Triazole-Based Ferrocenyl Dendrimers as a Medium for Encapsulated Palladium Nanoparticles

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Abstract: Novel ferrocenyl dendrimers with 1,3,5-tris(aminothiophenol)benzeneamide core has been synthesized through click chemistry under microwave-assisted solid-support technique. The higher-generation ferrocenyl dendrimers can 'sense' and bind palladium nanoparticles (PdNP) by encapsulation whereas the lower-generation dendrimers stabilize the PdNP.

Key words: ferrocenyl dendrimers, click chemistry, microwave, nanoparticles, palladium

Dendrimers which are peripherally functionalized with the electrochemically active ferrocene group can be used as potential multi-electron redox catalysts, electron reservoirs, electrode modifiers, ion sensors, mimics of biological redox processes,[1] and in nanosciences, such as nanoreactors[2] and nanomedicine.[3] The properties of such dendrimers are of great interest because the number of electrochemically active functional groups can be precisely controlled. The electrochemical properties of the ferrocenyl dendrimers are of particular interest in mimic-related nanometer-sized biological processes and provide useful energy-relevant devices. Microwave-assisted synthesis has been utilized as a powerful and effective technique to promote a group of chemical reactions.[4] Huisgen's 1,3-dipolar cycloaddition of alkyne to azide yielding triazole is, undoubtedly, the premier example of 'click chemistry' reactions.[5] The mechanistic proposal of the Cu(I)-catalyzed alkyne–azide 1,3-dipolar cycloaddition was reported and implicated a polar transition state, favorable for microwave activation.[6]

The dendrimer chemistry offers some significant advantages for preparing nanoparticles in the size range of 1–2 nm. One of the most remarkable examples of dendritic encapsulation is that of transition-metal nanoparticles (NP) that was disclosed more than a decade ago using polyamidoamine (PAMAM) dendrimer[7] and polypropyleneimine (PPI) dendrimer.[8] In particular, NP encapsulation has been applied to many transition metals including the use of a redox reaction between a NP and other metal cations. Most of the advantages arise by the presence of the dendrimer, which can template and stabilize the encapsulated nanoparticles. The synthesis and stabilization of transition-metal NP inside dendrimers has created a timely entry to their application in catalysis and nanosciences.[9] The 1,2,3-triazole branching unit in dendrimer synthesis has been achieved through click chemistry,[10] followed by reduction of Pd(II) to Pd(0) which can agglomerate as PdNP protected by the dendrimer frame.[11]

More recently, the synthesis of triazole ferrocenyl dendrimers, which can recognize and 'sense' several transition-metal ions by using the variation of the potential of the ferrocenyl wave, has been reported.[12] Astruc and coworkers[13] reported an interesting family of ferrocenyl triazolyl dendrimers by click reaction and applied them as templates and hosting agents for PdNP and found that 1,2,3-triazole units formed by click reaction are capable of binding $Pd(OAc)_2$ in one-to-one stoichiometry. As evidenced by the change of redox wave of ferrocenyl units in cyclic voltammetry, the complexation occurs in order, from inner to outer, if the dendrimer contains more than one layer of triazole units. Herein we report the synthesis of ferrocenyl dendrimers **1**–**4** (Figure 1) through click chemistry under microwave-assisted solid-support technique and their stabilization effect on palladium nanoparticles.

Reaction of 3,5-bis(propargyloxy)benzyl chloride (**6**) with two equivalents of azidomethyl ferrocene **5** under microwave-catalyzed click-reaction conditions using Na_2SO_4 as a solid support gave first-generation ferrocenyldendritic chloride **7** in 96% yield (AB_2-type). The use of NaN_3 in a mixture of acetone and water (4:1) at 60 °C allowed the transformation of the ferrocenyldendritic chloride **7** to the corresponding ferrocenyldendritic azide **8** in 98% yield (Scheme 1). 3,5-Bis(propargyloxy)benzylchloride (**6**)[14] and 3,4,5-tris(propargyloxy)benzylchloride (**9**)[14] were prepared by the conventional propargylation of methyl 3,5-dihydroxy benzoate and methyl 3,4,5-trihydroxy benzoate, respectively, followed by treatment with LAH and further with thionyl chloride and pyridine in dichloromethane. Reaction of 2-aminothiophenol with 3,5-bis(propargyloxy)benzyl chloride (**6**) or rather 3,4,5-tris(propargyloxy)benzyl chloride (**9**) in toluene and aqueous KOH in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB) as phase-transfer catalyst at reflux furnished 3,5-bis(propargyloxy)benzyl-2-aminothiophenol (**10**) and 3,4,5-tris(propargyloxy)-benzyl-2-aminothiophenol (**11**) in 86% and 79% yields, respectively.[15,16] Reaction of three equivalents of 3,5-bis(propargyloxy)benzyl-2-aminothiophenol (**10**) or rather 3,4,5-tris(propargyloxy)benzyl-2-aminothiophenol (**11**)

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with one equivalent of benzene-1,3,5-tricarboxylic acid chloride in the presence of Et_3N in dry dichloromethane at room temperature under N_2 afforded the amide-core-based propargylated dendritic wedges **12** and **13**[17,18] in 75% and 71% yields, respectively.

The ^1H NMR spectrum of propargylated dendritic wedge **13** displayed two different triplets for the two different acetylene protons at $\delta = 2.34$ and 2.45 ppm, and a singlet for *S*-methylene protons at $\delta = 3.89$ ppm and an NH proton as a broad singlet at $\delta = 9.\ 31$ ppm. In the ^{13}C NMR spectrum, the propargylated dendritic wedge **13** displayed the two different acetylene carbons at $\delta = 75.3$ and 75.9 ppm, the *S*-methylene carbon at $\delta = 41.8$ ppm, and the carbonyl carbon at $\delta = 168.7$ ppm. The FTIR spectrum also showed the carbonyl stretching frequency at 1639 cm^{-1} for the propargylated dendritic wedge **13**. The click chemistry on the propargylated dendritic wedge **12** and **13** with azidomethyl ferrocene **5** and dendritic azide **8** under microwave-assisted click-reaction conditions with solid support (Na_2SO_4) as mentioned earlier gave ferrocenyl dendrimers **1**–**4**[19–23] in 96%, 84%, 87%, and 77% yields, respectively (Scheme 2). The ^1H NMR spectrum of dendrimer **4** displayed a sharp singlet at $\delta = 4.94$ and 5.22 ppm for the *O*-mehtylene and *N*-methylene protons, the two different triazolyl protons and amide protons are represented as a singlet at $\delta = 7.57$, 7.61, and 9.51 ppm, respectively in addition to other aliphatic and aromatic protons. The ^{13}C NMR spectrum of **4** displayed ferrocenyl methylene carbons at $\delta = 61.8$ and 80.8 ppm, respectively, and the carbons at $\delta = 68.8$, 68.9, and 69.0 ppm, the *O*-methylene and *N*-carbons at $\delta = 68.8$, 68.9, and 69.0 ppm, the *O*-methylene and *N*-methylene carbons at $\delta = 61.8$ and 80.8 ppm, respectively. The triazole and amide carbons appeared at $\delta = 143.2$, 143.4, 143.8, and 163.1 ppm, respectively, in addition to other aliphatic and aromatic carbons. The appearance of the molecular ion peak at *m/z* = 7821 [M^+ + Na] also confirmed the structure of ferrocenyl dendrimer **4**. Similarly, the structure of the three other dendrimers **1**–**3** is confirmed from the spectral and analytical data.

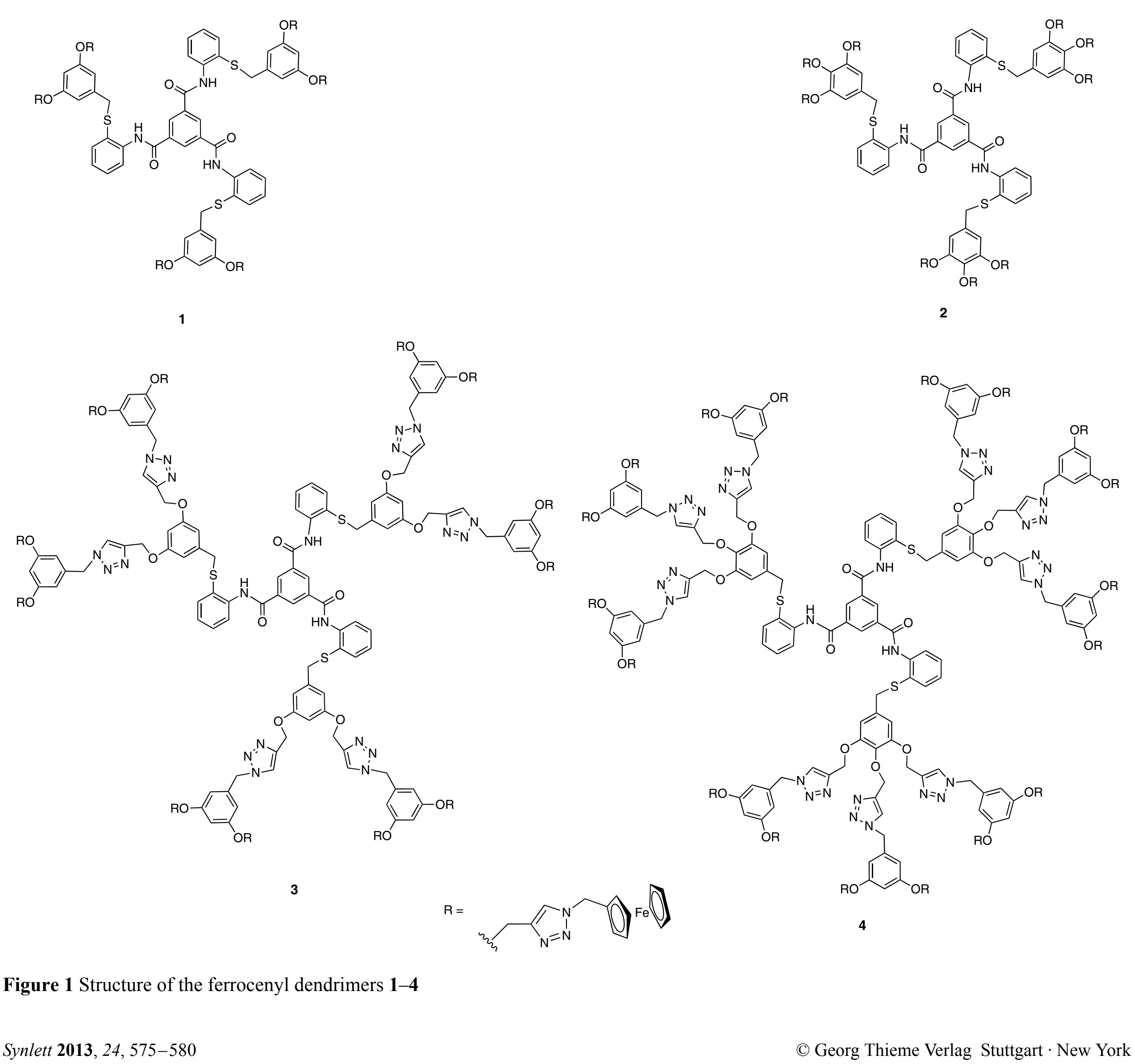
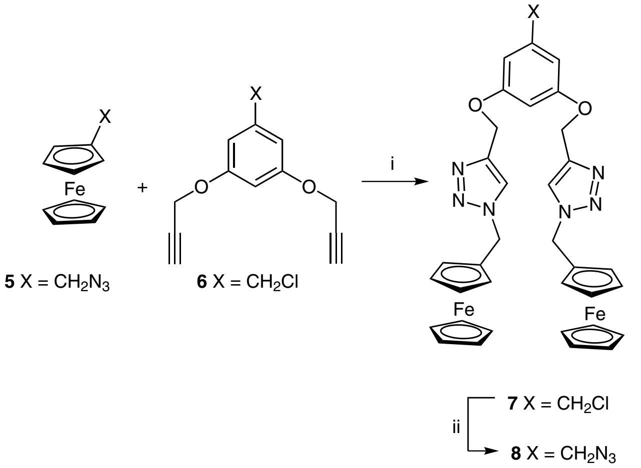


Figure 1 Structure of the ferrocenyl dendrimers **1**–**4**



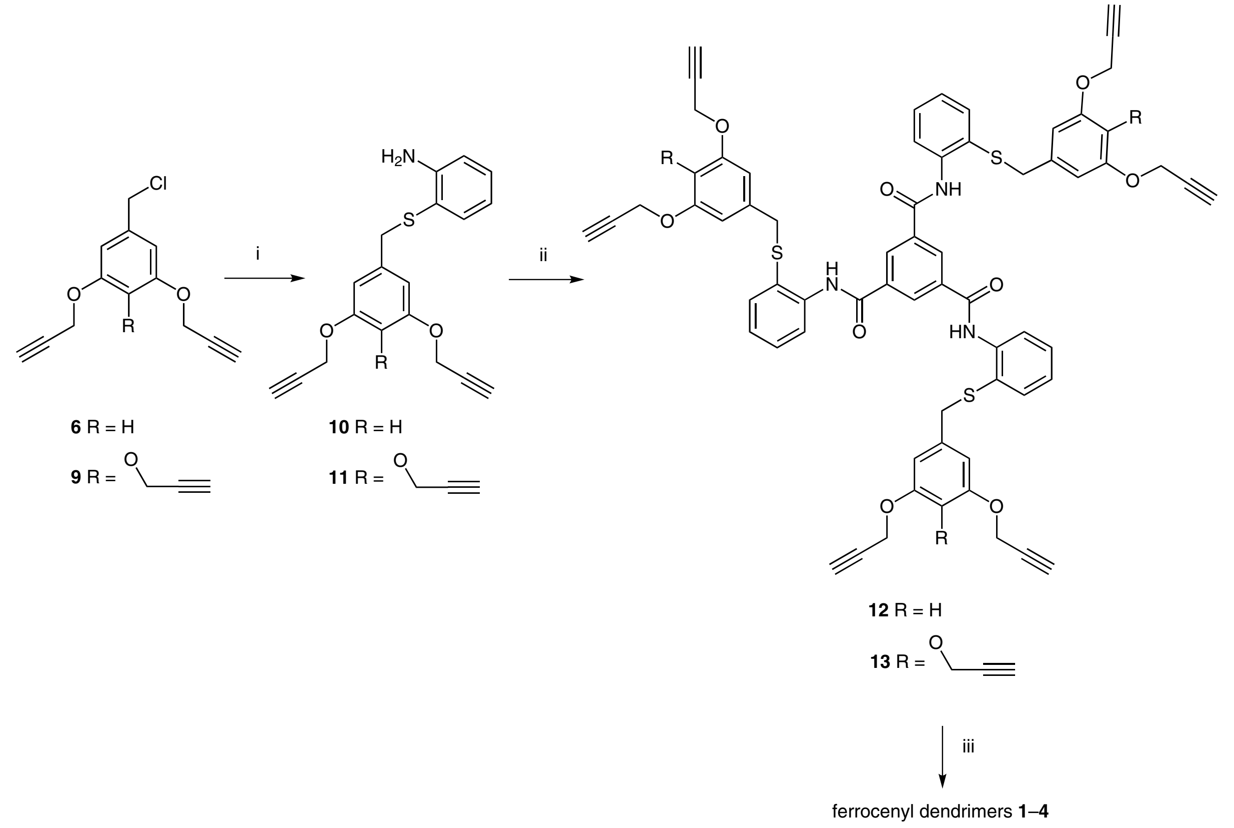
Scheme 1 *Reagents and conditions*: (i) Na_2SO_4, $CuSO_4$ (5 mol%), sodium ascorbate (10 mol%), MW (80 W), 1 min; (ii) NaN_3 (1.5 equiv), acetone–H_2O, 60 °C, 3 h.

The PdNP[24] were synthesized by reaction between the ferrocenyl dendrimers containing triazolyl groups with a stoichiometric amount of $PdCl_2$ (1 equiv per triazole unit) in a mixture of chloroform and methanol (2:1), followed by addition of $NaBH_4$ (10 equiv per Pd) as reducing agent. Though methanol is able to reduce $PdCl_2$ to Pd(0), which could retain the Pd(0) atoms inside the dendrimer, in the present investigation a combination of MeOH and $NaBH_4$ is used. Addition of $NaBH_4$ not only helps the reaction to proceed faster but also generates PdNP of smaller size. The formation of the NP was observed by the color change of the solution from yellow to golden brown and confirmed by UV-vis spectroscopy (Figure 2). The UV-vis spectrum of the ferrocenyl dendrimer **1** (DEN-6 tethers) and ferrocenyl dendrimer **4** (DEN-18 tethers) show a new band at 326 and 360 nm that corresponds to the formation of PdNP that are stabilized by adsorption of PdNP on the triazole unit of the dendrimers (Table 1).

Table 1 Optical Properties of Ferrocenyl Dendrimers **1** and **4** before and after Addition of $PdCl_2$ and $NaBH_4$ (PdNP)[a]

Entry	Dendrimers at λ_{max} (nm)	Dendrimers with $PdCl_2$ at λ_{max} (nm)	Dendrimers with PdNPs at λ_{max} (nm)
Dendrimer **1**	239	241	360
Dendrimer **4**	243	245	326

[a] PdNP that are stabilized by adsorption of PdNP on the triazole unit of the dendrimers.



Scheme 2 *Reagents and conditions*: (i) 2-aminothiophenol, TBAB, toluene–H_2O, reflux, 12 h; (ii) benzene-1,3,5-tricarboxylic acid chloride, Et_3N, CH_2Cl_2 (dry), 24 h; (iii) azidomethyl ferrocene **5** (6 and 9 equiv) and dendritic azide **8** (6 and 9 equiv), $CuSO_4$ (5 mol %), sodium ascorbate (10 mol%), MW (80 W), 1 min.

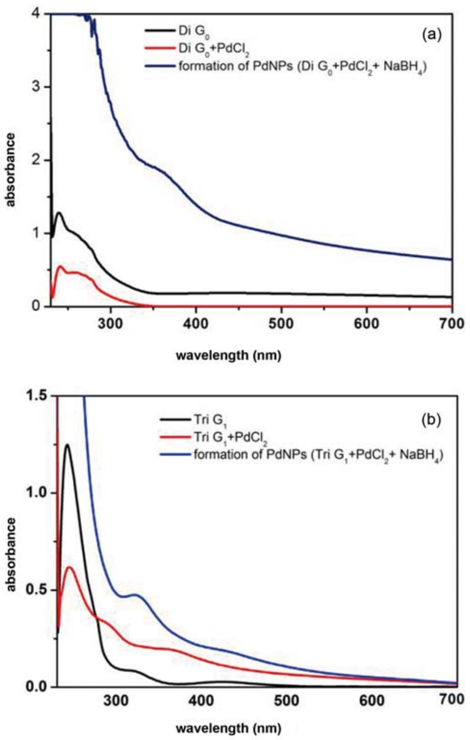


Figure 2 (a) UV-vis spectra of PdNP stabilized by ferrocenyl dendrimer **1**; (b) UV-vis spectra of PdNP stabilized by ferrocenyl dendrimer **4**.

The size of the PdNP generated using the ferrocenyl dendrimers is controlled due to the complexation of the ferrocenyltriazolyl unit to Pd(II) and thus the ferrocenyl group plays an important role. It blocks the periphery, which retains the Pd(0) atoms inside the dendrimer, and consequently leads to the formation of very small PdNP. Thus, the size of the generated PdNP is controlled by the dendrimer generations. Transmission electron microscopy (TEM) images show that lower-generation ferrocenyl dendrimers **1** and **2** (DEN-6 and DEN-9 tethers) are capable of stabilizing the PdNP of large size (5.3 ± 0.05 and 3.3 ± 0.05 nm). On the other hand, the higher-generation ferrocenyl dendrimers **3** and **4** (DEN-12 and DEN-18 tethers) are able to encapsulate PdNP of small size (1.64 ± 0.05 and 1.32 ± 0.05 nm, Figure 3).

Hence higher-generation ferrocenyl dendrimers **3** and **4** can sense the binding metal to the triazole and block the periphery by encapsulation of the nanoparticles inside the dendrimers better than the lower-generation dendrimers **1** and **2**.

In conclusion various ferrocenyl dendrimers **1**–**4** with an aminothiophenol core has been obtained through click chemistry under microwave-assisted solid-support synthesis. The size of the generated PdNP is controlled by the dendrimer generations. Ferrocenyl dendrimers **1** and **2** stabilizes the PdNP of larger size and ferrocenyl dendrimers **3** and **4** stabilizes the PdNP of smaller size by encapsulation.

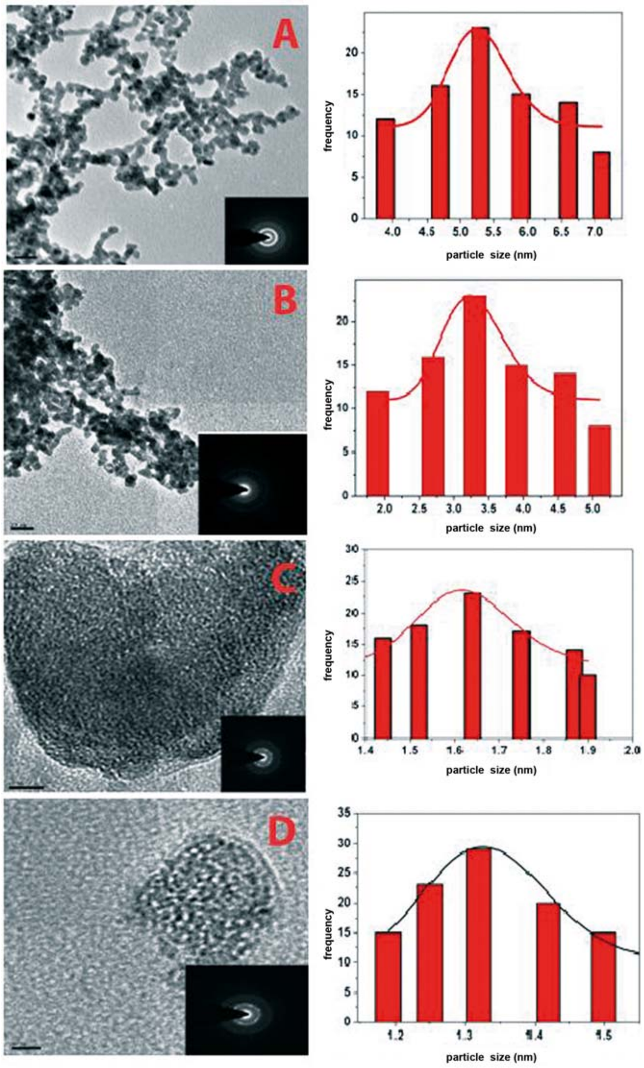


Figure 3 (a) Ferrocenyl dendrimer **1** DEN-6-G_0/PdNP: TEM image and size distribution; (b) ferrocenyl dendrimer **2** DEN-9-G_0/PdNP: TEM image and size distribution; (c) ferrocenyl dendrimer **3** DEN-12-G_1/PdNP: TEM image and size distribution; (d) ferrocenyl dendrimer **4** DEN-18-G_1/PdNP: TEM image and size distribution.

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(15) **General Procedure for the S-Alkylation**
A mixture of propargyloxybenzyl chloride derivatives **6** and **9** (1.0 mmol, 1 equiv), 2-aminothiophenol (1.2 mmol, 1.2 equiv), and TBAB (5 mg), KOH (1.5 mmol, 1.5 equiv), in a mixture of toluene–H_2O (1:1, 40 mL), was refluxed for 4 h. The toluene layer was separated, washed with 5% KOH solution (2 × 10 mL), H_2O (20 mL), and then dried over Na_2SO_4. Toluene was evaporated under vacuum, and the residue obtained was purified by column chromatography with hexane–$CHCl_3$ as eluent to give the corresponding propargyloxybenzyl-2-aminothiophenol.

(16) **3,5-Bis(propargyloxy)benzyl-2-aminothiophenol (10)**
Colorless liquid; yield 86%; R_f = 0.45 (hexane–$CHCl_3$ = 3:7). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.52 (t, J = 2.4 Hz, 2 H), 3.82 (s, 2 H), 4.25 (br s, 2 H), 4.57 (d, J = 2.4 Hz, 4 H), 6.37 (d, J = 2.4 Hz, 2 H), 6.47 (t, J = 2.4 Hz, 1 H), 6.63 (dt, J = 7.5, 1.5 Hz, 1 H), 6.70 (dd, J = 9.0 Hz, 1.2 Hz, 1 H), 7.11 (dt, J = 9.0 Hz, 1.8 Hz, 1 H), 7.23 (dd, J = 7.8 Hz, 1.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 39.7, 55.9, 75.6, 78.4, 101.5, 108.4, 114.9, 117.2, 118.5, 130.1, 136.6, 140.8, 148.7, 158.5 ppm. MS–FAB: *m/z* = 323 [M^+]. Anal. Calcd (%) for $C_{19}H_{17}NO_2S$: C, 70.56; H, 5.30; N, 4.33. Found: C, 70.49; H, 5.25; N, 4.31.

(17) **General Procedure for the Amide-Core-Based Propargylated Dendritic Wedge**
A solution of the benzene-1,3,5-tricarboxylic acid chloride (1.0 mmol) in dry CH_2Cl_2 (100 mL) and a solution of the propargyloxy benzyl-2-aminothiophenol derivative **10** or **11** (3.0 mmol) and Et_3N (3.1 mmol) in dry CH_2Cl_2 (100 mL) were simultaneously added dropwise to a well-stirred solution of dry CH_2Cl_2 (500 mL) during 6 h. After the addition was complete, the reaction mixture was stirred for another 6 h. The solvent was removed under reduced pressure, and the residue obtained was then dissolved in CH_2Cl_2 (300 mL), washed with H_2O (2 × 100 mL) to remove $Et_3N{\cdot}HCl$ and then dried over Na_2SO_4. CH_2Cl_2 was evaporated under vacuum, and the residue obtained was purified by column chromatography with $CHCl_3$–MeOH as eluent to give the corresponding amide-core-based propargylated dendritic wedge.

(18) **Dendritic Wedge 13**
Pale yellow solid; yield 71%; R_f = 0.54 ($CHCl_3$–MeOH = 99:1); mp 79 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (t, J = 2.4 Hz, 3 H), 2.45 (t, J = 2.4 Hz, 6 H), 3.90 (s, 6 H), 4.49 (d, J = 2.4 Hz, 12 H), 4.55 (d, J = 2.4 Hz, 6 H), 6.36 (s, 6 H), 7.13 (dt, J = 7.5, 0.9 Hz, 3 H), 7.44 (dt, J = 7.8 Hz, 1.2 Hz, 3 H), 7.52 (dd, J = 7.5 Hz, 1.2 Hz, 3 H), 8.47 (d, J = 7.8 Hz, 3 H), 8.70 (d, J = 1.5 Hz, 3 H), 9.31 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 41.8, 56.9, 60.2, 75.3, 75.9, 78.3, 79.0, 108.8, 120.8, 123.5, 125.0, 130.3, 130.6, 131.1, 131.4, 133.8, 135.8, 136.3, 139.9, 151.5, 163.1, 168.7 ppm. MS–FAB: *m/z* = 1287 [M^+]. Anal.Calcd (%) for $C_{75}H_{57}N_3O_{12}S_3$: C, 69.91; H, 4.46; N, 3.26. Found: C, 69.85; H, 4.40; N, 3.21.

(19) **General Procedure for the Microwave-Assisted Solid-Support Click Chemistry**
A mixture of azide **5** (2 equiv, 2.0 mmol)/ **5** (6 equiv, 6.0 mmol/ **5** (9 equiv, 9.0 mmol)/ **8** (6 equiv, 6.0 mmol)/ **8** (9 equiv, 9.0 mmol) and alkyne dendron **6**/**12**/**13**/**12**/**13** (1 equiv, 1.0 mmol) each in Na_2SO_4 (0.5 g) in the presence of $CuSO_4{\cdot}5H_2O$ (5 mol%) and NaAsc (10 mol%) was kept under microwave irradiation (80 W) for 1 min. The crude residue was treated with H_2O (150 mL) for 10 min in order to resume all the Cu(I) trapped in the dendrimer as $Cu(NH_3)_6^+$ and then extracted with $CHCl_3$ (2 × 150 mL). The organic layer was separated, washed with brine (1 × 150 mL), dried over Na_2SO_4, and evaporated to give the crude triazole, which was purified by column chromatography (SiO_2), using the eluent as mentioned under each compound.

(20) **Ferrocenyl Dendrimer 1**
Pale yellow solid; yield 96%; R_f = 0.52 ($CHCl_3$–MeOH, 25:3); mp 111–113 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 6 H), 4.14, 4.16, 4.18 (s, 54 H, Cp), 4.73 (s, 12 H), 5.18 (s, 12 H), 6.17 (s, 6 H), 7.13 (t, J = 7.5 Hz, 3 H), 7.37 (t, J = 7.2 Hz, 3 H), 7.47 (s, 6 H), 7.54 (t, J = 8.1 Hz, 3 H), 8.38 (s, 3 H), 8.41–8.47 (m, 6 H), 9.41 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.0, 61.8 [68.9, 69.0 (2 C), Cp], 80.9, 107.4, 121.0, 122.3, 122.5, 124.3, 125.1, 128.8, 130.2, 135.4, 135.9, 139.9, 140.0, 143.4, 159.3, 163.0 ppm. MS (MALDI-TOF): *m/z* = 2595 [M^+ + Na]. Anal. Calcd (%) for $C_{132}H_{117}Fe_6N_{21}O_9S_3$: C, 61.62; H, 4.58; N, 11.43. Found: C, 61.53; H, 4.54; N, 11.52.

(21) **Ferrocenyl Dendrimer 2**
Pale yellow solid; yield 84%; R_f = 0.65 ($CHCl_3$–MeOH, 25:1); mp 116–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.75 (s, 6 H), 4.12, 4.17, 4.18 (s, 81 H, Cp), 4.78 (s, 12 H),

4.87 (s, 6 H), 5.10 (s, 6 H), 5.17 (s, 12 H), 6.24 (s, 6 H), 7.11 (t, J = 7.5 Hz, 3 H), 7.36 (t, J = 7.8 Hz, 3 H), 7.43 (d, J = 7.8 Hz, 3 H), 7.53 (s, 6 H), 7.61 (s, 3 H), 8.32 (d, J = 8.4 Hz, 3 H), 8.43 (s, 3 H), 9.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.8, 50.0, 62.9 [68.9, 69.0 (2 C), Cp], 81.2, 81.6, 108.1, 122.9, 123.3, 124.3, 125.1, 128.9, 130.1, 130.2, 133.6, 135.6, 136.1, 136.6, 139.9, 143.4, 143.6, 152.0, 163.1 ppm. MS (MALDI-TOF): *m/z* = 3481 [M^+ + Na]. Anal. Calcd (%) for $C_{174}H_{156}Fe_9N_{30}O_{12}S_3$: C, 60.43; H, 4.53; N, 12.15. Found: C, 60.47; H, 4.50; N, 12.01.

(22) **Ferrocenyl Dendrimer 3**
Pale yellow solid; yield 87%; R_f = 0.50 ($CHCl_3$–MeOH, 20:3); mp 135–137 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.71 (s, 6 H), 4.13, 4.24, (s, 108 H, Cp), 4.67 (s, 12 H), 4.88–4.95 (m, 24 H), 5.22–5.32 (m, 36 H), 6.13 (s, 6 H), 6.39–6.46 (m, 21 H), 7.04 (s, 6 H), 7.24 (s, 3 H), 7.51 (s, 18 H), 8.28 (s, 3 H), 8.37 (s, 3 H), 9.39 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.1, 61.9, 61.88 [68.9, 69.0 (2 C), Cp], 80.9, 107.4, 107.8, 109.7, 115.5, 120.4, 122.7, 123.1, 122.8, 129.0, 131.0, 135.4, 137.8, 139.3, 144.1, 143.2, 143.5, 159.5, 159.7 ppm. MS (MALDI-TOF): *m/z* = 5490 [M^+ + Na]. Anal. Calcd (%) for $C_{276}H_{249}Fe_{12}N_{57}O_{21}S_3$: C, 60.64; H, 4.59; N, 14.60. Found: C, 60.51; H, 4.50; N, 14.48.

(23) **Ferrocenyl Dendrimer 4**
Pale yellow solid; yield 77%; R_f = 0.72 ($CHCl_3$–MeOH, 5:1); mp 163–164 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 4.13, 4.23 (s, 162 H, Cp), 4.94 (s, 54 H), 5.22 (s, 54 H), 6.43 (s, 33 H), 7.02–7.14 (m, 6 H), 7.28–7.30 (m, 3 H), 7.57 (s, 18 H), 7.61 (s, 9 H), 8.46–8.51 (m, 6 H), 9.51 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 50.1, 53.8, 54.6, 58.5, 61.7, 61.9 [68.8, 68.9, 69.0, 69.1, Cp], 80.8, 80.9, 100.9, 101.8, 107.4, 107.7, 122.6, 123.3, 123.5, 124.7, 125.2, 128.9, 130.3, 131.3, 133.6, 134.3, 135.3, 135.4, 136.1, 137.0, 137.4, 139.6, 140.0, 134.2, 143.4, 143.8, 159.3, 159.7, 159.8, 163.1 ppm. MS (MALDI-TOF): *m/z* = 7821 [M^+ + Na]. Anal. Calcd (%) for $C_{390}H_{354}Fe_{18}N_{84}O_{30}S_3$: C, 60.06; H, 4.58; N, 15.09. Found: C, 60.07; H, 4.44; N, 15.00.

(24) **General Procedure for the Preparation of the PdNP**
A solution of ferrocenyl dendrimers (1 mmol, 1 equiv) in $CHCl_3$ (3 mL) was placed in a round-bottom flask under an inert atmosphere. A solution of $PdCl_2$ (6 mmol, 9 mmol, 12 mmol, 18 mmol, 1 equiv per triazole) in a mixture of $CHCl_3$–MeOH (1:10, 0.5:5 mL) was added to this solution and stirred continuously r.t. for 3 h. The solution was stirred for 5 min and $NaBH_4$ (10 mmol, 10 equiv per Pd) was added dropwise, and the yellow solution turned to golden brown indicating the formation of PdNP.