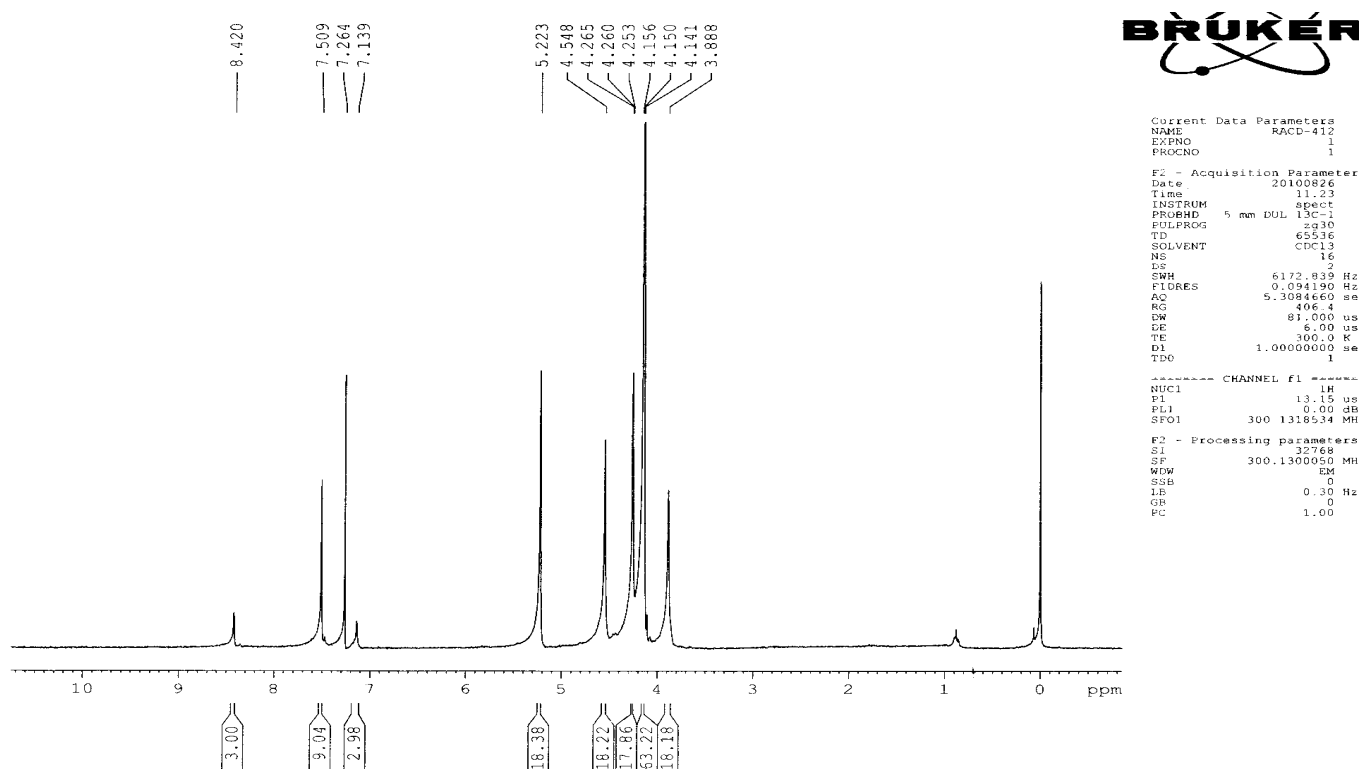
Mass spectrum (ESI) of dendritic azide 6



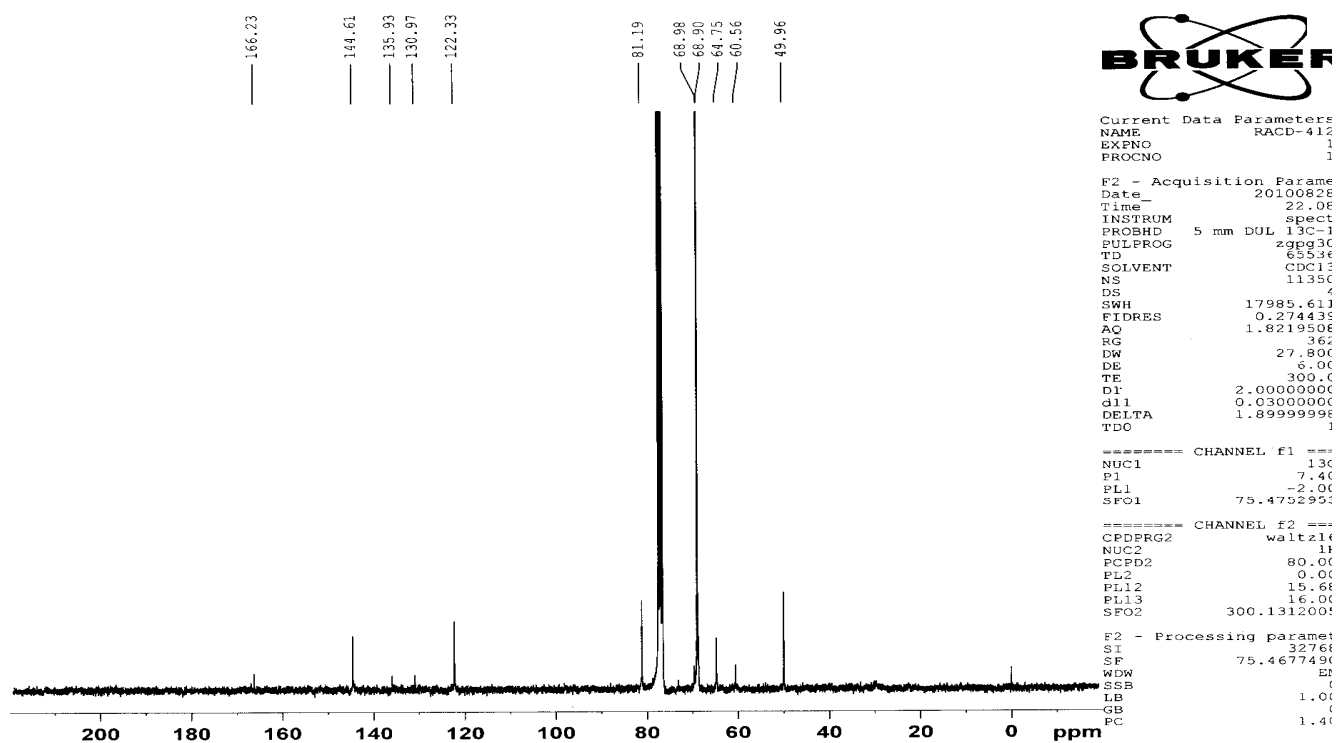
^1H NMR spectrum (300 MHz, CDCl_3) of dendritic azide 7



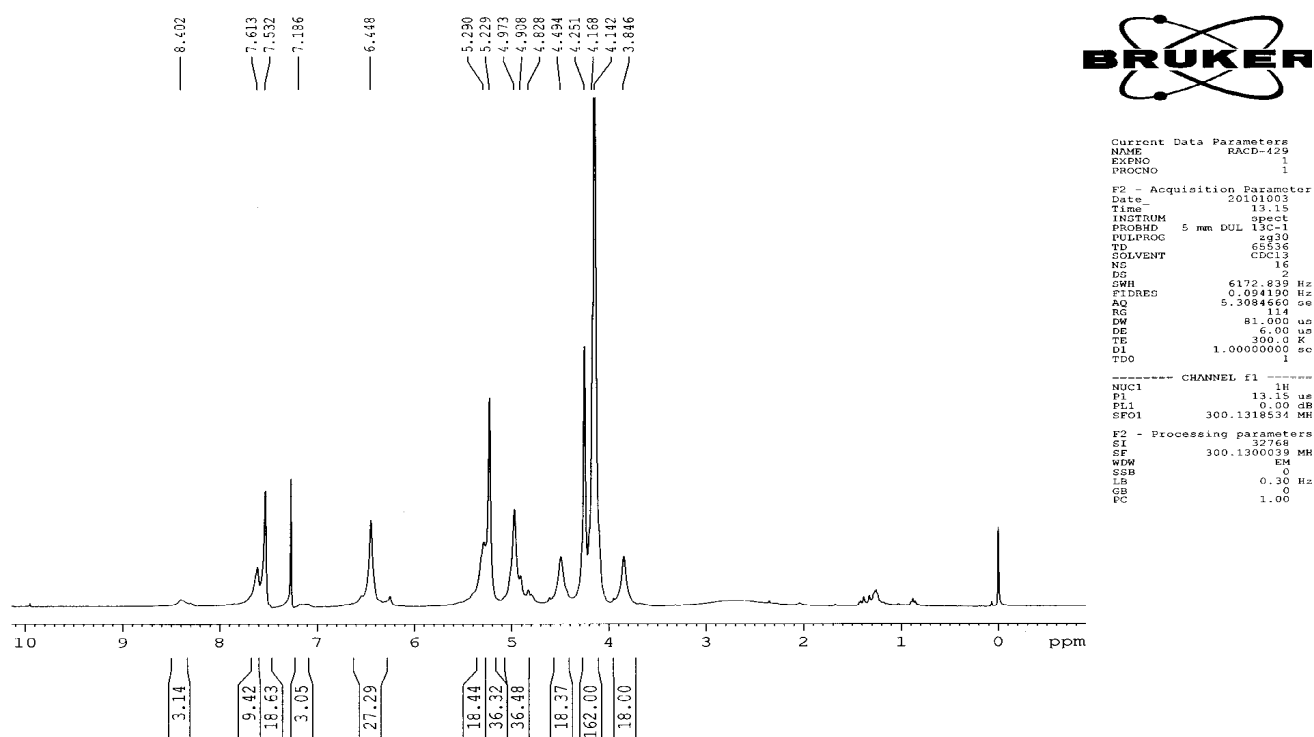
¹³C NMR spectrum (75 MHz, CDCl₃) of dendritic azide 7



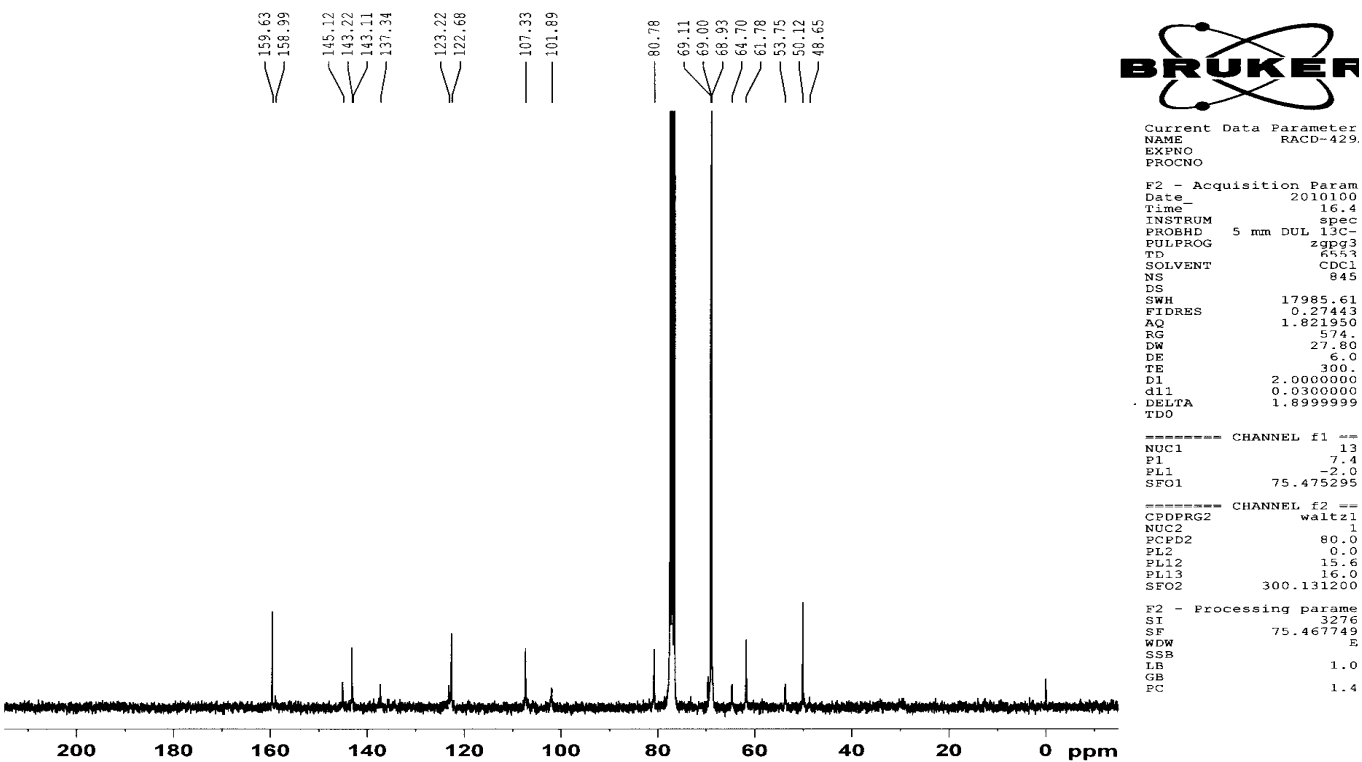
¹H NMR spectrum (300 MHz, CDCl₃) of ferrocenyldendrimer 1



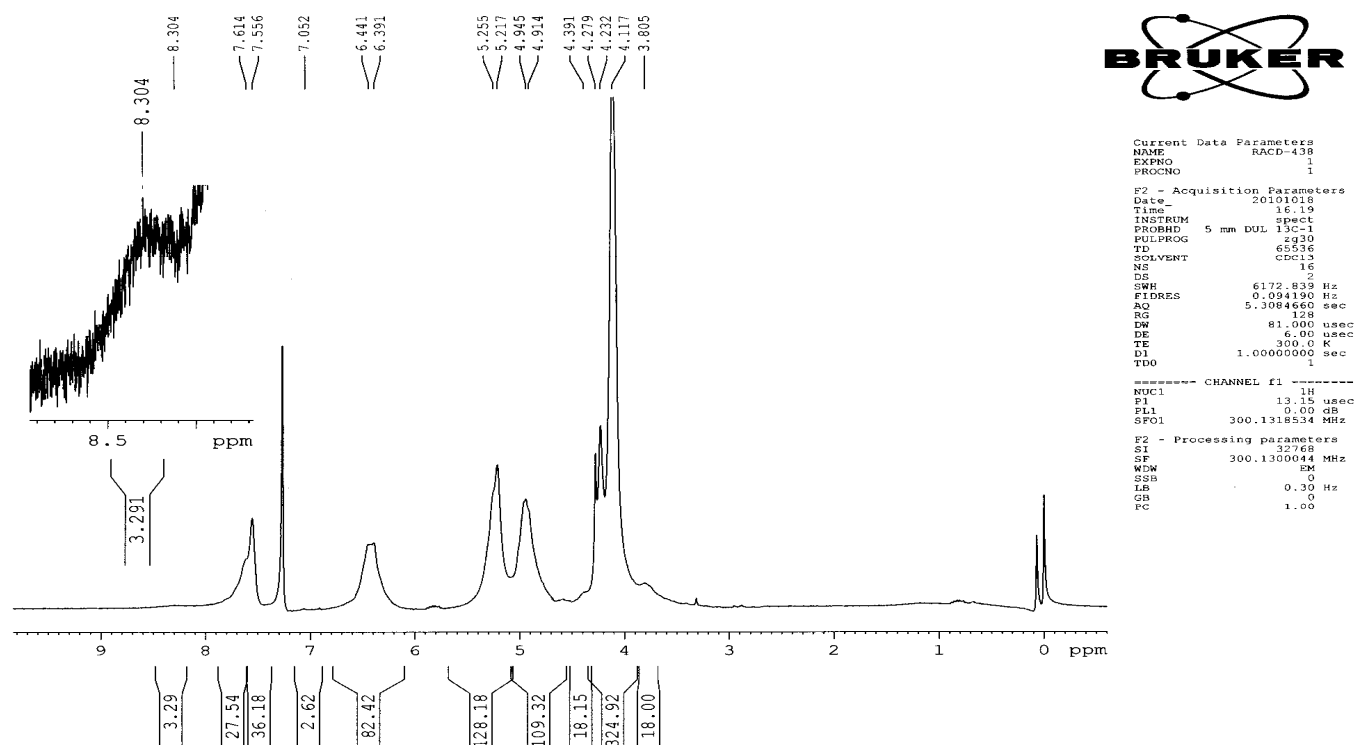
¹³C NMR spectrum (75 MHz, CDCl₃) of ferrocenyldendrimer 1



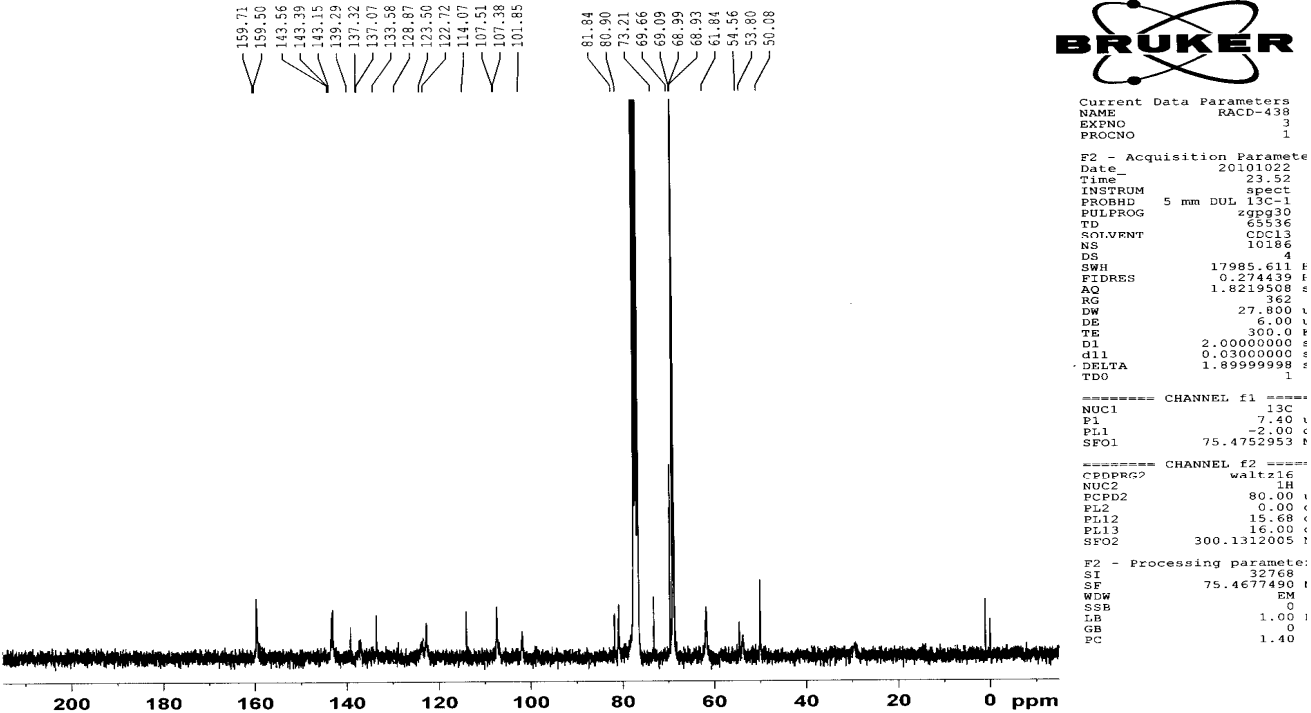
¹H NMR spectrum (300 MHz, CDCl₃) of ferrocenyldendrimer 2



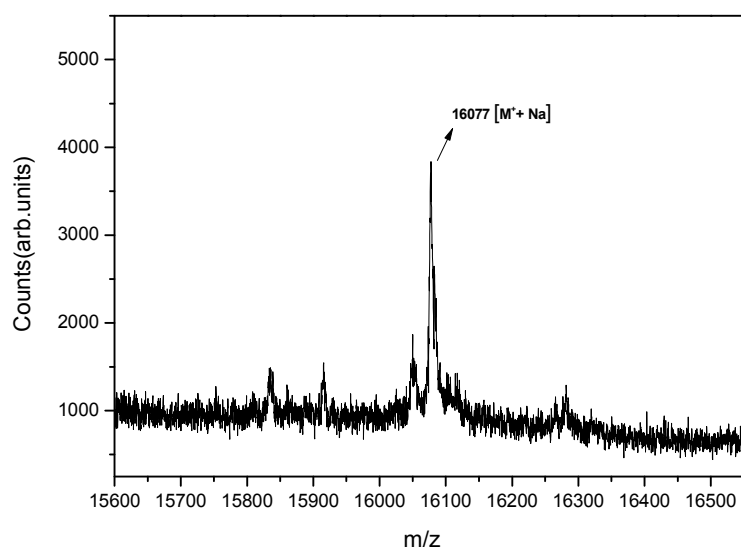
¹³C NMR spectrum (75 MHz, CDCl₃) of ferrocenyldendrimer 2



¹H NMR spectrum (300 MHz, CDCl₃) of ferrocenyldendrimer 3



¹³C NMR spectrum (75 MHz, CDCl₃) of ferrocenyldendrimer 3



Mass (MALDI-TOF) spectrum of ferrocenyldendrimer 3