Characteristics of Organic Transformations in a Confined Dendritic Core: Studies on the AIBN-Initiated Reaction of Dendrimer Cobalt(II) Porphyrins with Alkynes**

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Abstract: Cobalt(II) complexes of poly(aryl ester) dendrimer porphyrins [(*m*-[G*n*]TPP)Co^{II}] (generation number $n = 0-4$), in the presence of azobisisobutyronitrile (AIBN) at 60 °C, underwent alkenylation with several alkynes at the metal center. A complete inhibition of double-bond migration (secondary transformation) was observed for [(*m*-[G*n*]TPP)Co^{II}] ($n = 3$ and 4), which gave [(*m*-[G*n*]TPP)Co^{III}–C(=CH_2)R] ($n = 3$ and 4) exclusively. Overall reaction rates for [(*m*-[G*n*]TPP)Co^{II}] ($n = 0-3$) were hardly dependent on the size of the dendritic substituents, while a notable retardation was observed for the largest dendrimer, [(*m*-[G4]TPP)Co^{II}]. Mechanistic studies on double-bond migration with pure [(*m*-[G*n*]TPP)Co^{III}–C(=CH_2)Bu] ($n = 0-4$) demonstrated that the secondary transformation involves participation of [(*m*-[G*n*]TPP)Co^{III}H] ($n = 0-4$), derived from [(*m*-[G*n*]TPP)Co^{II}] and AIBN, rather than [(*m*-[G*n*]TPP)Co^{II}] alone. Crossover experiments using [(*m*-[G*n*]TPP)Co^{III}–C(=CH_2)Bu] ($n = 2-4$), in combination with nondendritic [(*m*-[G0]TPP)Co^{II}] and AIBN, indicated a high level of steric protection of the active center by a robust [G4]-dendritic cage, as suggested by a ^{1}H NMR pulse relaxation time profile of *m*-[G4]TPPH_2.

Keywords: alkenylation · cobalt · coenzymes · dendrimers · porphyrinoids

Introduction

Dendrimers are well-defined hyperbranched macromolecules with predictable three-dimensional shapes and are potential artificial substitutes for globular proteins.[1] Core-shell architectures of spherical dendrimers have also motivated chemists to explore the possibility of spatial reactivity control of active species encapsulated within such unique three-dimensional cages.[2] In 1996, we reported the first example of an iron(II) porphyrin complex encapsulated within a poly(benzyl ether) dendrimer cage as a mimic of O_2-carrying hemoproteins, in which a large dendrimer framework around the binding site inhibits μ-oxo dimer formation and enables reversible O_2 uptake.[3] Collman and Diederich et al. have reported a similar dendrimer effect on the O_2-binding reaction of an iron(II) porphyrin complex within an ether-amide dendrimer, for which a large affinity of the metal center toward O_2 has been highlighted.[4] In 1999, we extended these observations to the chemistry of nonheme metalloproteins, in which a highly labile bis(μ-oxo)dicopper(III) species is considerably stabilized by a large dendrimer cage.[5] From a synthetic point of view, in 1996 Suslick and co-workers reported shape-selective oxidation of olefins by means of a manganese porphyrin complex encapsulated within a poly(aryl ester) dendrimer framework.[6] More recently, Fréchet and co-workers reported an accelerated [4+2] cycloaddition of singlet oxygen to cyclopentadiene by using a benzophenone derivative encapsulated within an amphiphilic polyester dendrimer as a photosensitizer.[7]

In a previous paper,[8] we reported that a cobalt(II) porphyrin complex encapsulated within a large poly(aryl ester) dendrimer framework ([(*m*-[G3]TPP)Co^{II}]; Scheme 1d) undergoes highly chemoselective azobisisobutyronitrile(AIBN)-initiated alkenylation of the metal center by an alkyne such as propargyl alcohol (Scheme 2). Cobalt(II) porphyrin-mediated organic transformations involving free-radical species have been extensively studied from a biological as well as a synthetic point of view,[9, 10] because of their relevance to biological carbon-skeleton rearrangements mediated by coenzyme B_{12}.[11] In view of these studies, one of the challenges is to explore how to realize high chemo- and stereoselectivities in these organic transformations, as the selectivities with artificial model systems are usually much

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[**] AIBN = azobisisobutyronitrile.

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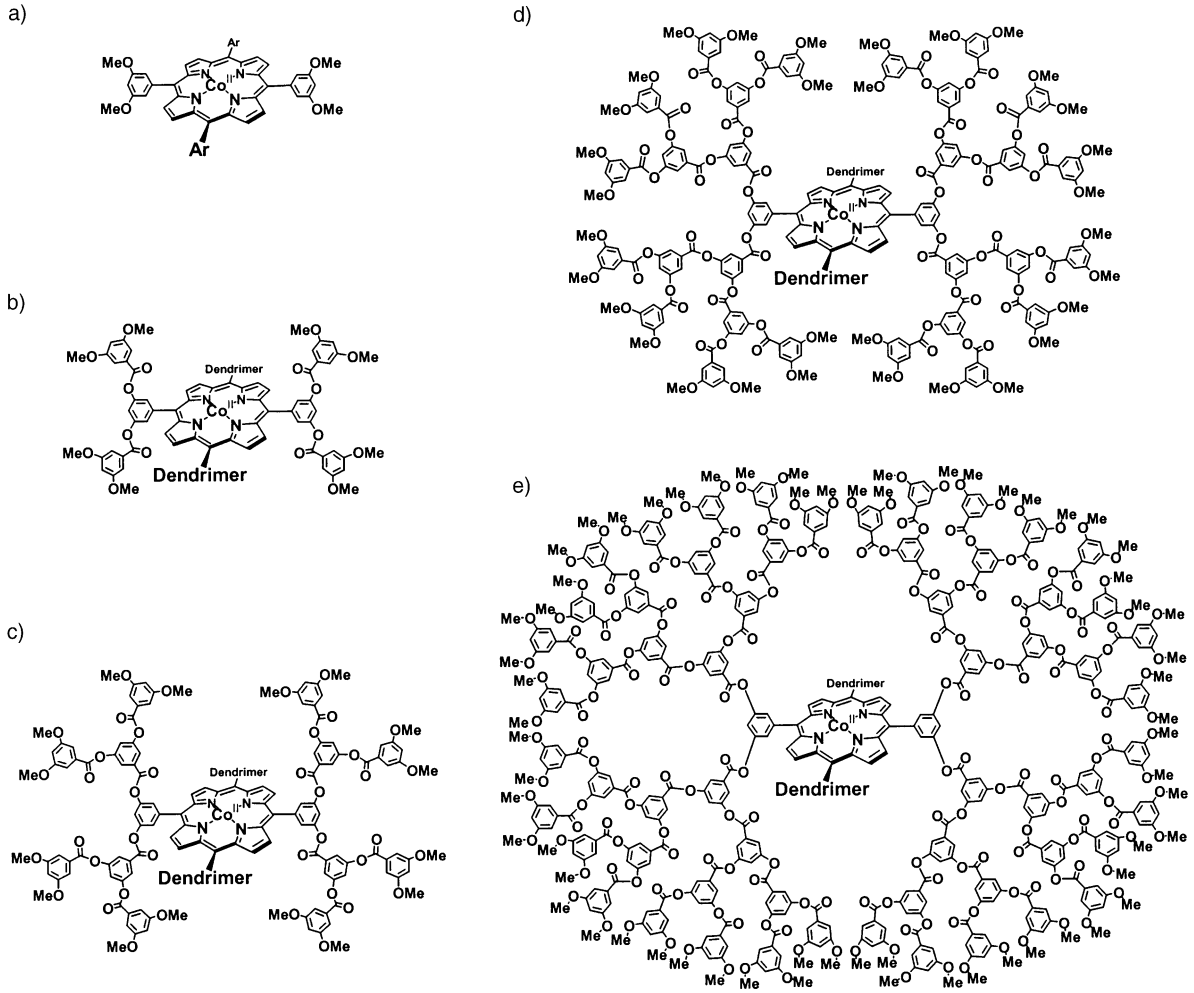
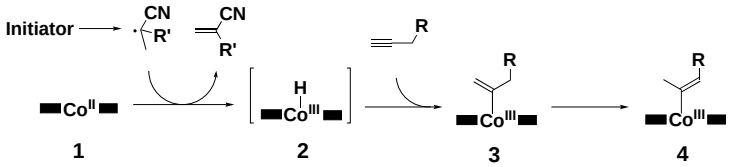


Scheme 1. Schematic structures of cobalt(II) porphyrins: a) [(*m*-[G0]TPP)Co^{II}]; b) [(*m*-[G1]TPP)Co^{II}]; c) [(*m*-[G2]TPP)Co^{II}]; d) [(*m*-[G3]TPP)Co^{II}]; e) [(*m*-[G4]TPP)Co^{II}].



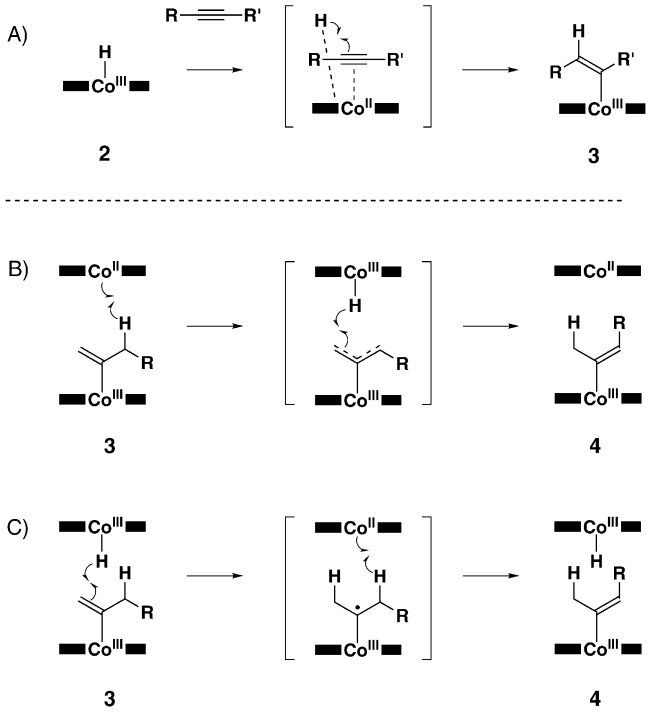
Scheme 2. Proposed reaction scheme for AIBN-initiated alkenylation of a cobalt(II) porphyrin complex encapsulated in a dendrimer framework [(*m*-[G3]TPP)Co^{II}].

inferior to those of biological systems.[10] For example, AIBN-initiated alkenylation of cobalt(II) porphyrins **1** involves addition of cobalt(III) hydride **2** to alkynes (Scheme 3A).[8, 12] However, in general, the products are not simple but rather complicated mixtures of different isomers, owing to the concomitant occurrence of double-bond migration. The participation of cobalt(III) hydride or cobalt(II) species has been considered to be responsible for this secondary transformation (Scheme 3B and 3C). On the other hand, in biological systems, structural aspects of the natural holoenzymes suggest that the steric isolation of the active species by the large protein matrices is important for highly selective transformations.[13] We have proposed a similar steric regulation for the selective alkenylation of large [(*m*-[G3]TPP)Co^{II}] with propargyl alcohol in the presence of AIBN.[8]

Herein, the AIBN-initiated transformation was further investigated by using a series of dendrimer-appended cobalt(II) porphyrin complexes with different generation numbers, including very large [(*m*-[G4]TPP)Co^{II}] (MW > 18900; Scheme 1e). Here, we would like to focus attention on the range of alkynes for the chemoselective transformation of the metal center, the mechanism of the isomerization using authentic terminal alkenylcobalt(III) species **3**, and a discussion of the characteristics of dendritic nano cages for the molecular design of core-active dendritic reagents and catalysts.

Results and Discussion

Synthesis and characterization of dendrimer cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] (*n* = 1–4) and nondendritic ref-



Scheme 3. Proposed mechanism for the AIBN-initiated alkenylation of **1**.

erence [(*m*-[G0]TPP)Co^{II}]: In a manner similar to that reported previously,[8] free-base porphyrin *m*-[G4]TPPH$_2$ with a large dendrimer framework (Scheme 1e) was newly synthesized by a dicyclohexylcarbodiimide(DCC)-mediated coupling of a carboxylic acid terminated poly(aryl ester) dendron with 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)porphine. It was unambiguously characterized by means of MALDI-TOF mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and electronic absorption spectroscopy. Dendrimer cobalt(II) porphyrin [(*m*-[G4]TPP)Co^{II}] was prepared by the reaction of *m*-[G4]TPPH$_2$ with anhydrous Co(OAc)$_2$ in CHCl$_3$/EtOH, in a manner similar to that reported for other dendrimer cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] ($n=1-3$) (Scheme 1b–1d) and nondendritic reference [(*m*-[G0]TPP)Co^{II}] (Scheme 1a).[8] Similar to the parent free-base porphyrins, all of these cobalt(II) porphyrins were unambiguously characterized spectroscopically.

Figure 1 shows the CPK models of the largest dendrimer [(*m*-[G4]TPP)Co^{II}] and that of one generation lower [(*m*-[G3]TPP)Co^{II}] for comparison. Evidently, the densely packed dendritic building units of [(*m*-[G4]TPP)Co^{II}] appear to provide a highly confined environment with regard to the cobalt(II) porphyrin moiety, while [(*m*-[G3]TPP)Co^{II}] still shows an open space around the metal center that allows access of small molecules. Figure 2 shows ^{1}H NMR pulse relaxation times (T_1) in CDCl$_3$ of the porphyrin pyrrole-β and dendritic aromatic protons (*p*-H) in free-base dendrimer porphyrins such as *m*-[G*n*]TPPH$_2$ ($n=2-4$) at 20 °C. The T_1 value of the pyrrole-β protons of the porphyrin macrocycle is longer when the generation number of the dendritic framework is larger, indicating a spatial suppression of the porphyrin functionality in large *m*-[G4]TPPH$_2$ from, for example, collision with solvent molecules. On the other hand,

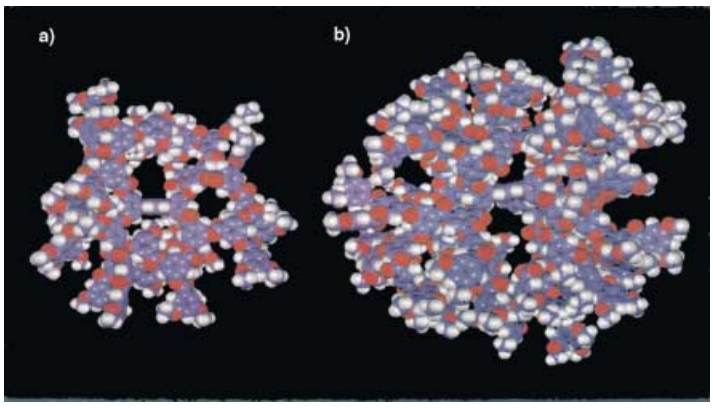


Figure 1. CPK models of dendrimer cobalt(II) porphyrins: a) [(*m*-[G3]TPP)Co^{II}]; b) [(*m*-[G4]TPP)Co^{II}].

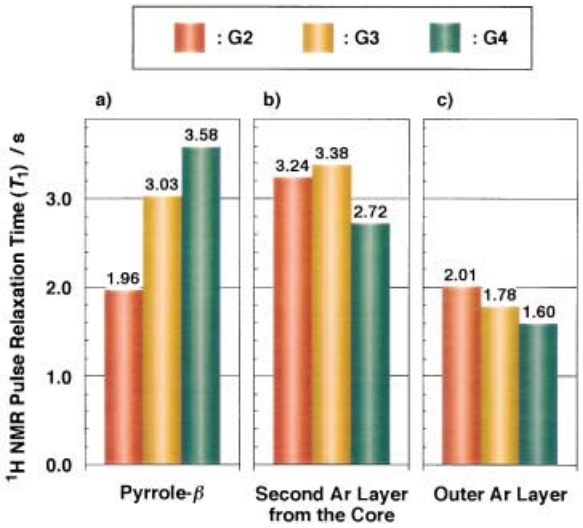


Figure 2. ^{1}H NMR pulse relaxation times (T_1) of pyrrole-β (porphyrin) and aromatic protons (dendritic Ar, *p*-H) of dendrimer free-base porphyrins *m*-[G*n*]TPPH$_2$ ($n=2-4$) in CDCl$_3$ at 20 °C.

the T_1 value of the aromatic protons in the outer layer of the dendrimer framework becomes shorter as the generation number increases, suggesting a dense packing of the building units on the exterior surface of *m*-[G4]TPPH$_2$.[14] These trends most likely reflect the structural characteristics of *m*-[G4]TPPH$_2$, in which the interior core of *m*-[G4]TPPH$_2$ in the CPK model (Figure 1b) is hardly visible owing to the complete cagelike architecture of the large dendrimer framework.

AIBN-initiated transformation of dendrimer cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] ($n=0-4$) with alkynes: The AIBN-initiated alkenylation of cobalt(II) porphyrin **1** with alkynes (Scheme 2)[12] involves the transient formation of the adduct [(porphinato)Co^{III}CMe$_2$CN] with a tertiary radical ($^{\bullet}$CMe$_2$CN), originating from AIBN, which immediately undergoes β-hydride abstraction to generate the [(porphinato)Co^{III}H] compound **2** with elimination of methacrylonitrile. Compound **2** subsequently undergoes addition of alkynes to give terminal alkenylcobalt(III) species **3**, which gradually isomerizes to internal alkenylcobalt(III) species **4**. As described in the introduction, the reaction of [(*m*-[G3]TPP)Co^{II}]

with AIBN and propargyl alcohol takes place chemoselectively, without any retardation, to give exclusively the corresponding terminal alkenylcobalt(III) species **3**.[8] To investigate the scope and limitation of this selective transformation, cobalt(II) porphyrins of varying steric bulk, such as [(*m*-[G0]TPP)Co^{II}] and [(*m*-[G3]TPP)Co^{II}], were treated with alkynes such as 1-hexyne, 1-phenyl-2-propyne, and 3-butyne-1-ol in the presence of AIBN, under identical conditions to those for propargyl alcohol. As summarized in Table 1, the use of nondendritic [(*m*-[G0]TPP)Co^{II}] as the substrate resulted in the formation of isomerized products **4** as well as terminal alkenyl compounds **3**. In sharp contrast, large [(*m*-[G3]TPP)Co^{II}] was selectively converted to compounds **3** in excellent yields (85–97%). Thus, the steric regulation observed for [(*m*-[G3]TPP)Co^{II}] in the reaction with propargyl alcohol[8] is generally operative for other alkynes.

Table 1. Reaction of cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] (*n* = 0 and 3) with alkynes in the presence of AIBN.[a]

Entry[b]	R group in RCH_2CCH[c]	*m*-[G0][d]		*m*-[G3][d]	
		3 [%][c]	**4** [%][c]	**3** [%][d]	**4** [%][c]
1	$-C_3H_7$	20	76	97	0
2	$-CH_2OH$	37	27	88	0
3	-OH	39	11	91	0
4	-Ph	75	5	85	0

[a] See Scheme 2. [b] in the presence of AIBN (40 μmol) in $CDCl_3$ (0.5 mL) at 60 °C. [c] 400 μmol. [d] 4.7 μmol. [e] ^{1}H NMR spectral yield in 200 min.

We further investigated the AIBN-initiated transformation of cobalt(II) porphyrins by selecting 1-hexyne as the substrate (Figure 3d–3f), first because it is nonpolar and thus different from the previously studied propargyl alcohol, and second because the product selectivities of [(*m*-[G0]TPP)Co^{II}] and

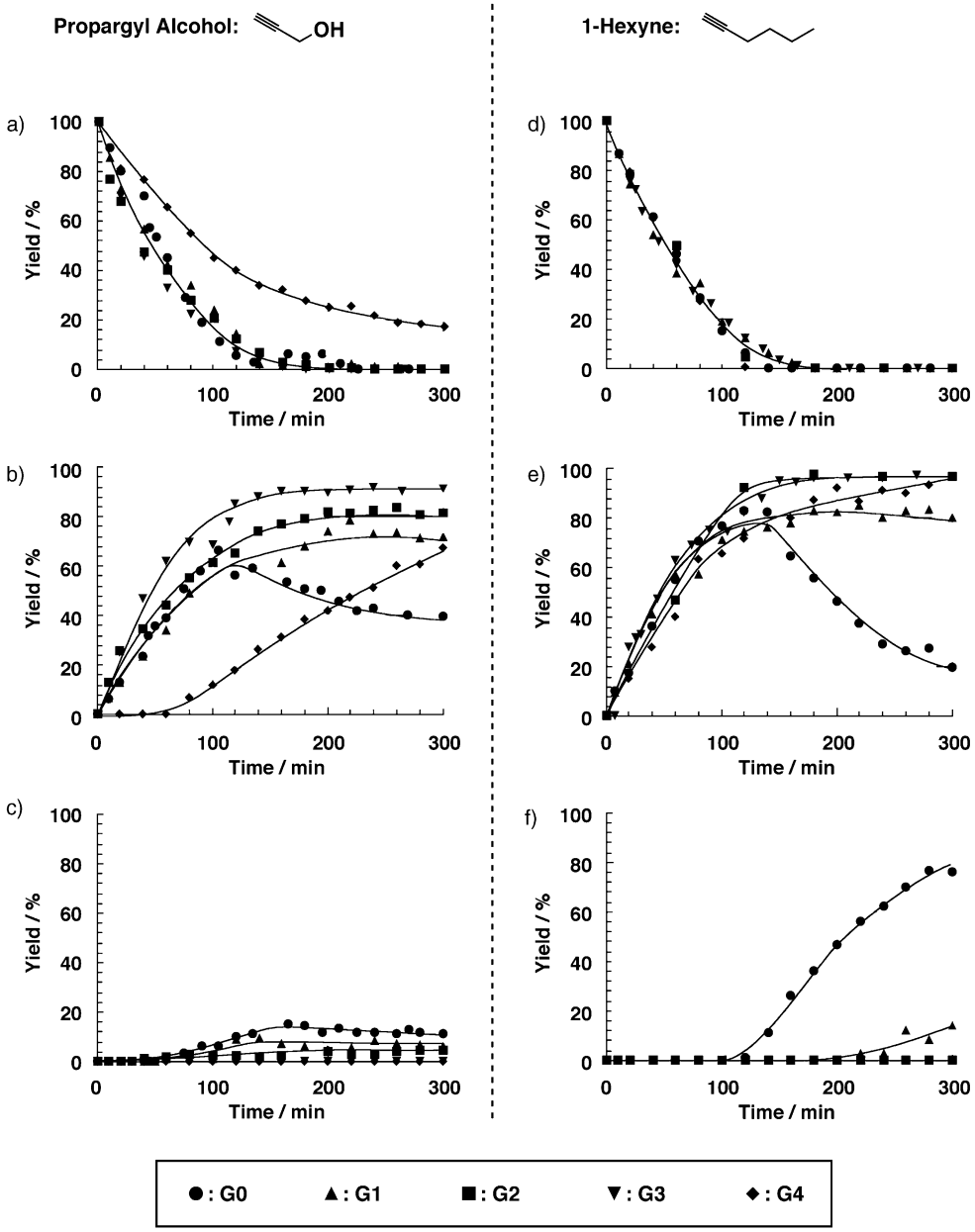


Figure 3. Time-courses of the reaction of cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] (*n* = 0 and 3; 4.7 μmol) with alkynes (450 μmol) in the presence of AIBN (40 μmol) in $CDCl_3$ (0.5 mL) at 60 °C: a), d) cobalt(II) porphyrin **1;** b), e) terminal-alkenylcobalt(III) porphyrin **3;** c), f) isomerized products.

[(*m*-[G3]TPP)Co^{II}] with this alkyne are very different from each other (Table 1). Thus, ^{1}H NMR studies were conducted on a mixture of [(*m*-[G*n*]TPP)Co^{II}] ($n = 0-4$) (4.7 μmol), AIBN (40 μmol), and 1-hexyne (450 μmol) in $CDCl_3$ (0.5 mL) at 60 °C. When nondendritic [(*m*-[G0]TPP)Co^{II}] was used, a ^{1}H NMR signal, initially observed at $\delta = 8.9$ ppm and due to *p*-H of the *meso*-Ar groups on the porphyrin macrocycle, gradually disappeared (●, Figure 3d) to give a new signal at $\delta = 8.7$ ppm, assignable to pyrrole-β-H of a diamagnetic cobalt(III) porphyrin species. At the same time, a new set of signals appeared in an upfield region ($\delta = 0$ to -4 ppm) at $\delta = -3.74$ (dt, $J = 1.6$, 7.6 Hz; β-CH_2), -2.58 (d, $J = 4.6$ Hz; *cis*-H to cobalt), -1.45 (tt, $J = 7.3$, 7.3 Hz; γ-CH_2), -0.68 (dt, $J = 1.6$, 4.6 Hz; *trans*-H to cobalt), -0.44 (tq, $J = 7.3$, 7.3 Hz; δ-CH_2), and -0.10 ppm (t, $J = 7.3$ Hz; ε-CH_3), which are due to the axial hexenyl group of compound **3** (●, Figure 3e). The spectral yield of **3** increased to 85% within the first 120 min, and then rapidly dropped to 20% in the following 180 min. The ^{1}H NMR spectrum of the reaction mixture also showed another set of signals at $\delta = -3.83$ (d, $J = 1.6$ Hz; β-CH_3), -2.83 (dt, $J = 1.6$, 7.3 Hz; *cis*-H to cobalt), and -0.3 (m, C_3H_7), which are assignable to isomerized compound **4** (●, J, Figure 3f). The spectral change profile related to these characteristic signals indicated that the yield of **4** starts to increase rapidly in 100 min and reaches 78% in 300 min. Thus, in contrast with the case of propargyl alcohol as the substrate, in which nonisomerized **3** remains a major product throughout the reaction (Figure 3b and 3c), the transformation of [(*m*-[G0]TPP)Co^{II}] with 1-hexyne is accompanied by considerable double-bond migration of the terminal alkenyl compound **3**, to give **4** as a major product in the final stage (Figure 3e and 3f).

Having this trend in mind, the reaction of the cobalt(II) center with 1-hexyne in the presence of AIBN was investigated for dendrimer cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] ($n = 1-3$) under identical conditions to those for nondendritic [(*m*-[G0]TPP)Co^{II}] (Figure 3d–3f and Figure 4). Similarly to the case with propargyl alcohol as the substrate, [(*m*-[G*n*]TPP)Co^{II}] ($n = 1-3$) reacted with 1-hexyne at rates comparable to that for nondendritic [(*m*-[G0]TPP)Co^{II}] (Figure 3a). Although the lower-generation dendrimer [(*m*-[G1]TPP)Co^{II}] (▲, Figure 3e) had an even high chemoselectivity for **3** (85% selectivity in 300 min), complete exclusion of the double-bond migration again required a larger dendrimer framework, where [(*m*-[G2]TPP)Co^{II}] (■) and [(*m*-[G3]TPP)Co^{II}] (▼) were selectively transformed into **3** in >96% spectral yield.

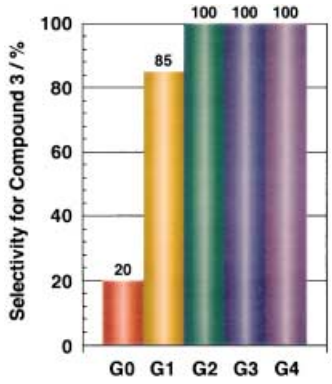


Figure 4. Reaction of cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] ($n = 0-4$; 4.7 μmol) with 1-hexyne (450 μmol) in the presence of AIBN (40 μmol) in $CDCl_3$ (0.5 mL) at 60 °C. Selectivities for nonisomerized **3** in 300 min, as determined by ^{1}H NMR.

The above observations prompted us to investigate the largest [(*m*-[G4]TPP)Co^{II}] (◆) in the AIBN-initiated reaction with 1-hexyne and propargyl alcohol. With 1-hexyne as the substrate, the reaction was highly chemoselective for **3**, but proceeded rather sluggishly relative to the lower-generation homologues. For example, in 180 min, compound **3** was formed in 87% yield from [(*m*-[G4]TPP)Co^{II}] (◆, Figure 3e), whereas [(*m*-[G3]TPP)Co^{II}] was transformed into **3** in 96% yield (▼, Figure 3e). On the other hand, in the reaction with propargyl alcohol, we found that the consumption of [(*m*-[G4]TPP)Co^{II}] is considerably retarded, such that 17% of starting [(*m*-[G4]TPP)Co^{II}] remained unreacted even in 300 min, whereas the lower generation homologues were completely consumed under identical conditions (◆, Figure 3a). Although the reaction of [(*m*-[G4]TPP)Co^{II}] proceeded without any indication of isomerization, the yield of **3** in 300 min was only 67% (◆, Figure 3b). Considering the low conformational change activity of the dendrimer framework, as suggested by the ^{1}H NMR T_1 profile of *m*-[G4]TPPH$_2$ (Figure 2), such a notable retardation of the overall reaction indicates that the four [G4]-poly(aryl ester) dendrons, attached to the cobalt(II) porphyrin moiety of [(*m*-[G4]TPP)Co^{II}] cooperatively form a cagelike architecture, and suppress not only the secondary transformation of **3** involving another cobalt porphyrin species, but also the access of even small molecules such as AIBN and propargyl alcohol to the interior metal center. Since 1) one generation lower [(*m*-[G3]TPP)Co^{II}] hardly shows any retardation in the reaction with propargyl alcohol (Figure 3a and 3b)[8] and 2) the retardation is less explicit even for [(*m*-[G4]TPP)Co^{II}] in the reaction with 1-hexyne (Figure 3d and 3e), it is likely that a complete dendritic cage, as indicated for the largest [(*m*-[G4]TPP)Co^{II}], may exhibit polarity-sensitive guest inclusion activity, which possibly affects the rate-determining step of the reaction.[2a–e, 15] This may be important for the molecular design of core-active dendritic reagents and catalysts.

Mechanistic aspects of isomerization: For the isomerization of terminal alkenylcobalt(III) species **3**, formed by hydride addition to alkynes, participation of another cobalt porphyrin complex, such as cobalt(II) or cobalt(III) hydride species, has been considered responsible (Scheme 3B and 3C).[8, 12] To determine which cobalt species is actually involved in this secondary transformation, a nondendritic terminal alkenylcobalt(III) porphyrin [(*m*-[G0]TPP)Co^{III}–C(=CH$_2$)Bu] (**3**, 2.3 μmol), synthesized according to a literature method using 1-hexyne and $NaBH_4$,[16] was heated in $CDCl_3$ (0.5 mL) at 60 °C in the presence of either [(*m*-[G0]TPP)Co^{II}] (0.46 μmol, 5 mol%) alone or with AIBN (40 μmol). In the absence of AIBN, no ^{1}H NMR signals assignable to isomerized product **4** were detected throughout an observation period of 200 min. The same was true for the reaction in the presence of AIBN (40 μmol) without any cobalt(II) species. In sharp contrast,

when [(*m*-[G0]TPP)Co^{III}–C(=CH$_2$)Bu] (2.3 μmol) was heated with both [(*m*-[G0]TPP)Co^{II}] (0.46 μmol, 5 mol%) and AIBN (40 μmol) under the same conditions as above, the ^{1}H NMR spectrum of the reaction mixture clearly showed the formation of isomerized compound **4**, whose spectral yield reached 38% in 300 min (Figure 5a). Therefore, it is clear that a cobalt(III) hydride species (Scheme 3C), rather than a cobalt(II) species (Scheme 3B), is responsible for the secondary transformation.

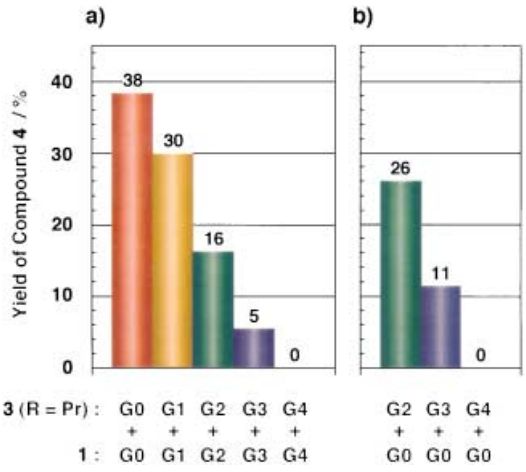


Figure 5. Reaction of hexenylcobalt(III) porphyrins [(*m*-[G*n*]TPP)Co^{III}–C(=CH$_2$)Bu] (**3**; $n = 0-4$; 2.3 μmol) with cobalt(II) porphyrins [(*m*-[G*n*]TPP)Co^{II}] ($n = 0-4$; 5 mol%) in the presence of AIBN (40 μmol) in $CDCl_3$ (0.5 mL) at 60 °C. Yields of isomerized **4** in 200 min, as determined by ^{1}H NMR.

By means of the above method, double-bond migration activities of dendritic [(*m*-[G*n*]TPP)Co^{III}–C(=CH$_2$)Bu] (**3**, $n = 1-4$)[12] were investigated in the presence of [(*m*-[G*n*]TPP)Co^{II}] ($n = 1-4$) and AIBN. For example, when a mixture of [(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)Bu] (2.3 μmol), [(*m*-[G4]TPP)Co^{II}] (0.46 μmol, 5 mol%), and AIBN (40 μmol) was heated in $CDCl_3$ (0.5 mL) at 60 °C, the ^{1}H NMR spectrum did not show any indication of isomerization (Figure 5a). In contrast, one generation lower [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)-Bu], in the presence of [(*m*-[G3]TPP)Co^{II}] and AIBN, underwent isomerization to give **4** in 5% spectral yield in 200 min. As expected, [(*m*-[G2]TPP)Co^{III}–C(=CH$_2$)Bu], [(*m*-[G1]TPP)Co^{III}–C(=CH$_2$)Bu], and nondendritic [(*m*-[G0]TPP)Co^{III}–C(=CH$_2$)Bu], in the presence of [(*m*-[G2]TPP)Co^{II}], [(*m*-[G1]TPP)Co^{II}], and [(*m*-[G0]TPP)Co^{II}], respectively, isomerized to a greater extent, forming compounds **4** in 16, 30, and 38% spectral yield after 200 min (Figure 5a). Thus, the steric effect of the dendrimer framework is again clear in this model secondary transformation. However, as already described, the dendrimer effect is less explicit than that observed for the transformation starting from [(*m*-[G*n*]TPP)Co^{II}] (Figure 3f), where nondendritic [(*m*-[G0]TPP)Co^{II}] is transformed with 1-hexyne to give isomerized compound **4** in 78% spectral yield, while no isomerization takes place for the lower-generation compound [(*m*-[G2]TPP)Co^{II}]. In relation to these observations, we found that the isomerization rate is sensitive to the concentration of cobalt(II) species **1**, that is, cobalt(III) hydride species **2**, which is determined by a balance between the rate of the reaction of **1** with AIBN and that of the resulting hydride **2** with 1-hexyne (Scheme 2). Although the overall reaction profiles in Figure 3 are hardly informative of this competitive situation, it is not surprising that the dendrimer framework around the cobalt center can affect the relative rates of elementary reaction steps involved in the transformation.[6, 7]

Along the lines of the above study, some crossover experiments were conducted under identical conditions, using dendritic terminal alkenylcobalt(III) porphyrins **3** such as [(*m*-[G*n*]TPP)Co^{III}–C(=CH$_2$)Bu] ($n = 2-4$) in combination with nondendritic [(*m*-[G0]TPP)Co^{II}] (Figure 5b). In the presence of AIBN, ^{1}H NMR spectroscopy showed isomerization of both [(*m*-[G2]TPP)Co^{III}–C(=CH$_2$)Bu] and [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)Bu], to give compounds **4** in 26 and 11% spectral yield, respectively, upon heating for 200 min at 60 °C. The observed yields of compounds **4** are clearly higher than those for [(*m*-[G2]TPP)Co^{III}–C(=CH$_2$)Bu] and [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)Bu], in conjunction with [(*m*-[G2]TPP)Co^{II}] (16%) and [(*m*-[G3]TPP)Co^{II}] (5%), respectively. In sharp contrast, the largest [(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)Bu] hardly underwent isomerization even with nondendritic [(*m*-[G0]TPP)Co^{II}] and AIBN, again indicating high-level steric protection of the interior active site by a robust cagelike dendritic architecture.

Conclusions

Herein, we have demonstrated a highly chemoselective AIBN-initiated organic transformation of dendrimer-appended cobalt(II) porphyrins with various alkynes such as 1-hexyne, 1-phenyl-2-propyne, 3-butyne-1-ol, and propargyl alcohol.[8] Such novel core-active dendrimers, when they carry optimum-sized dendritic frameworks, are rapidly and highly chemoselectively alkenylated by reaction with AIBN followed by alkynes. In contrast, when the dendrimer framework is too large, the overall reaction is clearly retarded owing to the limited access of even small molecules such as AIBN and alkynes to the interior active site. The fact that such retardation is more explicit for the transformation with propargyl alcohol bearing a hydroxyl functionality than with a nonpolar alkyne such as 1-hexyne (Figure 3) suggests an interesting molecular recognition ability of the highly confined dendritic core. These observations provide a new aspect for molecular design and utilization of core-active dendrimers for designer catalyses and artificial enzymes.

Experimental Section

General: ^{1}H NMR spectra were measured in $CDCl_3$ using a JEOL GSX-270 spectrometer and a JEOL EXcalibur-500 spectrometer operating at 270.05 MHz and 500.00 MHz, respectively. The chemical shifts were determined with respect to $CHCl_3$ ($\delta = 7.24$ ppm) as internal standard. ^{13}C NMR spectroscopy was performed in $CDCl_3$ using a JEOL EXcalibur-500 spectrometer operating at 125.65 MHz. The chemical shifts were determined with respect to $CDCl_3$ ($\delta = 77.00$ ppm) as internal standard. MALDI-TOF-MS spectra were recorded on an Applied Biosystems model Voyager DE STR. Preparative size-exclusion chromatography (SEC) was

performed at room temperature on a Japan Analytical Industry model LC-918 recycling preparative HPLC, equipped with a JASCO model MD-1510 multichannel photodiode array detector, using $CHCl_3$ as eluent at a flow rate of 3.5 mL min^{-1}. The column set consisted of two Polystyragel columns (20 (i.d.) × 600 mm (L)) of JAIGEL-1H (exclusion limit 1×10^3)/JAIGEL-2H (5×10^3) or JAIGEL-2H/JAIGEL-3H (3×10^4). Electronic absorption spectra were recorded on a JASCO model V-570 spectrophotometer. Fluorescence spectra were recorded on a JASCO model FP-777W spectrofluorometer.

Materials: CH_2Cl_2 was washed successively with concentrated H_2SO_4, water, and aqueous $NaHCO_3$, was dried over $CaCl_2$, and then distilled over CaH_2 under argon. THF was distilled under argon over sodium benzophenone ketyl just before use. MeOH was distilled over Mg coupled with iodine under argon. $CDCl_3$ was passed through alumina just before use. All alkynes were distilled before use. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) and 2′,2′,2′-trichloroethyl 3,5-dihydroxybenzoate were synthesized according to literature methods.[6] 2,2′-Azobis(isobutyronitrile) (AIBN) and 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) were purchased from Wako Chemicals and used as received. 4-(Dimethylamino)pyridine (DMAP), 1,3-dicyclohexylcarbodiimide (DCC), and $NaBH_4$ were purchased from Tokyo Chemical Industry and used as received. Anhydrous cobalt(II) acetate ($Co(OAc)_2$) was purchased from Nakalai Tesque and used as received. Cobalt(II) complexes of poly(aryl ester) dendrimer porphyrins [(*m*-[G*n*]TPP)Co^{II}] ($n = 1-3$) and nondendritic reference [(*m*-[G0]TPP)Co^{II}] were prepared as previously reported.[8]

[G3]Poly(aryl ester)-$CO_2CH_2CCl_3$ dendron: DCC (2.45 g, 12.0 mmol) was added to a solution of [G2]poly(aryl ester)-CO_2H dendron (10.8 g, 10.0 mmol), 2′,2′,2′-trichloroethyl 3,5-dihydroxybenzoate (1.40 g, 4.90 mmol), and DPTS (333 mg, 1.13 mmol) in distilled CH_2Cl_2 (30 mL) under argon at room temperature. After stirring overnight at room temperature, the reaction mixture was filtered through celite, washed with water (200 mL), and extracted with AcOEt and Et_2O. The combined extracts were dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure at room temperature. The residue was then chromatographed on silica gel with CH_2Cl_2 as eluent. After evaporation, 2′,2′,2′-trichloroethyl 3,5-bis{3′,5′-bis[3″,5″-bis(3‴,5‴-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoate ([G3]poly(aryl ester)-$CO_2CH_2CCl_3$ dendron) was obtained quantitatively as a white powder (11.9 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta = 3.84$ (s, 48H), 4.97 (s, 2H), 6.71 (t, 8H, $J = 2.5$ Hz), 7.32 (d, 16H, $J = 2.5$ Hz), 7.49 (m, 1H), 7.50 (t, 4H, $J = 2.5$ Hz), 7.54 (t, 2H, $J = 2.5$ Hz), 7.92 (d, 2H, $J = 2.5$ Hz), 8.00 (d, 8H, $J = 2.5$ Hz), 8.02 ppm (d, 4H, $J = 2.5$ Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C): $\delta = 55.7$, 74.7, 94.6, 106.8, 107.7, 120.9, 121.0, 121.1, 121.1, 121.2, 121.5, 130.3, 130.7, 130.9, 131.0, 150.9, 151.0, 151.3, 160.6, 162.4, 162.6, 162.8, 164.0 ppm; MS (MALDI-TOF, HABA): calcd for $C_{123}H_{95}Cl_3NaO_{46}$ ($[M + Na]^+$) 2435.41, found 2434.95.

[G3]Poly(aryl ester)-CO_2H dendron: Zinc powder (1.0 g) was slowly added to a THF/AcOH solution (10:9 mL) of [G3]poly(aryl ester)-$CO_2CH_2CCl_3$ dendron (2.90 g, 1.2 mmol) under argon at room temperature. After 15 min of vigorous stirring at 60 °C, the reaction mixture was filtered through celite to remove insoluble substances and extracted with AcOEt and Et_2O. The combined extract was evaporated to dryness under reduced pressure at room temperature, and the residue was dissolved in $CHCl_3$, washed with water (500 mL), and evaporated to dryness under reduced pressure at room temperature. The residue was dissolved in $CHCl_3$/2-PrOH (10%) and recrystallized upon addition of hexane to give 3,5-bis{3′,5′-bis[3″,5″-bis(3‴,5‴-dimethoxy-benzoyloxy)benzoyloxy]benzoyloxy}benzoic acid ([G3]poly(aryl ester)-CO_2H dendron) as a white powder in 82% yield (2.25 g). ^{1}H NMR (500 MHz, $CDCl_3$, 45 °C): $\delta = 3.83$ (s, 48H), 6.71 (t, 8H, $J = 2.5$ Hz), 7.32 (d, 16H, $J = 2.5$ Hz), 7.50–7.51 (m, 5H), 7.56 (t, 2H, $J = 2.5$ Hz), 7.90 (d, 2H, $J = 2.5$ Hz), 7.99 (d, 4H, $J = 2.5$ Hz), 8.02 ppm (d, 2H, $J = 2.5$ Hz); ^{13}C NMR (126 MHz, $CDCl_3$, 45 °C): $\delta = 55.7$, 106.9, 107.8, 120.6, 121.0, 121.0, 121.4, 130.5, 130.9, 131.2, 131.6, 150.9, 151.1, 151.4, 158.1, 160.7, 160.9, 162.4, 162.6, 164.0, 167.2 ppm; MS (MALDI-TOF, HABA): calcd for $C_{121}H_{94}NaO_{46}$ ($[M + Na]^+$) 2305.49, found 2305.22.

***m*-[G4]TPPH_2**: DCC (110 mg, 533 μmol) was added to a mixture of [G3]poly(aryl ester)-CO_2H dendron (1.14 g, 500 μmol), 5,10,15,20-tetrakis(3′,5′-dihydroxyphenyl)-21*H*,23*H*-porphine (33.3 mg, 44.7 μmol), and DMAP (8.1 mg, 67 μmol) in distilled THF (5 mL) under argon at room temperature. The reaction mixture was stirred for 60 min at 60 °C, and then evaporated to dryness under reduced pressure at room temperature. The residue was chromatographed on silica gel with CH_2Cl_2 as eluent, and subjected to SEC with $CHCl_3$ as eluent. A fraction containing the desired product was isolated and evaporated to dryness under reduced pressure at room temperature, and the residue was dissolved in $CHCl_3$/2-PrOH (10%) and recrystallized upon addition of hexane to give 5,10,15,20-tetrakis[3′,5′-bis(3″,5″-bis{3‴,5‴-bis[3⁗,5⁗-bis(3⁗′,5⁗′-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy)phenyl]-21*H*,23*H*-porphine (*m*-[G4]TPPH_2) as a purple powder in 70% yield (593 mg). ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): $\delta = -2.96$ (s, 2H), 3.70 (s, 384H), 6.57 (s, 64H), 7.18 (s, 128H), 7.42 (s, 32H), 7.50 (s, 24H), 7.72 (s, 4H), 7.87 (s, 64H), 7.91 (s, 32H), 8.06 (s, 24H), 9.12 ppm (s, 8H); ^{13}C NMR (126 MHz, $CDCl_3$, 45 °C): $\delta = 55.5$, 106.7, 107.7, 114.9, 118.3, 120.7–120.9 (br m), 121.2, 126.1, 128.2, 130.4, 131.0, 131.5, 143.8, 149.5, 151.1, 151.3, 160.6, 160.8, 162.4, 162.5, 162.9, 163.9 ppm; UV/vis ($CHCl_3$): $\lambda_{max} = 423$, 518, 553, 593, 649 nm; MS (MALDI-TOF, dithranol): calcd for $C_{1012}H_{766}N_4O_{368}$ ($[M + H]^+$) 18871.72, found 18876.55.

[(*m*-[G4]TPP)Co^{II}]: A saturated solution of anhydrous $Co(OAc)_2$ in EtOH (3 mL) was added to a solution of *m*-[G4]TPPH_2 (200 mg, 10.6 μmol) in $CHCl_3$ (10 mL) and the mixture was stirred at room temperature until it became nonfluorescent. Then, the reaction mixture was evaporated to dryness under reduced pressure at room temperature, and the residue was chromatographed on silica gel with $CHCl_3$ as eluent. A fraction containing the desired product was isolated and evaporated to dryness under reduced pressure at room temperature. The residue was dissolved in $CHCl_3$ and recrystallized upon addition of 2-PrOH, to give {5,10,15,20-tetrakis[3′,5′-bis(3″,5″-bis{3‴,5‴-bis[3⁗,5⁗-bis(3⁗′,5⁗′-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy)phenyl]porphinato}cobalt(II) ([(*m*-[G4]TPP)Co^{II}]) as a dark purple powder in 82% yield (165 mg). ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C): $\delta = 3.70$ (s, 384H), 6.56 (br s, 64H), 7.17 (br s, 160H), 7.40 (br s, 32H), 7.57 (br s, 16H), 7.92 (d, $J = 1.4$ Hz, 64H), 9.40 (br s, 12H), 12.90 (br s, 8H), 15.89 (br s, 8H); UV/Vis ($CHCl_3$): $\lambda_{max} = 415$, 532 nm; MS (MALDI-TOF, dithranol): calcd for $C_{1012}H_{764}CoN_4O_{368}$ ($[M^+]$) 18927.63, found 18927.31.

Reaction of cobalt(II) porphyrins with alkynes in the presence of AIBN: A solution of a mixture of cobalt(II) porphyrin (4.7 μmol), alkyne (450 μmol), and AIBN (6.57 mg, 40 μmol) in $CDCl_3$ (0.5 mL) was transferred to an NMR tube. After three freeze-pump-thaw cycles, the NMR tube was sealed off under reduced pressure. The mixture was then heated to 60 °C, and the reaction was monitored by ^{1}H NMR spectroscopy. After a designated time, the reaction mixture was evaporated to dryness under reduced pressure at room temperature, and the residue was subjected to SEC with $CHCl_3$ as eluent. A fraction containing the desired product was isolated and evaporated to dryness under reduced pressure at room temperature.

3-(1-Hydroxy-3-butenyl)[5,10,15,20-tetrakis(3′,5′-bis{3″,5″-bis[3‴,5‴-bis-(3⁗,5⁗-dimethoxy-benzoyloxy)benzoyloxy]benzoyloxy}phenyl)porphinato]cobalt(III) ([(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)CH$_2$CH$_2$OH]): The use of 1-hydroxy-3-butyne and [(*m*-[G3]TPP)Co^{II}] for the reaction gave [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)CH$_2$CH$_2$OH] as a dark purple powder. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -3.56$ (t, $J = 5.9$ Hz, 2H), −2.57 (d, $J = 2.7$ Hz, 1H), −0.69 (d, $J = 2.7$ Hz, 1H), 0.32 (t, $J = 5.9$ Hz, 1H), 0.82 (t, $J = 6.8$ Hz, 1H), 3.68 (s, 192H), 6.54 (t, $J = 2.2$ Hz, 32H), 7.14 (d, $J = 2.2$ Hz, 64H), 7.36 (t, $J = 2.2$ Hz, 16H), 7.42 (t, $J = 2.2$ Hz, 8H), 7.62 (t, $J = 2.2$ Hz, 4H), 7.83 (br s, 32H), 7.99 (m, 24H), 9.01 ppm (s, 8H).

2-(1-Phenyl-2-propenyl)[5,10,15,20-tetrakis(3′,5′-bis{3″,5″-bis[3‴,5‴-bis-(3⁗,5⁗-dimethoxy-benzoyloxy)benzoyloxy]benzoyloxy}phenyl)porphinato]cobalt(III) ([(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)CH$_2$Ph]): The use of 1-phenyl-2-propyne and [(*m*-[G3]TPP)Co^{II}] for the reaction gave [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)CH$_2$Ph] as a dark purple powder. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -2.55$ (br s, 2H), −2.41 (br s, 1H), −0.92 (br s, 1H), 3.67 (s, 192H), 4.61 (d, $J = 7.3$ Hz, 2H), 6.24–6.38 (m, 3H), 6.55 (t, $J = 2.2$ Hz, 32H), 7.21 (d, $J = 2.2$ Hz, 64H), 7.38 (t, $J = 2.2$ Hz, 16H), 7.44 (t, $J = 2.2$ Hz, 8H), 7.63 (t, $J = 2.2$ Hz, 4H), 7.86 (br s, 32H), 8.00 (m, 24H), 9.01 ppm (s, 8H).

2-(1-Hexenyl)(5,10,15,20-tetrakis{3′,5′-bis[3″,5″-bis(3‴,5‴-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}porphinato)cobalt(III) ([(*m*-[G2]TPP)Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G2]TPP)Co^{II}] for the reaction gave [(*m*-[G2]TPP)Co^{III}–C(=CH$_2$)Bu)] as a dark purple powder. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -3.81$ (t, $J = 7.0$ Hz, 2H), −2.70 (d, $J = 4.9$ Hz, 1H), −1.43 (tt, $J = 7.0$, 7.0 Hz, 2H), −0.83 (br d, $J = 4.9$ Hz, 1H), −0.56 (qt, $J = 7.3$, 7.0 Hz, 2H), −0.18 (t, $J = 7.3$ Hz, 3H), 3.75 (s, 192H),

6.62 (t, $J = 2.2$ Hz, 32H), 7.23 (d, $J = 2.2$ Hz, 64H), 7.45 (t, $J = 2.2$ Hz, 16H), 7.53 (t, $J = 2.2$ Hz, 8H), 7.72 (t, $J = 2.2$ Hz, 4H), 7.91 (brs, 32H), 8.07 (m, 24H), 9.06 ppm (s, 8H).

2-(1-Hexenyl)[5,10,15,20-tetrakis(3′,5′-bis{3″,5″-bis[3‴,5‴-bis(3⁗,5⁗-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}phenyl)porphinato]cobalt(III) ([(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G3]TPP)Co^{II}] for the reaction gave [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)Bu] as a dark purple powder. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -3.91$ (t, $J =$ 7.0 Hz, 2H), −2.78 (d, $J = 4.9$ Hz, 1H), −1.57 (tt, $J = 7.0$, 7.0 Hz, 2H), −0.96 (brd, $J = 4.9$ Hz, 1H), −0.67 (qt, $J = 7.3$, 7.0 Hz, 2H), −0.29 (t, $J = 7.3$ Hz, 3H), 3.75 (s, 192H), 6.62 (t, $J = 2.2$ Hz, 32H), 7.23 (d, $J = 2.2$ Hz, 64H), 7.45 (t, $J = 2.2$ Hz, 16H), 7.53 (t, $J = 2.2$ Hz, 8H), 7.72 (t, $J = 2.2$ Hz, 4H), 7.91 (brs, 32H), 8.07 (m, 24H), 9.06 ppm (s, 8H).

2-(1-Hexenyl){5,10,15,20-tetrakis[3′,5′-bis(3″,5″-bis{3‴,5‴-bis[3⁗,5⁗-bis(3⁗⁗,5⁗⁗-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy)phenyl]porphinato}cobalt(III) ([(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G4]TPP)Co^{II}] for the reaction gave [(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)Bu] as a dark purple powder. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -3.88$ (brs, 2H), −2.75 (brs, 1H), −1.55 (brs, 2H), −0.97 (brs, 1H), −0.64 (brs, 2H), −0.29 (t, $J = 7.0$ Hz, 3H), 3.71 (s, 384H), 6.58 (brs, 64H), 7.19 (brs, 128H), 7.31 (brs, 8H), 7.44 (brs, 32H), 7.53 (brs, 16H), 7.61 (brs, 4H), 7.88 (brs, 64H), 7.92 (brs, 32H), 8.05 (m, 24H), 9.04 ppm (s, 8H).

2-(1-Hydroxy-2-propenyl){5,10,15,20-tetrakis[3′,5′-bis(3″,5″-bis{3‴,5‴-bis[3⁗,5⁗-bis(3⁗⁗,5⁗⁗-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy)phenyl]porphinato}cobalt(III) ([(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)-CH$_2$OH]): The use of 1-hexyne and [(*m*-[G4]TPP)Co^{II}] for the reaction gave [(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)CH$_2$OH] as a dark purple powder. ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -2.43$ (brs, 1H), −1.92 (brs, 2H), −1.79 (brs, 1H), −0.29 (brs, 1H), 3.71 (s, 384H), 6.59 (brs, 64H), 7.19 (brs, 128H), 7.32 (t, $J = 2.4$ Hz, 8H), 7.43 (brs, 32H), 7.52 (brs, 16H), 7.62 (brs, 4H), 7.87 (brs, 64H), 7.92 (brs, 32H), 8.04 (m, 24H), 9.07 ppm (s, 8H).

2-(1-Hexenyl){5,10,15,20-tetrakis(3′,5′-dimethoxyphenyl)-porphinato}cobalt(III) ([(*m*-[G0]TPP)Co^{III}–C(=CH$_2$)Bu]): Argon was briefly bubbled through a round-bottom flask containing a mixture of [(*m*-[G0]TPP)Co^{II}] (20 mg, 22.0 μmol), 1-hexyne (51.7 μL, 450 μmol), and $NaBH_4$ (30 mg, 0.8 mmol) in C_6H_6/MeOH (30:1, 20 mL). The reaction mixture was stirred at room temperature for 12 h and then evaporated to dryness under reduced pressure at room temperature. Hexane (30 mL) was added to a solution of the residue in $CHCl_3$ (0.5 mL), and the resulting dark purple precipitate was isolated, washed with hexane, and dried under reduced pressure at room temperature to give [(*m*-[G0]TPP)Co^{III}–C(=CH$_2$)Bu] as a dark purple powder in 89% yield (19.4 mg). ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -3.74$ (dt, $J = 1.6$, 7.6 Hz; β-CH$_2$), −2.58 (d, $J = 4.6$ Hz; *cis*-H to cobalt), −1.45 (tt, $J = 7.3$, 7.3 Hz; γ-CH$_2$), −0.68 (dt, $J = 1.6$, 4.6 Hz; *trans*-H to cobalt atom), −0.44 (tq, $J = 7.3$, 7.3 Hz; δ-CH$_2$), −0.10 (t, $J = 7.3$ Hz; ε-CH$_3$), 3.92 (s, 24H), 6.84 (t, $J = 2.2$ Hz, 4H), 7.23 (d, $J = 2.2$ Hz, 8H), 8.88 ppm (s, 8H).

Reaction of cobalt(II) porphyrins with 1-hexyne in the presence of V-70: Typically, a degassed $CHCl_3$ solution (0.5 mL) of a mixture of cobalt(II) porphyrin (4.7 μmol), 1-hexyne (450 μmol), and V-70 (10.02 mg, 40 μmol) was stirred for 5 h at room temperature and the reaction mixture was evaporated to dryness under reduced pressure at room temperature. The residue was subjected to SEC with $CHCl_3$ as eluent and a fraction containing the desired product was isolated and evaporated to dryness under reduced pressure at room temperature.

2-(1-Hexenyl)(5,10,15,20-tetrakis[3′,5′-bis{3″,5″-bis(3‴,5‴-dimethoxybenzoyloxy)benzoyloxy}phenyl]-porphinato)cobalt(III) ([(*m*-[G1]TPP)-Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G1]TPP)Co^{II}] (9.93 mg, 4.7 μmol) for the reaction gave [(*m*-[G1]TPP)Co^{III}–C(=CH$_2$)Bu]) as a dark purple powder quantitatively (10.3 mg). ^{1}H NMR (270 MHz, $CDCl_3$, 60 °C): $\delta = -3.81$ (t, $J = 7.0$ Hz, 2H), −2.69 (d, $J = 5.1$ Hz, 1H), −1.43 (tt, $J = 7.0$, 7.0 Hz, 2H), −0.83 (brd, $J = 5.1$ Hz, 1H), −0.55 (qt, $J =$ 7.3, 7.0 Hz, 2H), −0.17 (t, $J = 7.0$ Hz, 3H), 3.75 (s, 48H), 6.69 (t, $J = 2.2$ Hz, 8H), 7.39 (d, $J = 2.2$ Hz, 16H), 7.63 (t, $J = 2.2$ Hz, 4H), 7.92 (d, $J = 2.2$ Hz, 8H), 9.08 ppm (s, 8H).

2-(1-Hexenyl)(5,10,15,20-tetrakis{3′,5′-bis[3″,5″-bis(3‴,5‴-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}porphinato)cobalt(III) ([(*m*-[G2]TPP)-Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G2]TPP)Co^{II}] (21.6 mg, 4.7 μmol) for the reaction quantitatively gave [(*m*-[G2]TPP)Co^{III}–C(=CH$_2$)Bu] as a dark purple powder (21.6 mg).

2-(1-Hexenyl)[5,10,15,20-tetrakis(3′,5′-bis{3″,5″-bis[3‴,5‴-bis(3⁗,5⁗-dimethoxybenzoyloxy)-benzoyloxy]benzoyloxy}phenyl)porphinato]cobalt(III) ([(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G3]TPP)Co^{II}] (43.7 mg, 4.7 μmol) for the reaction gave [(*m*-[G3]TPP)Co^{III}–C(=CH$_2$)Bu]) as a dark purple powder in 98% yield (43.3 mg).

2-(1-Hexenyl){5,10,15,20-tetrakis[3′,5′-bis(3″,5″-bis{3‴,5‴-bis[3⁗,5⁗-bis(3⁗⁗,5⁗⁗-dimethoxybenzoyloxy)benzoyloxy]benzoyloxy}benzoyloxy)phenyl]porphinato}cobalt(III) ([(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)Bu]): The use of 1-hexyne and [(*m*-[G4]TPP)Co^{II}] (89.0 mg, 4.7 μmol) for the reaction gave [(*m*-[G4]TPP)Co^{III}–C(=CH$_2$)Bu]) as a dark purple powder in 98% yield (88.0 mg).

Reaction of [(*m*-[G*n*]TPP)Co^{III}–C(=CH$_2$)Bu] ($n = 0-4$) with [(*m*-[G*n*]TPP)Co^{II}] ($n = 0-4$) in the presence of AIBN: Typically, a solution of a mixture of [(*m*-[G*n*]TPP)Co^{III}–C(=CH$_2$)Bu] ($n = 0-4$) (2.3 μmol), 5 mol% of [(*m*-[G*n*]TPP)Co^{II}] ($n = 0-4$), and AIBN (6.57 mg, 40 μmol) in $CDCl_3$ (0.5 mL) was transferred to an NMR tube. After three freeze-pump-thaw cycles, the NMR tube was sealed off under reduced pressure, and subjected to ^{1}H NMR spectroscopy at 60 °C.

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