Design, Synthesis and Self-Assembly of Functional Amphiphilic Metalloendrimers

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Dedicated to Prof. Jean-Marie Lehn on the occasion of his 80th birthday

A new family of alkynylated, amphiphilic dendrimers consisting of amidoamine linkers connected to 2,2'-bipyridine cores has been developed and evaluated in the formation of metalloendrimers of different generations and in self-assembly protocols. A convergent synthetic strategy was applied to provide dumbbell-shaped amphiphilic dendrimers, where the 2,2'-bipyridine cores could be coordinated to Fe³⁺ centers to afford corresponding metalloendrimers. The ability of the metallic- and non-metallic dendritic structures to self-assemble into functional supramolecular aggregates were furthermore evaluated in aqueous solution. Spherical aggregates with sizes of a few hundred nanometers were generally produced, where controlled disassembly of the metalloendrimers through decomplexation could be achieved.

1. Introduction

Dendrons and dendrimers are well-defined, branched molecular structures with typically wedge-like or spherical shapes. These highly tunable structures are generally prepared via divergent or convergent syntheses, where especially the multiple end groups at the peripheries can be straightforwardly functionalized.[1–3] Dendrimer surface modification improves many properties such as improved solubilities and increased reactivities,[4–6] as well as enhanced structural stabilities.[7] This facilitates many potential applications, including liquid crystal formation,[7] catalysis,[8,9] biosensing/biorecognition,[10,11] light-emitting materials,[12–14] and targeted delivery.[15–19] Various biomolecular structures have furthermore been conjugated to dendrimer surfaces for various biomedical applications.[20–23] Dendritic molecules have moreover been pursued in the fabrication of supramolecular self-assemblies.[24,25] Assembly of the primary units into larger and more complex entities thus leads to a wide range of potential applications, for example, in the fields of drug delivery, biomedicine and nanotechnology.[26,27] However, adequate supramolecular interactions are generally required for dendrimer self-assembly,[28] for example, H-bonding, π-π interactions, donor-acceptor interactions, or metal-ligand coordination.[29] Therefore, appropriate amphiphilic dendritic structures consisting of hydrophilic and hydrophobic segments, able to assemble through van der Waals’ interactions and solvophobic effects, have witnessed great interest as building blocks, and have been employed to create a variety of functional materials.[30] In addition, reversible binding that can be controlled by external stimuli is of primary importance in dynamic assembly applications, where non-covalent interactions and reversible covalent bonds are key to achieve the desired effects.[30–32] In this context, metal coordination occupies an established position for building discrete and well-defined structures with controlled formation and disassembly profiles.[33,34] Supramolecular metal coordination complexes thus provide a useful foundation for self-assembly protocols, where a large variety of coordination geometries can be employed, with bond strengths ranging from very labile coordination to covalent bond energies.[35] In principle, these features enable tunable and controllable formation of aggregates that are assembled through metal coordination, amenable for a wide variety of applications.[36,37]

Despite tremendous achievements in generating self-assembled structures based on, for example, amphiphilic effects, H-bonding or metal coordination, the development of dendrimers as building blocks for well-organized supramolecular architectures remains challenging. Examples include assembly of oligo(amidoamine) dendrimers,[35] and prototypic peptide-based amphiphilic dendrimers showing similarities with globular proteins.[36] This has been addressed in the present study, where we describe the design and development of a new family of amphiphilic dendrimer structures based on 2,2'-bipyridine cores functionalized with amidoamine branches carrying multiple alkynylated aryl ether end-groups (Figure 1a). The resulting dumbbell-shaped amphiphilic structures were subsequently evaluated for self-assembly into functional supramolecular nanostructures controlled by metal complexion with Fe³⁺-ions (Figure 1b).
2. Results and Discussion

2.1. Synthesis

The amphiphilic dendrimers were designed as indicated in Figure 1, composed of three different elements: 1) 2,2'-bipyridine cores; 2) hydrophilic amidoamine branches; and 3) alkynylated aryl ether end groups. This results in rod-like, dumbbell-shaped dendrimers with either eight or 16 alkyne groups that can be used for further functionalization, e.g., through alkyne-azide cycloaddition. In addition, the 2,2'-bipyridine core structures enable metal coordination for metallo-dendrimer formation. A convergent synthesis method was adopted, where the dendron branches were first produced, functionalized with aryl ether group, and subsequently conjugated to the 2,2'-bipyridine cores. This modular strategy enables the synthesis of a variety of structures in short time, also applicable to other core structures. The metallocdendrimers could finally be produced from the dendritic structures through metal complexation.

Preparation of the internal, hydrophilic amidoamine dendron branches were achieved through a traditional sequence based on repeated conjugate addition and amidation.[36] One of the amino groups of ethylenediamine (1) was thus first Boc-protected to give compound 3, from which double conjugate addition to acrylic ester 4 yielded compound 5. This diester was subsequently allowed to react with ethylenediamine 1 to provide diamide structure D1G1 (generation 1 dendron). Dendrons of generation 2 (D1G2) could then be synthesized by repeating the conjugate addition and amidation steps of structure D1G1. Both dendron generations were obtained in excellent yields as presented in Figure 2.

Synthesis of the alkynylated, hydrophobic exterior started from esterification of dihydroxybenzoic acid 7 giving ester 8. This ester was then deprotonated and subjected to reaction with propargyl bromide (9) to provide compound 10. Finally, hydrolysis of ester 10 resulted in structure AK in good yield (Figure 3).

Amide coupling of the hydrophilic interior structures (D1G1 and D1G2) with the alkynylated hydrophobic exterior molecule (AK) gave Boc-protected amphiphilic dendrons of generation 1 (11) and 2 (12), respectively. These were then deprotected to provide dendrons D1G1AK and D1G2AK dendrons in excellent yields (Figure 4). Finally, amide coupling of both dendron structures D1G1AK and D1G2AK with core element 2,2'-bipyridine-5,5'-dicarboxylic acid (13) using (benzotriazol-1-yl)tris(dimethylamino)phosphonium hexafluorophosphate (BOP) as coupling agent in dimethylformamide provided the non-metallated (series I) amphiphilic dendrimers of generation 1 and 2 in moderate yields (Figure 5).

Figure 1. Structures of amphiphilic dendrimers and overview of synthetic pathways to supramolecular aggregates.

Figure 2. Synthesis of hydrophilic amidoamine structures (D1G1 and D1G2).

Figure 3. Synthesis of hydrophobic exterior structure AK.

Figure 4. Synthesis of amphiphilic dendrons generation 1 and 2.
The resulting amphiphilic series I-dendrimers (D1G1AK)$_2$BPy and (D1G2AK)$_2$BPy were subsequently subjected to coordination with Fe$^{II}$-ions (metal/ligand 1:3) resulting in both metalodendrimer (series II) complexes (D1G1AK)$_2$BPy-Fe and (D1G2AK)$_2$BPy-Fe) in excellent yields (Figure 6). Complex formation between the dendrimers and Fe$^{II}$ resulted in purple structures, of which the generation 1 structure showed especially deep color. The recorded electronic spectra also displayed remarkably intense charge-transfer (MLCT) bands in the visible region (500–600 nm), in analogy to typical transition-metal bipyridine complexes (Figure 7).[37,38]

**Self-assembly.** Having successfully synthesized the targeted dendritic structures of series I, (D1G1AK)$_2$BPy and (D1G2AK)$_2$BPy, and the metalodendrimers of series II, (D1G1AK)$_2$BPy-Fe and (D1G2AK)$_2$BPy-Fe, their self-assembly properties were investigated. The structures were thus evaluated for their abilities to form large, functional structures through reversible aggregation in aqueous solution. The processes were followed using dynamic light scattering (DLS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).

The results are displayed in Figure 8, clearly showing aggregate formation from all dendritic structures. The obtained amphiphilic dendrimers (series I) and their metal coordination complexes (series II) thus self-assembled into smaller spherical aggregates ranging in size of approximately 125, 200, 155, and 190 nm (DLS), and 100–130, 80–150, 100–200, and 150–200 nm (TEM), for the four different structures (D1G1AK)$_2$BPy, (D1G2AK)$_2$BPy, (D1G1AK)$_2$BPy-Fe, and (D1G2AK)$_2$BPy-Fe, respectively. SEM showed somewhat broader distributions with
assemblies of 100–150, 100–200, 150–500, and 200–800 nm. In all cases, larger aggregates were also seen.

The generation 1-structure of series I (\((D1G1AK)_{2}BPy\)) displayed the smallest size with a low degree of larger assemblies (Figure 8 far left), whereas the analogous generation 2-structure (\((D1G2AK)_{2}BPy\)) showed a broader distribution with assemblies up to approximately 850 nm (Figure 8 middle left). In both cases, the particles showed core-shell morphologies by TEM. Interestingly, the generation 1 metallodendrimer (\((D1G1AK)_{2}BPy-Fe\)) showed a bimodal distribution with a relatively large amount of aggregates around 970 nm in size (Figure 8 middle right). In contrast, the larger metallodendrimers exhibited a narrower distribution, with larger aggregates of approximate 600 nm diameter (Figure 8 far right).

This unique self-assembly behavior, where both the average particle size and distribution varies between the dendritic structures, is effectuated by building block generation and metal complexation. The balance between the hydrophilic amidoamine segments and the lipophilicity of the alkynylated aryl ether segments thus plays a significant role in the control of the resulting supramolecular self-assemblies. This is seen by the size increase of the aggregated structures as a consequence of the larger dendrimers in those two series. In addition, increased sizes of the metallodendrimer assemblies in comparison to their non-metallic counterparts were produced. The metallodendrimers also displayed different properties in terms of morphology, where TEM indicated solid generation 1-structures and hollow generation 2-spheres. Further, from inspection of the SEM micrographs (Figure 8), the presence of concave features (white arrows) in some particles of (\((D1G2AK)_{2}BPy-Fe\)) indicates the possible formation of hollow spherical structures. The proportion of broken spheres is also very low, suggesting that the dendrimeric spheres are robust and difficult to break. This indicates that aggregation of the dendritic structures is dynamically reversible,[39] resulting in the formation of spheres in aqueous solution prior to vacuum treatment during SEM analysis.[39,41]

Supramolecular disassembly. Due to the intriguing self-assembly results, especially regarding the hollow nanostructures obtained with the generation 2 metallodendrimer (\((D1G2AK)_{2}BPy-Fe\)), the disassembly behavior of the spheres was further studied. Both metallodendrimer preparations, (\((D1G1AK)_{2}BPy-Fe\) and (\((D1G2AK)_{2}BPy-Fe\), were thus selected for evaluation of controlled disassembly in the presence of an external stimulus. Based on the metallodendrimer Fe(ii)-bipyridine coordination, competitive binding of ethylenediaminetetraacetate (EDTA) towards iron(II) would thus trigger the supramolecular aggregates to disassemble into the basic dendritic (series I) ligands, thereby changing the expression of the overall system. The process was followed by absorption spectroscopy, but could also be directly observed by the naked eye (Figure 9). Interestingly, the two metallodendrimer systems displayed different behavior in response to the metal complexation competitor. The absorption spectra obtained of the system based on metallodendrimer (\((D1G1AK)_{2}BPy-Fe\) demonstrated a rapid, but partial, decrease of the absorption intensity of the MLCT band over the first 30 min, after which time only minor changes occurred over 30 h (Figure 9a).

In the case of the system based on metallodendrimer (\((D1G2AK)_{2}BPy-Fe\), on the other hand, the MLCT absorption...
intensity progressively decreased as a function of time, reaching nearly complete decomplexation over 30 h (Figure 9b). Moreover, the photographic images in Figure 9c clearly show the metallodendrimer color quenches after exposure to EDTA over 30 h. These results are indicative of stronger complexes between the smaller generation 1-dumbbell dendrimers and iron(II), likely owing to a higher degree of steric hindrance of the larger generation 2-dendrimers around the metal core. The results also support the findings from microscopy, inasmuch as the generation 1-metallodendrimers displayed a more solid appearance, thereby being more resistant to ligand exchange, whereas the hollow generation 2-dendrimers were more accessible to decomplexation.

3. Conclusions

We have developed a new class of amphiphilic, dendritic structures based on a modular approach involving three design elements. The structures thus include 2,2'-bipyridine core structures, amenable to transition metal complexation, linked to internal amidoamine branches of different generation, which are capped with alkynylated aryl ether groups. The structures could be straightforwardly synthesized following a convergent strategy, and showed efficient and branch-dependent metal complexation with iron(II). All structures formed supramolecular aggregates in aqueous solution, showing distinct differences with respect to dendrimer size and metal complexation. Spherical structures of either core-shell, solid or hollow nature were thus observed by microscopy. The metallodendrimers were furthermore responsive to an external stimulus, where decomplexation and associated structural rearrangement occurred in the presence of competitive complexation ligands. These results show that metal coordination not only enables the construction of flexible supramolecular dendrimers, but also possesses the advantage of controlled disassembly and potential release of contained molecules. The structures further provide the opportunity for straightforward modification through the alkyne groups at the dendrimer periphery, giving access to a wide range of structures with various properties. Thus, these multifunctional metallodendrimers constitute an important step toward tunable nanomaterials, offering a means to future applications of functional materials.

Experimental Section

Materials. Triethylamine (Et$_3$N) was distilled over calcium hydride under inert atmosphere, and stored under nitrogen. Anhydrous solvents used in air- and moisture sensitive reactions were dried using a solvent dispensing system (Glass-contour, Inc.) by passing over alumina columns. Water used for supramolecular assembly was obtained from a Millipore Milli-Q system with at least 18.2 MΩ resistivity. Other commercially available compounds and solvents were of HPLC, certified ACS, or reagent grade, and used as received unless otherwise specified. Air- and moisture sensitive reactions were carried out in flame-dried, septum-capped flasks under an atmospheric pressure of nitrogen.

Instrumentation. $^1$H and $^{13}$C NMR spectra were recorded on Bruker Ascend$^{TM}$ 400 or Bruker DMX 500 spectrometers at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) with (residual) solvent as internal reference. J-values are given in hertz (Hz). Thin layer chromatography (TLC) was performed on pre-coated Croma-tosilolos AL Silica gel 60 F254 plates (Merck). Flash column chromatography was carried out on silica gel 60, 0.040–0.063 mm (SDS). Size exclusion column chromatography was performed using Sephadex G-10 columns with methanol as eluent. Electrospray mass spectrometry was performed in positive mode on a Finnigan LCQ Advantage Max LC-MS/MS spectrometer (Thermo Fisher Science). Matrix-assisted laser desorption ionization with time-of-flight (MALDI-TOF) MS spectra were recorded on a Bruker Ultraflex TOF/TOF instrument using 2,5-dihydroxybenzoic acid as matrix. Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer Nano ZS at 20 °C with a backscattering detector at 173°. TEM measurements were performed on a Hitachi H-7650 transmission electron microscope. SEM measurements were performed on a field emission scanning electron microscope with Zeiss Ultra-55 scanning electron microscope. UV absorption spectra were recorded using a Cary 300Bio spectrophotometer.

Synthesis of Amphiphilic Dendrimers
tert-Butyl (2-aminophenyl)carbamate (3). To a solution of ethylendiamidine 1 (5.51 mL, 82.47 mmol) in dichloromethane (40 mL) at 0 °C was added dropwise a solution of di-tert-butyl dicarbonate 2 (3.00 g, 13.74 mmol) in dichloromethane (80 mL). The mixture was stirred overnight at ambient temperature. Following evaporation to dryness under reduced pressure, the resulting solid was redissolved in distilled water (40 mL), filtered, and subsequently extracted with dichloromethane (2 × 40 mL). Evaporation of the solvent and drying afforded product 3 as a white solid (1.80 g, 82 %). $^1$H NMR (500 MHz, CDCl$_3$) δ: 5.31 (br, 1H), 3.03 (t, J = 6.0 Hz, 2H), 2.66 (t, J = 6.0 Hz, 2H), 1.31 (s, 9H), 1.19 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ: 156.3, 79.0, 43.1, 41.6, 28.3.

Diethyl 3,3'-(2-((tert-butoxycarbonyl)amino)ethylazenediyldi)propanoate (5). A methanol solution (4 mL) of N-Boc-ethylenediamine 3 (1.00 g, 6.26 mmol) was added dropwise to a stirred solution of ethyl acrylate 4 (2.67 mL, 25.05 mmol) in methanol (4 mL) at 0 °C. The reaction mixture was allowed to reach room temperature and was kept stirred for 2 d. The volatiles were removed by evaporation and the resulting product dried under vacuum for 3 d, providing compound 5 as a viscous pale yellow oil
tert-Butyl (2-bis((2-aminoethyl)amino)-3-oxopropyl)amine (ethylcarbamate (D1G1)).

To a cold solution (0°C) of ethylenediamine 1 (5.70 mL, 85.49 mmol) in methanol (10 mL), a methanol solution (10 mL) of ethyl ester-terminated amidoamine dendron 5 (2.05 g, 5.70 mmol) was added dropwise within 1 h. The resulting reaction mixture was allowed to reach room temperature and was kept stirred for 5 d. The reaction solvent was removed by evaporation, after which the excess ethylenediamine 1 was removed by azotropic distillation with toluene/methanol, followed by vacuum distillation to remove the remaining toluene. The desired product was further dried under vacuum for 2 d to afford product D1G1 as a viscous amber oil (1.12 g, 96 %).

**Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK)).** Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK) was slowly added to a cold solution (0°C) of diethyl acrylate (126 MHz, CDCl₃) δ: 173.0, 156.4, 79.1, 50.2, 49.0, 45.4, 41.1, 40.9, 33.9, 28.5.

**Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK)).** Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK) was slowly added to a cold solution (0°C) of diethyl acrylate (126 MHz, CDCl₃) δ: 173.0, 156.4, 79.1, 50.2, 49.0, 45.4, 41.1, 40.9, 33.9, 28.5.

**Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK)).** Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK) was slowly added to a cold solution (0°C) of diethyl acrylate (126 MHz, CDCl₃) δ: 173.0, 156.4, 79.1, 50.2, 49.0, 45.4, 41.1, 40.9, 33.9, 28.5.

**Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK)).** Diethyl 11-(2-bis((2-aminoethyl)amino)-3-oxopropyl)-dibromo-1,1-dioxo-(3,5-bis(prop-2-yn-1-yloxy)benzamide (D1G1AK) was slowly added to a cold solution (0°C) of diethyl acrylate (126 MHz, CDCl₃) δ: 173.0, 156.4, 79.1, 50.2, 49.0, 45.4, 41.1, 40.9, 33.9, 28.5.
tert-Butyl (9-(3-(2-((2-yn-1-yloxy)benzamido)(ethyl)amino)-3-oxopropyl)-16-(1-((2,5-bis(prop-2-yn-1-yloxy)phenyl)-1,6,13-trioxo-2,5,12,16-pentaaazaoctadecan-18-yl)carbamate (12). Acid AK (0.33 g, 1.42 mmol) was mixed and dissolved in dry DBO (0.63 g, 1.42 mmol) and was added to a solution of NaH (0.25 g, 41 %). 1H NMR (500 MHz, CDCl3): δ = 7.90–7.61 (m, 10H), 7.08 (s, 8H), 6.70 (s, 4H), 6.59 (br, 1H), 4.66 (d, J = 2.0 Hz, 16H), 3.51–3.34 (m, 20H), 3.18–3.13 (m, 4H), 2.65 (br, 8H), 2.56 (t, J = 2.0 Hz, 8H), 2.51 (t, J = 6.0 Hz, 2H), 2.46 (t, J = 5.5 Hz, 4H), 2.30–2.26 (m, 12H), 2.21 (t, J = 6.0 Hz, 2H), 1.39 (s, 3H).13C NMR (126 MHz, CDCl3): δ = 173.9, 167.6, 158.7, 136.3, 106.9, 105.4, 78.1, 76.1, 56.1, 50.6, 41.0, 39.2, 34.3, 28.5. MS (ESI-MS, positive mode): Calculated for C48H34N6O24; [M + H]+ m/z = 819.7943. Found: [M + H+] m/z = 819.76.

Amphiphilic dendron D1G2AK. Boc-protected aminooamine dendron 12 (0.24 g, 0.14 mmol) was dissolved in dichloromethane (0.9 mL), to which trifluoroacetic acid (TFA) (0.22 mL, 2.83 mmol) was added dropwise at 0 ºC. After stirring at room temperature for 18 h, the volatiles were removed by evaporation. The residue was redissolved in dichloromethane (10 mL), washed with an aqueous solution of Na2SO4 (25 %, 3 mL), and the organic phase dried over anhydrous MgSO4. Removal of the solvent by evaporation and drying under vacuum for 3 d provided product D1G2AK as a viscous pale yellow oil (0.22 g, yield: 99 %). 1H NMR (500 MHz, CDCl3): δ = 7.64–7.97 (m, 10H), 7.09 (d, J = 2.5 Hz, 8H), 6.72 (t, J = 2.5 Hz, 4H), 4.66 (d, J = 1.5 Hz, 16H), 3.51–3.34 (m, 20H), 3.12–3.05 (m, 4H), 2.55–2.50 (m, 22H), 2.33–2.17 (m, 14H).13C NMR (126 MHz, CDCl3): δ = 158.7, 107.0, 106.8, 78.1, 76.0, 56.1, 29.7. MS (ESI-MS, positive mode): Calculated for C64H32N10O16; [M + H]+ m/z = 1593.7418. Found: [M + H+] m/z = 1593.76.

Amphiphilic dendrimer (D1G1AK).BPy. Dicarboxylic acid 13 (0.04 g, 0.16 mmol) and BOP (0.18 g, 0.42 mmol) were mixed and dissolved in dry dimethylformamide (4 mL), to which solution Et3N (0.06 mL, 0.42 mmol) and compound D1G1AK (0.23 g, 0.32 mmol) were successively added. The resulting solution was stirred at ambient temperature for 16 h. After removal of the solvent by evaporation, the residue was dissolved in dichloromethane (2 × 30 mL) and the solution subsequently washed with water (2 × 10 mL) and brine (10 mL). Drying over Na2SO4, evaporation to dryness, and purification by column chromatography (eluent: DCM-MeOH, 9: 1 v/v), yielded the desired product D1G1AK, BPy as a pale yellow solid (0.10 g, 42 %). 1H NMR (500 MHz, CD3OD): δ = 9.08 (s, 2H), 8.45 (d, J = 8.0 Hz, 2H), 8.30 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 2.0 Hz, 16H), 6.75 (t, J = 2.0 Hz, 8H), 4.74 (d, J = 2.5 Hz, 32H), 3.46–3.39 (m, 44H), 3.18 (br, 8H), 2.99 (t, J = 2.5 Hz, 16H), 2.82–2.70 (m, 24H), 2.51–2.30 (m, 28H). HRMS (MALDI-TOF MS, positive mode): Calculated for C56H38N10O24; [M + H]+ m/z = 3394.5031. Found: [M + H+] m/z = 3395.64.

Synthesis of Metalloendodrimers

Dendrimeric complex (D1G1AK),BPy-Fe. 2,2’-bipyridine-dendrimeric ligand (D1G1AK),BPy (0.058 g, 0.035 mmol) and iron(II) perchlorate hydrate (0.003 g, 0.012 mmol) were dissolved in dichloromethane/methanol (5 mL, 1: 1, v/v) and the mixture was stirred at room temperature for 1 h. The precipitated purple product was purified by centrifugation from methanol 3 times. Drying under vacuum afforded product (D1G1AK),BPy-Fe as a deep purple solid (0.054 g, 92 %). 1H NMR (500 MHz, CD3C1D3OD, 8.1): δ = 9.20 (s, 6H), 8.47 (d, J = 8.0 Hz, 6H), 8.38 (d, J = 7.5 Hz, 6H), 6.98 (br, 24H), 6.65 (br, 12H), 6.65 (br, 30H), 4.62 (br, 48H), 3.92–2.08 (m, 144H).13C NMR (126 MHz, CD3C1D3OD, 8.1): δ = 163.3, 160.2, 141.9, 131.9, 115.0, 111.0, 109.7, 106.1, 104.5, 82.8, 60.1, 56.4, 35.8, 32.9, 21.7. HRMS (MALDI-TOF MS, positive mode): Calculated for C56H38FeN10O24; [M + H]+ m/z = 4954.96. Found: [M + H+] m/z = 4955.54.

Dendrimeric complex (D1G2AK),BPy-Fe. 2,2’-bipyridine-dendrimeric ligand (D1G2AK),BPy (0.04 g, 0.012 mmol) and iron(II) perchlorate hydrate (0.001 g, 0.004 mmol) were dissolved in dichloromethane: methanol (5 mL, 1: 1, v/v) and the mixture was stirred at room temperature for 1 h. The precipitated purple product was purified by centrifugation from methanol 3 times. Drying under vacuum afforded product (D1G2AK),BPy-Fe as a purple complex (0.037 g, 90 %).1H NMR (400 MHz, CD3C1D3OD, 8.1): δ = 9.09 (s, 6H), 8.71 (br, 6H), 8.68 (br, 6H), 8.28–7.67 (m, 12H), 7.02 (br, 48H), 6.66 (br, 24H), 6.54 (br, 15H), 4.63 (d, J = 4.0 Hz, 96H), 3.43–2.45 (m, 360H).13C NMR (100 MHz, CD3C1D3OD, 8.1): δ = 168.0, 158.6, 136.2, 107.0, 105.3, 78.2, 76.1, 56.1, 39.2, 36.7, 36.6. HRMS (MALDI-TOF MS, positive mode): Calculated for C56H32FeN10O24; [M + H]+ m/z = 10237.44. Found: [M + H+] m/z = 10237.64.

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Conflict of Interest

The authors declare no conflict of interest.
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