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Coherently Aligned Porphyrin-Appended Polynorbornenes

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Dedicated to Professor Armin de Meijere on the occasion of his 70th birthday

Abstract: Six different kinds of coherently aligned porphyrin-appended polynorbornenes derived from 5,6-*endo*-fused *N*-arylpyrrolidenonorbornenes have been synthesized. π–π interactions between the pendant groups are essential for dictating the photophysical properties of the polymers and the mechanism for the stereoselective formation of polymers. Splitting of the Soret band of polymers **2a**–**c**, which have alkyl-substituted porphyrin pendant groups, suggests strong exciton coupling between chromophores. No splitting of the Soret band is observed for polymers **2d**–**f**, which have tetraaryl substituents on the porphyrin moiety. Significant fluorescence quenching is found in polymers **2a**–**e**, whereas only slightly reduced quantum yield is observed for **2f**. Time-resolved fluorescence measurements also indicate a similar trend. The AFM image of **2d** on graphite shows aggregation to form a two-dimensional, ordered pattern.

Keywords: Arylpyrrolidenes · photophysics · polynorbornene · porphyrinoids · ring-opening polymerization

Introduction

The photosynthetic system of purple bacteria has been shown to contain a supramolecular array of chlorophyll moieties and pigments within protein matrices, in which efficient capture of solar energy and electron transfer take place.[1] Relative orientations and distances between chromophores may be crucial for these important, efficient, and ultrafast photoinduced processes. Numerous model systems with different cofacial alignments of porphyrin derivatives have been designed to mimic this important biological process.[2] For example, cofacial bisporphyrin dyads,[2f] multiple deck oligoporphyrins,[3] multiporphyrinic dendrimers,[4] and porphyrin-appended macromolecules[5] have been extensively examined for through-space singlet and/or triplet energy transfers. A molecular assembly based on derivatized polystyrenes with pendant polypyridine complexes of Ru^{II} has been used to mimic both the light-harvesting and energy-conversion steps of photosynthesis.[6] More rigid polynorbornenes with electroactive pendants have also been employed for photoinduced electron transfer investigations.[7] The use of tetraphenylporphyrin pendant groups in a norbornene-based block copolymer has been briefly explored for a possible molecular switch device.[8] It has recently been shown that polynorbornenes with *N*-aryl-substituted 5,6-*endo*-fused pyrrolidine, obtained by ring-opening metathesis polymerization (ROMP) of the corresponding norbornene monomers catalyzed by the Grubbs I catalyst, may have homogeneous stereochemistry in which all pendants align coherently in

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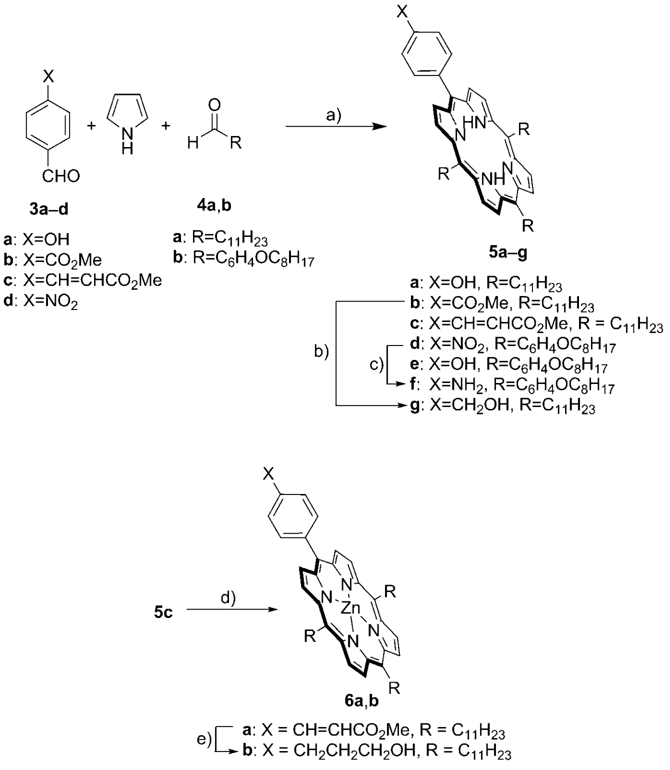
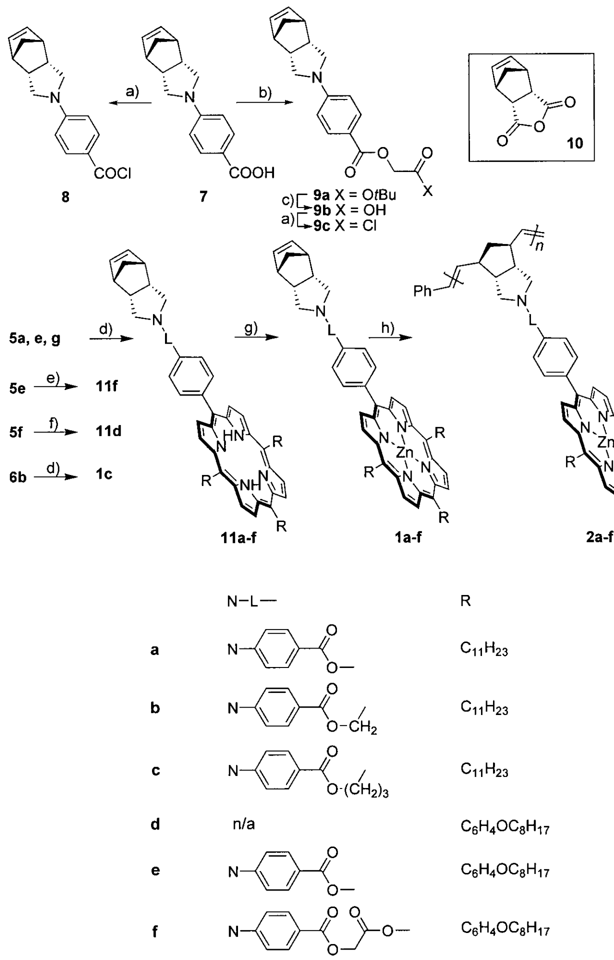
the same direction.[9] In addition, the double bonds in these polymers were predominantly, if not exclusively, *trans*. The space occupied by each of the monomeric units in these polymers is about 5.5 Å.[9] This strategy has been employed for the design and synthesis of double-stranded polybisnorbornenes.[10] Electrochemical and magnetic investigations of these double-stranded polymers showed that there are strong interactions between the ferrocene linkers due to their close proximity.[11] It is envisaged that the incorporation of porphyrin pendants in polynorbornenes would provide an intriguing model in which all porphyrin moieties would be aligned in a similar direction and that interactions between these pendant macrocyclic aromatic rings might offer intriguing photophysical behavior. Herein we wish to report the synthesis and photophysical properties of porphyrin-appended polynorbornenes.

Results and Discussion

Synthesis: The porphyrin moieties in norbornene monomers **1a**–**f** were prepared by using the Lindsey procedure (Schemes 1 and 2) and the details are described in the Experimental Section.[12] Polymerization of **1a**–**f** in the presence of the Grubbs I catalyst afforded the corresponding dark purple polymers **2a**–**f** (Scheme 2) in good yields. The ^{13}C NMR spectra of **2a**–**f** were similar to those of corresponding monomers **1a**–**g** and consistent with the structures.



Scheme 1. Synthesis of substituted porphyrins **5**: a) $BF_3{\cdot}OEt_2$ or TFA (trifluoroacetic acid), then DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), then NEt_3, RT; b) DIBAL-H (diisobutylaluminum hydride); c) $SnCl_2{\cdot}2H_2O$, concd HCl; d) $Zn(OAc)_2{\cdot}2H_2O$; e) H_2, Pd/C, then DIBAL-H.



Scheme 2. Synthesis of **1** and **2** (n/a = no linker). a) $(COCl)_2$; b) Cs_2CO_3, $BrCH_2CO_2Bu$; c) TFA; d) **8**, NEt_3, DMAP (4-dimethylaminopyridine); e) **9**, NEt_3, DMAP; f) Compound **10**, then LAH (lithiumaluminum hydride); g) $Zn(OAc)_2{\cdot}2H_2O$; h) $[(Cy_3)_2Cl_2Ru{=}CHPh]$.

^{1}H NMR spectra: The partial ^{1}H NMR spectra of the aromatic regions of **2a**–**f** are compared with those of **1a**–**f** in Figure 1. Besides severe line broadening,[13] the signals for the protons on porphyrin moieties in **2a**–**f** were shifted upfield compared with those of the corresponding monomers **1a**–**c** due to anisotropic shielding by the neighboring porphyrin moieties. Similar behavior was found in cofacial multiple deck oligoporphyrins[3] and related systems.[14] These results suggest that the neighboring porphyrin pendants in **2a**–**c** may be in close proximity and, therefore, these chromophores may align coherently in a similar direction.

As can be seen from Figure 1, the signals for the β protons on the porphyrin rings in **2a**–**c** were more affected than those in **2d**–**f**. These results suggest that the neighboring porphyrin chromophores would be in closer proximal relationships for **2a**–**c** than those for **2d**–**f**. It is worth noting that polymers **2d**–**f** have aryl substituents at the other *meso*-positions of the porphyrin skeleton whereas **2a**–**c** have alkyl

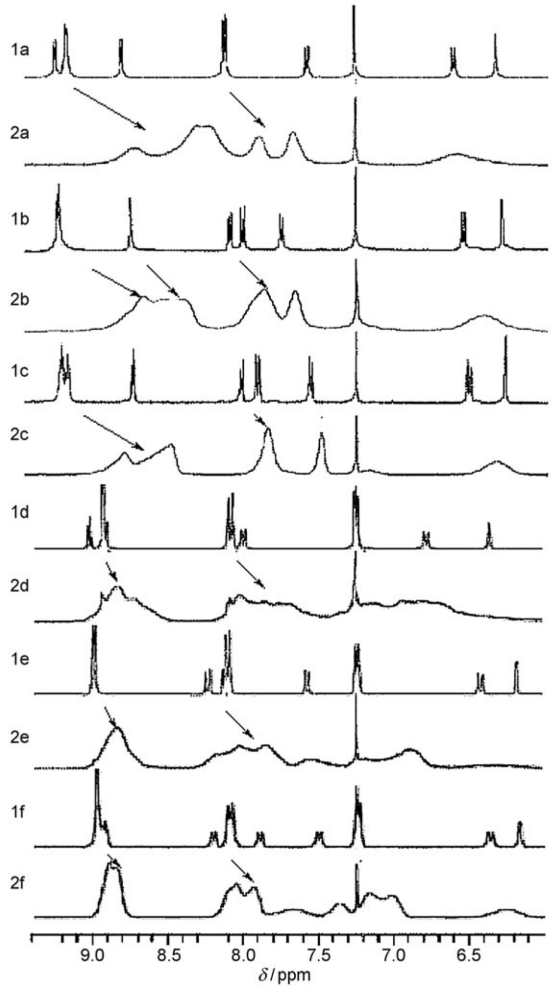


Figure 1. Partial ^{1}H NMR spectra (aromatic region) of **1a**–**f** and **2a**–**f** in $CDCl_3$.

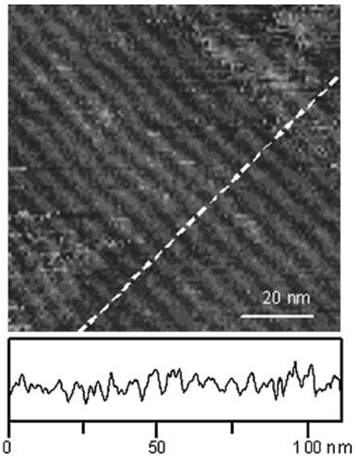


Figure 2. Top: TMAFM image of **2d** on highly ordered pyrolytic graphite. Bottom: The section profile of the dash line showing the spacing of about 5 nm. Imaging conditions: 257 kHz for the drive frequency of the tip.

substituents at the same positions. Tetraphenylporphyrin is known to be nonplanar.[15] As mentioned in the Introduction Section, the spacing occupied by each of the monomeric units in **2** would be around 5.5 Å. Steric repulsion between neighboring pendant groups in **2d**–**f** might be expected if they were in more eclipsed conformations. It seems likely that the porphyrin pendants in **2d**–**f** might be more staggered than those in **2a**–**c**. These characteristics might also be reflected in their photophysical properties as discussed below.

Tapping-mode atomic force microscopy (TMAFM) images: TMAFM was carried out to morphologically assess the cofacial stacking of the appended porphyrins. To facilitate the imaging, the sample was subjected to shear treatment[16] immediately after it was dropcast on the freshly cleaved surface of highly ordered pyrolytic graphite. A typical image of polymer **2d**, which is a prototype for this series of polynorbornenes, is displayed in Figure 2 and shows a long-range ordered pattern with stripes significantly longer than the apparent length of **2d**. Such an assembly is common for double-stranded polybisnorbornenes[10,11] and is ascribed to intermolecular interactions, such as π–π stacking between terminal groups along the longitudinal dimension and van der Waal interactions between the polymeric backbones and pendant groups in the horizontal direction. The aligned stripes have a uniform width of around 5 nm. The uniformity and the dimension suggest the porphyrin pendants are cofacially attached to the bisnorbornene backbone.

Photophysical properties: The absorption spectra of **1a**–**f** and **2a**–**f** in CH_2Cl_2 are shown in Figure 3 and selected photophysical properties are summarized in Table 1. It is worth noting that the Soret band of polymers **2a**–**c** split into two bands, which indicates that there may be significant exciton coupling between neighboring porphyrin chromophores even though the distance between these neighboring pendant moieties would be around 5.5 Å. In addition, the relative intensities of the shorter wavelength absorption versus the longer wavelength absorption in the split Soret band decreased as the number of methylene moieties in the linkers of **2a**–**c** increased. The incorporation of methylene groups in the pendants may increase its flexibility and the exciton coupling between meighboring chromophores may be affected.

It is known that intramolecular interactions between two porphyrin moieties leading to the splitting of the Soret band may depend on the distance and dihedral angle between the two chromophores.[8,17,18] In general, the exciton interaction between two porphyrins is relatively weak if the face-to-face distance between porphyrins in cofacial bisporphyrins is more than 5 Å.[19] The 5.5 Å distance between the cofacial porphyrin chromophores in **2a**–**c** would be rather large to exhibit exciton coupling.[20] Slight flexibility in the linkers of **2a**–**c** might result in a closer face-to-face distance between the neighboring porphyrin moieties or adjust the dihedral angle between two transition dipoles and lead to exciton coupling.

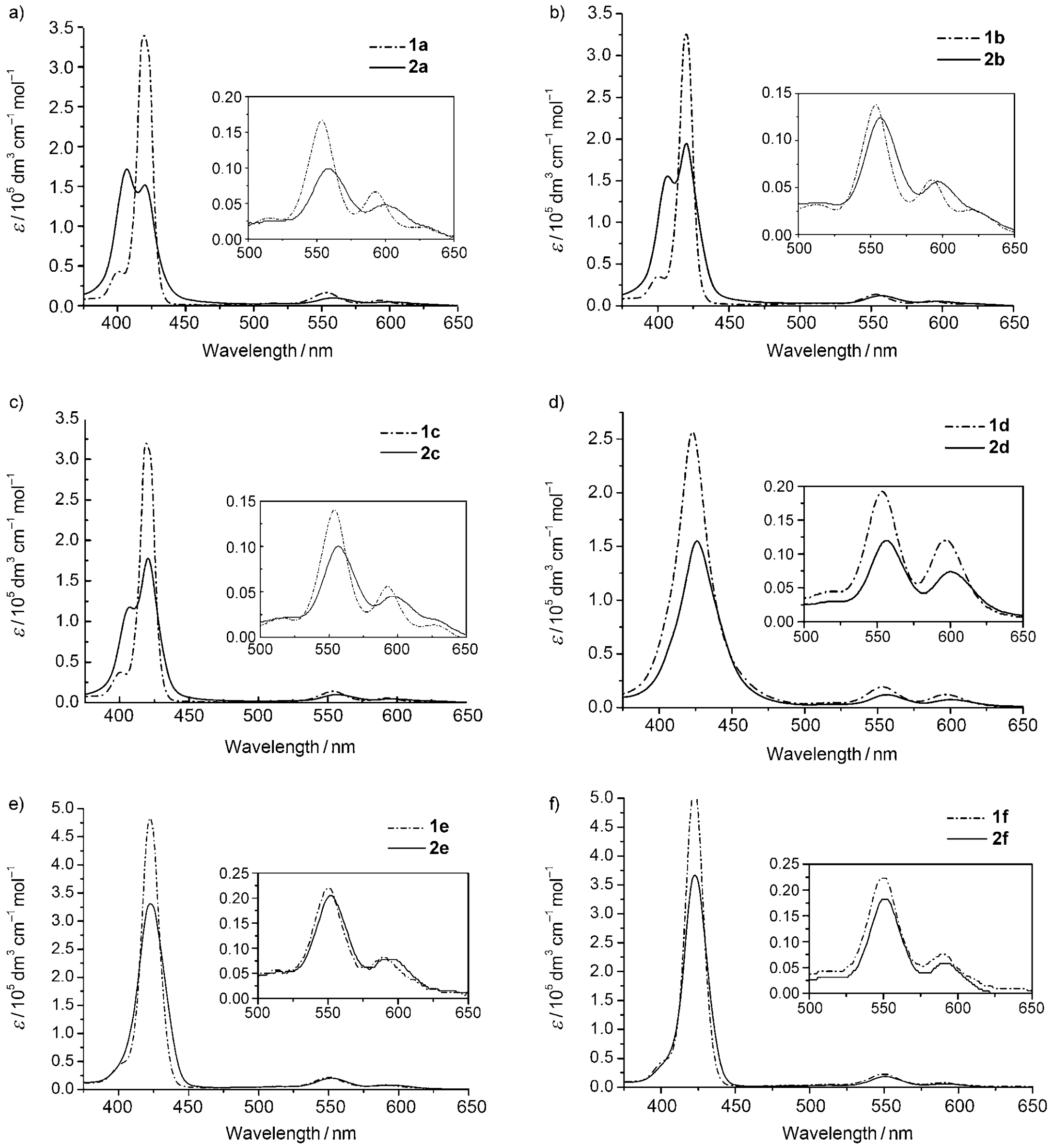


Figure 3. Absorption spectra of **1a**–**f** and **2a**–**f** in CH_2Cl_2.

Table 1. UV/Vis absorption and fluorescent spectral data for **1** and **2** in CH_2Cl_2.

	M_n (PDI)	Absorption		Emission		Lifetime
		Soret band λ_{max}[a] [nm]	Q-band λ_{max}[a] [nm]	λ_{max}[b] [nm]	Φ_f[c]	τ [ps]
1a	1164	420 (3.39)	554 (0.17), 593 (0.07)	599	0.036	1450
2a	18900 (1.08)	407 (1.71), 420 (1.51)	558 (0.10), 600 (0.05)	614	0.004	158 (73%), 1450(27%)
1b	1177	420 (3.26)	554 (0.14), 593 (0.06)	600	0.036	1420
2b	17000 (1.19)	407 (1.55), 420 (1.94)	557 (0.12), 596 (0.06)	605	0.007	182 (72%), 1420 (28%)
1c	1206	419 (3.21)	554 (0.14), 593 (0.06)	600	0.034	1470
2c	15300 (1.13)	407 (1.78), 420 (1.17)	557 (0.10), 597 (0.05)	603	0.008	190 (74%), 1470 (26%)
1d	1193	423 (2.57)	553 (0.19), 596 (0.12)	619	0.041	1360
2d	10600 (1.38)	426 (1.55)	557 (0.12), 600 (0.07)	624	0.010	97 (60%), 1370 (40%)
1e	1313	423 (4.85)	550 (0.22), 589 (0.08)	602	0.040	1340
2e	51400 (1.58)	423 (3.31)	552 (0.21), 592 (0.08)	610	0.025	228 (72%), 1350 (28%)
1f	1372	422 (5.14)	550 (0.26), 590 (0.16)	601	0.031	1360
2f	9500 (1.16)	423 (3.66)	551 (0.18), 592 (0.06)	604	0.027	310 (26%), 1360 (74%)

[a] The molar extinction coefficient ($10^5\,\text{M}^{-1}\text{cm}^{-1}$) based on the molecular weight of the monomeric unit is shown in parentheses. [b] Excitation at λ_{max} around 550 nm. [c] The quantum yield for ZnTPP in toluene, used as a reference, is 0.033 (see ref. [12b]).

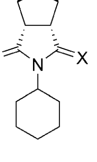
As shown in Figure 3, the Soret bands of **2d–f** showed essentially no change compared with those of the corresponding monomers **1d–f**. Presumably, little aggregation resulting in exciton coupling may take place for **2d–f** because of the presence of four aryl substituents on the porphyrin ring.[15]

The fluorescence quantum yields of polymers **2a–c** were significantly reduced compared with those of the corresponding monomers **1a–c**, presumably due to self quenching. It is interesting to note that the reduction in quantum yield for polymers **2d–f** compared with those of the corresponding monomers **1d–f** were, relatively speaking, smaller than for those of alkyl-substituted analogues **2a–c**. These results appear to be consistent with other photophysical data and the NMR results described above.

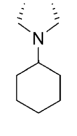
Time-resolved fluorescence spectroscopy: Time-resolved fluorescence decays for both monomers **1a–f** and polymers **2a–f** in CH_2Cl_2 were measured. Using two-exponential fittings, the fluorescence lifetimes are also summarized in Table 1.

The longer lifetimes for **2a–f** were comparable with those of corresponding monomers **1a–f**. The major route for the fluorescence decay (60–73 %) occurred via the shorter lifetime path, presumably because of self-quenching between neighboring porphyrin moieties in **2a–f**. As can be seen from Table 1, these lifetimes fall within the same range as those obtained from related cofacial porphyrin dyads.[21] Similar quenching behavior can also be found in chlorophyll- and dye-based systems.[22] These results again suggest that all porphyrin pendants are coherently aligned in a similar direction.

Importance of the *endo*-fused *N*-arylpyrrolidine moiety: In spite of the large porphyrin pendant groups in **2**, the stereoselectivity (*trans* double bonds) and *syn* orientation of the pendants appeared to be similar to those of simple aryl-substituted 5,6-*endo*-pyrrolidine-fused polynorbornenes.[9] It seems likely that π–π interactions would be essential for controlling the stereochemistry of the polymerization during the course of the ROMP process. To test the validity of this hypothesis, ROMP of **12** was carried out under the usual conditions to give **13** containing a mixture of *cis* and *trans* double bonds (21:79) in 81 % yield.



12a (X=O)
12b (X=H,H)



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Conclusions

We have demonstrated direct evidence to show that porphyrin-appended polynorbornenes derived from 5,6-*endo*-fused *N*-aryl-pyrrolidenonorbornenes may have coherently aligned pendant groups that exhibit exciton coupling and fluorescence quenching in the absorption and emission profiles. π–π interactions between the pendant groups were essential to dictate the photophysical properties of the polymers and the mechanism for the stereoselective formation of **2**. Our results suggest that the presence of the *N*-aryl group is essential for dictating the stereoselectivity of the ROMP of **1**. Because of the close proximity between the porphyrin moieties, these polymers may provide a versatile model system for studying light harvesting and photoinduced electron transfer processes.

Experimental Section

General: High-resolution mass spectrometric measurements were obtained by using a Jeol-JMS-700 mass spectrometer using the FAB method with a 3-nitrobenzyl alcohol matrix. Gel permeation chromatography (GPC) was performed by using a Waters GPC machine with an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1.0 mL min^{-1}). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for determining the relative molecular weight with polystyrene as the standard (M_n values ranged from 375 to 3.5×10^6). Absorption spectra were measured by using a Hitachi U-3310 spectrophotometer and emission spectra were recorded by using a Hitachi F-4500 fluorescence spectrophotometer. Quantum yields were obtained with ZnTPP in toluene as the reference ($\Phi = 0.033$).

21*H*,23*H*-5-(4-Hydroxyphenyl)-10,15,20-tris(undecyl)porphyrin (5a): TFA (1.5 mL, 10^{-2} M) was added slowly to a mixture of **3a** (1.22 g, 10 mmol), **4a** (6.01 g, 30 mmol), and pyrrole (2.79 mL, 40 mmol) in CH_2Cl_2 (2 L), then the mixture was stirred for 2 h before being quenched by the addition of DDQ (6.81 g, 30 mmol). After stirring for 1 h at RT, NEt_3 (5 mL) was added to neutralize TFA. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2) to give **5a** as a purple solid (650 mg, 8 %). M.p. 87–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.65$ (s, 2H; NH), 0.87–0.92 (m, 9H; CH_3), 1.17–1.45 (m, 36H; CH_2), 1.48–1.56 (m, 6H; CH_2), 1.75–1.88 (m, 6H; CH_2), 2.47–2.58 (m, 6H; CH_2), 4.90–5.00 (m, 6H; CH_2), 7.11 (d, ^3J(H,H) = 8.1 Hz, 2H; ArH), 7.99 (d, ^3J(H,H) = 8.1 Hz, 2H; ArH), 8.83 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.38 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.49 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.52 ppm (d, ^3J(H,H) = 4.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 29.3, 29.4, 29.64, 29.66, 29.71, 29.73, 30.6, 30.7, 31.9, 35.4, 35.8, 38.7, 38.9, 113.5, 117.7, 119.1, 119.3, 127.9, 128.2, 135.1, 135.5, 136.3, 155.2 ppm; IR (KBr): $\tilde{\nu} = 3383$, 3318, 3129, 2954, 2923, 2852, 1609, 1513, 1479, 1467, 1353, 1264, 1238, 964, 913, 791 cm^{-1}; HRMS (FAB): m/z calcd for $C_{59}H_{85}N_4O$: 865.6720 [M^++H]; found: 865.6723.

21*H*,23*H*-5-{4-[2-(Methoxycarbonyl)-1-vinyl]phenyl)-10,15,20-tris(undecyl)porphyrin (5c): Boron trifluoride etherate (0.8 mL) was added slowly to a solution of **3c** (1.00 g, 5.26 mmol), **4a** (3.16 g, 15.78 mol), and pyrrole (1.5 mL, 21.03 mmol) in dry CH_2Cl_2 (2 L) under nitrogen and the mixture was stirred at RT for 1 h. DDQ (7.16 g, 31.54 mmol) was added and the mixture was stirred at RT for 1 h. The reaction mixture was neutralized with NEt_3 (5 mL) and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2 1:1) to give **5c** (0.41 g, 8 %). M.p. 56–57 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.65$ (s, 2H), 0.85–0.92 (m, 9H), 1.27–1.33 (br s, 36H), 1.50–1.56 (m, 6H), 1.76–1.81 (m, 6H), 2.49–2.53 (m, 6H), 3.94 (s, 3H), 4.90–4.99 (m, 6H), 6.76 (d, ^3J(H,H) = 16.1 Hz, 1H), 7.90 (d, ^3J(H,H) = 8.1 Hz, 2H), 8.06 (d, ^3J(H,H) = 16.1 Hz, 1H), 8.19 (d, ^3J(H,H) = 8.1 Hz, 2H), 8.79 (d, ^3J(H,H) = 4.8 Hz, 2H), 9.39 (d, ^3J(H,H) = 4.8 Hz, 2H), 9.50 (d, ^3J(H,H) = 4.8 Hz, 2H), 9.53 ppm (d, ^3J(H,H) = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 29.36, 29.38, 29.65, 29.69, 29.7, 30.5, 30.6, 31.9, 35.3, 35.7, 38.7, 38.9, 51.8, 53.4, 116.6, 118.3, 119.2, 119.6, 126.2, 127.9, 128.1, 130.6, 130.7, 133.5, 134.9, 144.8, 144.9, 167.5 ppm; IR (KBr): $\tilde{\nu}=3317$, 3123, 3028, 2952, 2923, 2852, 1723, 1635, 1480, 1466, 1434, 1321, 1312, 1203, 1168, 983, 917, 790, 732 cm^{-1}; HRMS (FAB): m/z calcd for $C_{63}H_{89}N_4O_2$: 933.6986 [M^++H]; found: 933.6978.

21*H*,23*H*-5-(4-Nitrophenyl)-10,15,20-tris(4-octyloxyphenyl)-porphyrin (5d):[12] TFA (0.75 mL, 5×10^{-3} M) was added to a mixture of **3d** (0.76 g, 5 mmol), **4b**[23] (3.52 g, 15 mmol), and pyrrole (1.34 g, 20 mmol) in CH_2Cl_2 (2 L) and stirred for 2.5 h, then quenched with DDQ (3.40 g, 15 mmol) for 1 h at RT. The solution was concentrated and filtered through an alumina pad to remove the quinone and polypyrrylmethine species. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2 7:3) to give **5d** (0.42 g, 8%). M.p. 202–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-2.74$ (s, 2H; NH), 0.94 (t, ^3J(H,H) = 6.3 Hz, 9H; CH_3), 1.35–1.64 (m, 30H; CH_2), 1.95 (quint, ^3J(H,H) = 6.3 Hz, 6H; CH_2), 4.18 (t, ^3J(H,H) = 5.9 Hz, 6H; OCH_2), 7.22 (d, ^3J(H,H) = 8.4 Hz, 6H; ArH), 8.06 (dd, ^3J(H,H) = 8.4, 3.3 Hz, 6H; ArH), 8.31 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 8.55 (d, $J=8.4$ Hz, 2H; ArH), 8.67 (d, $J=4.8$ Hz, 2H; β-H), 8.87 (s, 4H; β-H), 8.89 ppm (d, ^3J(H,H) = 4.8 Hz, 2H; β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 26.3, 29.3, 29.5, 31.9, 68.4, 112.9, 114.8, 116.2, 120.5, 121.0, 121.8, 129.8, 131.4, 132.0, 134.1, 134.2, 135.1, 135.6, 146.9, 147.7, 149.4, 159.2 ppm; IR (KBr): $\tilde{\nu}=2925$, 2855, 1606, 1510, 1469, 1347, 1284, 1245, 1174, 1108, 966, 847, 801, 735 cm^{-1}; LRMS (MALDI): m/z (%): 1044.0 (100) [M^+], 1045.0 (80) [M^++H]; elemental analysis calcd (%) for $C_{68}H_{77}N_5O_5$: C 78.20, H 7.43, N 6.71; found: C 78.34, H 7.84, N 5.90.

21*H*,23*H*-5-(4-Hydroxyphenyl)-10,15,20-tris(4-octyloxyphenyl)-porphyrin (5e);[24] TFA (1.5 mL, 10^{-2} M) was added slowly to a mixture of **4b** (7.02 g, 30 mmol), **3a** (1.22 g, 10 mmol), and pyrrole (2.68 g, 40 mmol) in CH_2Cl_2 (2 L) and the mixture was stirred for 2.5 h, then quenched by addition of *p*-chloranil (7.44 g, 30 mmol). After 3 h at RT, $NaHCO_3$ (10 g) was added to neutralize TFA. The crude mixture was concentrated and filtered through an alumina pad to remove quinone and polypyrrylmethene species. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2) to give **5e** as a purple solid (1.217 g, 12%). M.p. 228–229 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-2.74$ (s, 2H; NH), 0.93 (t, ^3J(H,H) = 6.6 Hz, 9H; CH_3), 1.35–1.52 (m, 24H; CH_2), 1.60 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 1.95 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 4.19 (t, ^3J(H,H) = 6.6 Hz, 4H; OCH_2), 4.20 (t, ^3J(H,H) = 6.6 Hz, 2H; OCH_2), 5.01 (s, 1H; OH), 7.02 (d, ^3J(H,H) = 8.4 Hz, 2H), 7.22 (d, ^3J(H,H) = 8.4 Hz, 4H), 7.24 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.00 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.07 (d, ^3J(H,H) = 8.4 Hz, 4H), 8.09 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.82 (d, ^3J(H,H) = 5.1 Hz, 2H; β-H), 8.85 (d, ^3J(H,H) = 5.1 Hz, 2H; β-H), 8.86 ppm (s, 4H; β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.4$, 22.9, 26.4, 29.5, 29.7, 32.1, 68.3, 112.5, 113.42, 113.43, 119.3, 119.68, 119.72, 130.8, 134.15, 134.18, 134.5, 135.33, 135.38, 135.41, 155.0, 158.61, 158.62 ppm; IR (KBr) $\tilde{\nu}=3357$, 2924, 2852, 1605, 1571, 1509, 1467, 1349, 1283, 1244, 1174, 1108, 966, 840, 803, 738 cm^{-1}; LRMS (MALDI): m/z (%): 1015.6 (100) [M^++H], 1016.6 (72) [M^++2]; HRMS (MALDI): m/z calcd for $C_{68}H_{79}N_4O_4$: 1015.6053 [M^++H]; found: 1015.6096.

21*H*,23*H*-5-(4-Aminophenyl)-10,15,20-tris(4-octoxyphenyl)-porphyrin (5f):[25] A mixture of **5d** (522 mg, 0.5 mmol), $SnCl_2\cdot2H_2O$ (564 mg, 2.5 mmol), and HCl (35%, 3 mL) in THF (25 mL) was stirred at RT under argon for 24 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (50 mL). Sodium hydroxide (10%) was added until the pH value was basic, then the organic layer was separated and dried ($MgSO_4$) and the solvent was removed in vacuo to give a residue that was purified by column chromatography on silica gel (eluent CH_2Cl_2) to give **5f** as a purple solid (0.38 g, 75%). M.p. 203–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-2.73$ (s, 2H; NH), 0.93 (t, ^3J(H,H) = 6.6 Hz, 9H; CH_3), 1.35–1.49 (m, 24H; CH_2), 1.60 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 1.95 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 3.93 (brs, 2H; NH_2), 4.19 (t, ^3J(H,H) = 6.6 Hz, 6H; OCH_2), 6.99 (d, ^3J(H,H) = 7.8 Hz, 2H; ArH), 7.23 (d, ^3J(H,H) = 8.4 Hz, 6H; ArH), 7.96 (d, ^3J(H,H) = 7.8 Hz, 2H; ArH), 8.09 (d, ^3J(H,H) = 8.4 Hz, 6H; ArH), 8.85 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 8.86 (s, 4H; β-H), 8.91 ppm (d, ^3J(H,H) = 4.8 Hz, 2H; β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.2$, 22.7, 26.3, 29.4, 29.5, 31.9, 68.3, 112.7, 113.4, 119.7, 119.8, 120.5, 130.7, 131.0, 132.6, 134.5, 135.6, 135.7, 146.0, 159.0 ppm; IR (KBr): $\tilde{\nu}=3390$, 3318, 2923, 2852, 1606, 1561, 1509, 1466, 1243, 1175, 966, 805, 741 cm^{-1}; LRMS (MALDI): m/z (%): 1016.5 (100) [M^++3H]; HRMS (MALDI): m/z calcd for $C_{68}H_{80}N_5O_3$: 1014.6232 [M^++H]; found: 1014.6256; elemental analysis calcd (%) for $C_{68}H_{79}N_5O_3$: C 80.51, H 7.85, N 6.90; found: C 80.29, H 8.26, N 6.35.

5-{4-[2-(Methoxycarbonyl)-1-vinyl]phenyl}-10,15,20-tris-(undecyl)porphyrinzinc(II) (6a): Zinc acetate (730 mg, 3.32 mmol) was added to a solution of **5c** (620 mg, 0.66 mmol) in methanol (10 mL) and CH_2Cl_2 (30 mL). The mixture was stirred at RT in the dark for 3 h and then washed with $NaHCO_3$ (5%) and brine and then dried ($MgSO_4$). The solvent was removed in vacuo to give a residue that was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2/NEt_3 1:1:0.05) to afford **6a** (580 mg, 88%). M.p. 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.86$–0.91 (m, 9H), 1.25–1.49 (m, 36H), 1.49–1.60 (m, 6H), 1.72–1.90 (m, 6H), 2.33–2.48 (m, 6H), 3.93 (s, 3H), 4.58 (t, ^3J(H,H) = 7.8 Hz, 2H), 4.72 (t, ^3J(H,H) = 7.8 Hz, 4H), 6.76 (d, ^3J(H,H) = 16.1 Hz, 1H), 7.93 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.06 (d, ^3J(H,H) = 16.1 Hz, 1H), 8.21 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.84 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.19 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.22 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.37 ppm (d, ^3J(H,H) = 4.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.3$, 22.8, 29.5 29.80, 29.85, 29.88, 30.9, 32.0, 35.3, 35.5, 38.9, 39.0, 51.9, 117.3, 117.9, 119.7, 126.1, 128.0, 128.2, 128.4, 131.1, 133.1, 134.9, 144.8, 145.4, 148.1, 148.5, 148.8, 149.1, 167.4 ppm; IR (KBr): $\tilde{\nu}=3123$, 3060, 3025, 2952, 2923, 2852, 1723, 1633, 1603, 1466, 1435, 1322, 1205, 1167, 1078, 1007, 986, 932, 787, 712 cm^{-1}; HRMS (FAB): m/z calcd for $C_{63}H_{86}N_4O_2Zn$: 994.6042 [M^+]; found: 994.6044.

5-[4-(3-Hydroxy-1-propyl)phenyl]-10,15,20-tris-(undecyl)-porphyrinzinc(II) (6b): A mixture of **6a** (500 mg, 0.50 mmol) and Pd/C (10 wt%, 50 mg, 0.05 mmol) in EtOH (10 mL) and THF (20 mL) was purged three times with hydrogen. The reaction system was then charged with hydrogen to 1 atm and stirred at RT for 24 h. After filtration through Celite, the filtrate was evaporated in vacuo to give the corresponding hydrogenated product (410 mg, 83%). M.p. 46–47 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.86$–0.91 (m, 9H), 1.24–1.45 (m, 36H), 1.75–1.86 (m, 6H), 1.75–1.86 (m, 6H), 2.35–2.49 (m, 6H), 2.98 (t, ^3J(H,H) = 7.8 Hz, 2H), 3.34 (t, ^3J(H,H) = 7.8 Hz, 2H), 3.84 (s, 3H), 4.65 (t, ^3J(H,H) = 7.6 Hz, 2H), 4.79 (t, ^3J(H,H) = 7.8 Hz, 2H), 7.59 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.11 (d, ^3J(H,H) = 8.0 Hz, 2H), 8.88 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.26 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.29 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.41 ppm (d, ^3J(H,H) = 4.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 29.4, 29.7, 29.8, 30.68, 30.74, 31.0, 31.9, 35.2, 35.4, 36.0, 38.7, 38.8, 51.8, 118.5, 119.6, 126.3, 128.0, 128.2, 128.3, 131.6, 134.6, 139.4, 141.3, 148.2, 148.9, 149.3, 149.4, 173.6 ppm; IR (KBr) $\tilde{\nu}=3123$, 3018, 2958, 2923, 2852, 1743, 1526, 1502, 1466, 1437, 1344, 1210, 1077, 1008, 788, 712 cm^{-1}; HRMS (FAB): m/z: calcd for $C_{63}H_{88}N_4O_2Zn$: 996.6199 [M^+]; found: 996.6192.

DIBAL-H (4.0 mL, 1.0 M in THF, 4.0 mmol) was added slowly to a solution of hydrogenated product (800 mg, 0.8 mmol) in THF (20 mL) at 0 °C and stirred under a N_2 atmosphere. The reaction mixture was allowed to stir for 2 h at RT, then quenched by slowly pouring into saturated NH_4Cl. After the remaining DIBAL-H was completely quenched, the gel-like organic layer was acidified with 6 M HCl and extracted with CH_2Cl_2. The combined organic layers were washed with NaOH (10%) and brine and then dried ($MgSO_4$) and evaporated in vacuo to afford **6b** (730 mg, 94%). M.p. 50–51 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.86$–0.91 (m, 9H), 1.13 (t, ^3J(H,H) = 5.3 Hz, 1H), 1.27–1.48 (m, 36H), 1.49–1.60 (m, 6H), 1.76–1.86 (m, 6H), 1.98–2.13 (m, 2H), 2.38–2.51 (m, 6H), 2.95 (t, ^3J(H,H) = 7.7 Hz, 2H), 3.61–3.67 (m, 2H), 4.65 (t, ^3J(H,H) = 8.1 Hz, 2H), 4.77 (t, ^3J(H,H) = 8.1 Hz, 4H), 7.51 (d, ^3J(H,H) = 7.9 Hz, 2H), 8.09 (d, ^3J(H,H) = 7.9 Hz, 2H), 8.88 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.25 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.27 (d, ^3J(H,H) = 4.7 Hz, 2H), 9.39 ppm (d, ^3J(H,H) = 4.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 29.4, 29.7, 29.8, 30.8, 31.8, 31.9, 33.9, 35.37, 35.44, 38.8, 38.9, 62.1, 118.7, 119.55, 119.62, 126.4, 128.1, 128.28, 128.33, 131.7, 134.5, 140.5, 140.8, 148.4, 149.0, 149.3, 149.4 ppm; IR (KBr): $\tilde{\nu}=3326$, 3123, 3018, 2955, 2923, 2852, 1608, 1557, 1525, 1502, 1466, 1343, 1298, 1209, 1076, 1056, 1009, 788, 712 cm^{-1};

HRMS (FAB): *m*/*z* calcd for $C_{62}H_{88}N_4OZn$: 968.6250 [M^+]; found: 968.6257.

4-{4-[(*tert*-Butoxycarbonyl)methoxycarbonyl]phenyl}-4-azatri-cyclo[5.2.1.0^{2,6}]dec-8-ene (9a): *tert*-Butyl bromoacetate (0.97 g, 5.0 mmol) was added to a mixture of **7** (1.02 g, 4.0 mmol) and Cs_2CO_3 (0.65 g, 2.0 mmol) in DMF (25 mL), then the mixture was heated to 50 °C for 30 min before being cooled to RT. CH_2Cl_2 (70 mL) was added and the mixture was poured into saturated $NaHCO_3$. The organic layer was separated and washed with aqueous $NaHCO_3$ (3×50 mL) and water (2×50 mL) and then dried ($MgSO_4$), and the solvent was removed in vacuo to give a residue that was flash purified by using column chromatography (eluent hexane/EtOAc 2:1) to give **9a** (1.40 g, 95 %). M.p. 160–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.48$ (s, 9H; CH_3), 1.52 (d, ^2J(H,H) = 8.1 Hz, 1H; *anti*-10-H), 1.62 (d, ^2J(H,H) = 8.1 Hz, 1H; *syn*-10-H), 2.94–2.95 (m, 2H), 2.8 (s, 2H), 3.08–3.10 (m, 2H), 3.27–3.33 (m, 2H), 4.67 (s, 2H, CH_2O), 6.17 (s, 2H; vinyl-H), 6.39 (d, ^3J(H,H) = 9.0 Hz, 2H), 7.91 ppm (d, ^3J(H,H) = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 28.0, 45.4, 46.6, 50.4, 52.1, 61.1, 82.0, 110.9, 115.3, 131.6, 135.8, 150.6, 166.3, 167.6 ppm; IR (KBr): $\tilde{\nu} = 2978$, 2942, 2867, 1745, 1696, 1609, 1526, 1482, 1426, 1386, 1368, 1298, 1230, 1166, 1106, 771 cm^{-1}; LRMS (ESI): *m*/*z* (%): 370.2 (60) [M^++H]; HRMS (ESI): *m*/*z* calcd for $C_{22}H_{27}NO_4$: 370.2026 [M^++H]; found: 370.2013.

4-{4-[(Hydroxycarbonyl)methoxycarbonyl]phenyl}-4-azatri-cyclo [5.2.1.0^{2,6}]dec-8-ene (9b): A solution of **9a** (1.11 g, 3.0 mmol) and CF_3CO_2H (50 %) in CH_2Cl_2 (30 mL) was stirred for 3 h and then evaporated in vacuo to afford an oily residue. A small amount of water was added and the mixture was neutralized with saturated $NaHCO_3$. The white precipitate was collected and washed with water and hexane and then dried under vacuum to give **9b** (1.0 g, 91 %). M.p. 200–201 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.49$ (apparent s, 2H; bridging CH_2), 2.90–2.94 (m, 4H), 3.06–3.8 (m, 2H), 3.25–3.29 (m, 2H), 4.70 (s, 2H; CH_2O), 6.17 (s, 2H; vinyl-H), 6.45 (d, ^3J(H,H) = 9.0 Hz, 2H), 7.75 (d, ^3J(H,H) = 9.0 Hz, 2H), 12.99 ppm (brs, 1H; COOH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 44.7$, 46.0, 50.0, 51.5, 60.3, 111.0, 114.4, 130.9, 135.7, 150.3, 165.4, 169.5 ppm; IR (KBr): $\tilde{\nu} = 3060$, 2964, 2941, 2886, 2848, 1735, 1714, 1608, 1526, 1477, 1433, 1411, 1379, 1278, 1244, 1188, 1122, 767 cm^{-1}; LRMS (ESI): *m*/*z* (%): 312.2 ([M^+−H] (100); HRMS (ESI): *m*/*z* calcd for $C_{18}H_{20}NO_4$: 314.1397 [M^++H]; found: 314.1387; elemental analysis calcd (%) for $C_{18}H_{19}NO_4$: C 68.99, H 6.11, N 4.47; found: C 68.44, H 6.12, N 4.28.

Compound 11a: Oxalyl chloride (0.31 mL, 3.7 mmol) and DMF (one drop) were added to a solution of **7** (390 mg, 1.5 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was gradually warmed to RT and stirred for 1 h, then the solvent was removed in vacuo to give **8**, which was used for the next reaction without further purification.

Next, compound **8** in CH_2Cl_2 (20 mL) was added to a mixture of **5a** (880 mg, 1.0 mmol), NEt_3 (2.0 mL), and DMAP (trace amount) in CH_2Cl_2 (20 mL) at 0 °C. The mixture was stirred at RT for 17 h, then saturated $NaHCO_3$ was added and the solution was washed with water and brine and then dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2/NEt_3 1:1:0.05) to give **11a** (1.03 g, 93 %). M.p. 92–93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.64$ (s, 2H; NH), 0.87–0.93 (m, 9H; CH_3), 1.25–1.47 (m, 36H; CH_2), 1.47–1.62 (m, 7H; CH_2; CH on norbornene), 1.65 (d, ^2J(H,H) = 8.2 Hz, 1H; CH on norbornene), 1.78–1.87 (m, 6H; CH_2), 2.50–2.58 (m, 6H; CH_2), 3.00–3.04 (m, 4H; H on norbornene), 3.06–3.09 (m, 2H; H on norbornene), 3.29–3.34 (m, 2H; H on norbornene), 4.91–4.98 (m, 6H; CH_2), 6.21 (s, 2H; alkenyl H on norbornene), 6.53 (d, ^3J(H,H) = 8.9 Hz, 2H; ArH), 7.61 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 8.20 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 8.21 (d, ^3J(H,H) = 8.9 Hz, 2H; ArH), 8.90 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 9.40 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 9.51 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 9.54 ppm (d, ^3J(H,H) = 4.8 Hz, 2H; β-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.3$, 22.8, 29.5, 29.77, 29.84, 29.86, 30.7, 30.8, 32.0, 35.5, 35.9, 38.8, 39.0, 45.4, 46.7, 50.5, 52.1, 111.0, 115.2, 117.1, 119.0, 119.3, 120.0 127.9, 128.3, 132.0, 135.0, 135.6, 139.4, 150.6, 151.0, 165.6 ppm; IR (KBr): $\tilde{\nu} = 3313$, 3126, 3060, 2955, 2923, 2852, 1721, 1603, 1527, 1474, 1380, 1272, 1205, 1175, 1164, 1058, 967, 791, 734 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{75}H_{100}N_5O_2$: 1102.7877 [M^++H]; found: 1102.7886.

Compound 11b: In a manner similar to that described above for **11a**, compound **5g**[15] was converted to **11b** (0.37 g, 74 %). M.p. 90–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -2.65$ (s, 2H; NH), 0.86–0.92 (m, 9H; CH_3), 1.27–1.42 (m, 36H; CH_2), 1.45–1.56 (m, 7H; CH_2; CH on norbornene), 1.63 (d, ^2J(H,H) = 8.3 Hz, 1H; CH on norbornene), 1.77–1.85 (m, 6H; CH_2), 2.50–2.56 (m, 6H; CH_2), 2.97–3.01 (m, 4H; H on norbornene), 3.07–3.10 (m, 2H; H on norbornene), 3.29–3.32 (m, 2H; H on norbornene), 4.91–4.98 (m, 6H; CH_2), 5.70 (s, 2H; OCH_2), 6.19 (s, 2H; alkenyl H on norbornene), 6.47 (d, ^3J(H,H) = 9.0 Hz, 2H; ArH), 7.81 (d, ^3J(H,H) = 8.0 Hz, 2H; ArH), 8.10 (d, ^3J(H,H) = 9.0 Hz, 2H; ArH), 8.17 (d, ^3J(H,H) = 8.0 Hz, 2H; ArH), 8.83 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 9.38 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 9.50 (d, ^3J(H,H) = 4.9 Hz, 2H; β-H), 9.53 ppm (d, ^3J(H,H) = 4.9 Hz, 2H; β-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.3$, 22.8, 29.46, 29.48, 29.75, 29.77, 29.8, 29.9, 30.7, 30.8, 32.0, 35.5, 35.9, 38.8, 39.0, 45.4, 46.6, 50.4, 52.1, 65.8, 110.7, 110.9, 116.1, 117.4, 119.0, 119.3, 125.9, 127.8 (br), 131.0, 131.4, 134.4, 135.6, 136.1, 142.0, 150.3, 166.9 ppm; IR (KBr): $\tilde{\nu} = 3316$, 3120, 3053, 2952, 2923, 2852, 1704, 1605, 1524, 1475, 1376, 1271, 1177, 1097, 969, 917, 792, 768 cm^{-1}; HRMS (FAB): *m*/*z*: calcd for 1116.8034 ($C_{76}H_{102}N_5O_2$, [M^++H]); found: 1116.8024.

21*H*,23*H*-5-[(4-Aza-tricycle[5.2.1.0$^{2,6\text{-}endo}$]dec-8-ene-3,5-dione-4-yl)phenyl]-10,15,20-tris(4-octoxyphenyl)porphyrin (11d): A solution of **10** (43 mg, 0.26 mmol) and **5f** (267 mg, 0.26 mmol) in DMF (5 mL) was heated at reflux for 18 h. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2) to give the corresponding imide **11d′** as a purple solid (201 mg, 67 %). M.p. >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.76$ (s, 2H; NH), 0.94 (t, ^3J(H,H) = 6.6 Hz, 9H; CH_3), 1.36–1.50 (m, 24H; CH_2), 1.61 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 1.67 (d, ^2J(H,H) = 9.0 Hz, 1H; *anti*-10-H), 1.86 (d, ^2J(H,H) = 9.0 Hz, 1H; *syn*-10-H), 1.96 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 3.55 (brs, 2H; H on norbornene), 3.62 (brs, 2H; H on norbornene), 4.22 (t, ^3J(H,H) = 6.6 Hz, 6H; 3×OCH_2), 6.43 (s, 2H; vinyl-H), 7.25 (d, ^3J(H,H) = 8.1 Hz, 6H; ArH), 7.55 (d, ^3J(H,H) = 8.1 Hz, 2H; ArH), 8.09 (d, ^3J(H,H) = 8.1 Hz, 6H; ArH), 8.26 (d, ^3J(H,H) = 8.1 Hz, 2H; ArH), 8.87 ppm (brs, 8H; β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 14.2, 22.7, 26.2, 29.3, 29.5, 29.7, 31.9, 45.6, 45.9, 52.3, 68.2, 112.7, 118.3, 120.0, 120.3, 124.7, 130.7, 131.0, 131.4, 134.2, 134.8, 135.0, 135.6, 142.4, 158.9, 177.0 ppm; IR (KBr): $\tilde{\nu} = 2925$, 2854, 1713, 1606, 1509, 1468, 1376, 1283, 1245, 1174, 1108, 966, 738, 723 cm^{-1}; LRMS (MALDI): *m*/*z* (%): 1161.6 (100) [M^++2H]; HRMS (MALDI): *m*/*z* calcd for $C_{77}H_{86}N_5O_5$: 1160.6615 [M^++H]; found: 1160.6624.

A solution of imide **11d′** (200 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) was added slowly to a suspension of $LiAlH_4$ (26 mg, 0.68 mmol) in Et_2O (10 mL), and the mixture was stirred at RT for 4 h. Water (1 mL) and NaOH (10 %, 1 mL) were then added sequentially and the resulting suspension was filtered. The solid was repeatedly triturated with CH_2Cl_2 and then filtered. The CH_2Cl_2 solution was dried (Na_2SO_4) and filtered and the filtrate was concentrated in vacuo to give a residue that was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2 1:1) to give **11d** as a purple solid (135 mg, 70 %). M.p. 204–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -2.69$ (s, 2H; NH), 0.94 (t, ^3J(H,H) = 6.6 Hz, 9H; CH_3), 1.35–1.71 (m, 32H; CH_2 on alkyl chain and norbornene), 1.97 (quint., ^3J(H,H) = 6.6 Hz, 6H; CH_2), 3.09–3.21 (m, 6H; H on norbornene), 3.45–3.51 (m, 2H; H on norbornene), 4.22 (t, ^3J(H,H) = 6.6 Hz, 6H; OCH_2), 6.34 (t, ^3J(H,H) = 1.5 Hz, 2H; alkenyl H on norbornene), 6.78 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 7.25 (d, ^3J(H,H) = 8.4 Hz, 6H; ArH), 8.01 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 8.10 (d, ^3J(H,H) = 8.4 Hz, 2H; ArH), 8.83 (d, ^3J(H,H) = 4.8 Hz, 2H; β-H), 8.84 (s, 4H; β-H), 8.93 ppm (d, ^3J(H,H) = 4.8 Hz, 2H; β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 22.7, 26.3, 29.4, 29.5, 29.7, 31.9, 45.8, 46., 51.0, 52.3, 68.4, 110.4, 112.7, 119.3, 119.6, 121.5, 129.4, 130.8, 130.8, 130.9, 131.0, 131.2, 131.2, 131.3, 134.6, 134.7, 135.6, 135.9, 136.1, 147.2, 158.9 ppm; IR (KBr): $\tilde{\nu} =$ 2924, 2853, 1607, 1509, 1469, 1367, 1284, 1244, 1174, 965, 803, 738 cm^{-1}; LRMS (MALDI): *m*/*z* (%): 1067.1 (100) [M^+−$C_4H_3N^{2-}$], 1132.1 (6) [M^+], 1133.1 (10) [M^++H], 1134.1 (10) [M^++2H]; HRMS (MALDI): *m*/*z* calcd for $C_{77}H_{90}N_5O_3$: 1132.7015 [M^++H]); found: 1132.7038.

Compound 11e: Compound **8** in CH_2Cl_2 (10 mL) was added dropwise to a mixture of **5e** (507 mg, 0.5 mmol) and DMAP (0.75 mol, 92 mg) in CH_2Cl_2 (10 mL) at 0°C under argon. The mixture was allowed to warm to RT and was stirred for an additional 24 h. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2/hexane 3:1) to give **11e** as a purple solid (594 mg, 95%). M.p. 229–231°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-2.76$ (s, 2H; NH), 0.94 (t, ^3J(H,H)=6.6 Hz, 9H; CH_3), 1.36–1.67 (m, 32H; CH_2), 1.99 (quint., ^3J(H,H)=6.6 Hz, 6H; CH_2), 3.03–3.07 (m, 4H), 3.12–3.15 (m, 2H), 3.35–3.41 (m, 2H), 4.25 (t, ^3J(H,H)=6.6 Hz, 6H; 3×OCH_2), 6.22 (s, 2H), 6.52 (d, ^3J(H,H)=9.0 Hz, 2H), 7.27 (d, ^3J(H,H)=9.0 Hz, 6H), 7.59 (d, ^3J(H,H)=9.0 Hz, 2H), 8.11 (d, ^3J(H,H)=9.0 Hz, 6H), 8.18 (d, ^3J(H,H)=9.0 Hz, 2H), 8.23 (d, ^3J(H,H)=9.0 Hz, 2H), 8.87 (s, 4H, β-H), 8.89 (d, ^3J(H,H)=5.1 Hz, 2H, β-H), 8.90 ppm (d, ^3J(H,H)=5.1 Hz, 2H, β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.2$, 22.7, 26.2, 29.3, 29.5, 31.9, 45.4, 46.6, 50.5, 52.1, 68.3, 111.1, 112.7, 115.2, 118.9, 119.9, 120.1, 120.2, 131.0 (br), 132.1, 134.3, 134.4, 135.3, 135.6, 135.8, 139.3, 150.8, 151.3, 158.9, 165.8 ppm; IR (KBr): $\tilde{\nu}=2924$, 2851, 1722, 1604, 1558, 1506, 1471, 1379, 1277, 1244, 1175, 1057, 966, 802, 720 cm^{-1}; LRMS (MALDI): *m*/*z* (%): 1252.7 (100) $[M^++H]$; HRMS (MALDI): *m*/*z* calcd for $C_{84}H_{94}N_5O_5$: 1252.7222 $[M^++H]$; found: 1252.7250; elemental analysis calcd (%) for $C_{84}H_{94}N_5O_5$: C 80.54, H 7.48, N 5.59; found: C 80.07, H 7.51, N 5.11.

Compound 11f: A mixture of **9b** (250 mg, 0.8 mmol) and oxalyl chloride (0.75 mL, 8 mmol) in CH_2Cl_2 (10 mL) was stirred at RT for 3 h and dried in vacuo to give **9c**, which was used for the next reaction without further purification. A mixture of **5e** (507 mg, 0.5 mmol) DMAP (96 mg, 0.8 mol) and **9c** in CH_2Cl_2 (20 mL) was stirred at RT for 24 h. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2 3:7) to give **11f** (622 mg, 95%). M.p. 202–204°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-2.78$ (s, 2H; NH), 0.94 (t, ^3J(H,H)=6.6 Hz, 9H; CH_3), 1.36–1.67 (m, 32H; CH_2), 1.98 (quint., ^3J(H,H)=6.6 Hz, 6H; CH_2), 2.97–3.00 (m, 4H; H on norbornene), 3.08–3.11 (m, 2H; H on norbornene), 3.29–3.35 (m, 2H; H on norbornene), 4.24 (t, ^3J(H,H)=6.6 Hz, 6H; 3×OCH_2), 5.20 (s, 2H; OCH_2CO), 6.18 (s, 2H; vinyl-H), 6.44 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 7.26 (d, ^3J(H,H)=8.4 Hz, 6H; ArH), 7.54 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 8.03 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 8.09 (d, $J=8.4$ Hz, 6H; ArH), 8.21 (d, $J=8.7$ Hz, 2H; ArH), 8.81–8.88 ppm (m, 8H, β-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.2$, 22.7, 26.2, 29.3, 29.46, 29.47, 31.9, 45.3, 46.5, 50.3, 52.0, 60.9, 68.2, 111.0, 112.6, 112.7, 114.8, 118.4, 119.6, 119.8, 120.0, 120.2, 131.1, 131.8, 134.26, 134.29, 134.34, 135.3, 135.5, 135.6, 135.7, 140.1, 150.1, 150.7, 158.9, 166.5, 167.3 ppm; IR (KBr): $\tilde{\nu}=2926$, 2853, 1745, 1712, 1605, 1507, 1470, 1378, 1283, 1245, 1169, 1104, 966, 801, 768, 720 cm^{-1}; LRMS (MALDI): *m*/*z* (%): 1310.7 $[M^++H]$ (81); HRMS (MALDI): *m*/*z* calcd for $C_{86}H_{96}N_5O_7$: 1310.7318 $[M^++H]$; found: 1310.7304.

Compound 1a: A mixture of **11a** (700 mg, 0.63 mmol) and zinc acetate (690 mg, 3.15 mmol) in methanol (20 mL) and CH_2Cl_2 (40 mL) was stirred at RT in the dark for 3 h and then washed with $NaHCO_3$ and brine and dried ($MgSO_4$). The solvent was removed in vacuo to give a residue that was purified by column chromatography on silica gel (eluent hexane/CH_2Cl_2/NEt_3 1:1:0.05) to afford **1a** (680 mg, 92%). M.p. 136–137°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.85$–0.90 (m, 9H; CH_3), 1.27–1.42 (m, 36H; CH_2), 1.46–1.61 (m, 7H; CH_2; CH on norbornene), 1.65 (d, ^2J(H,H)=8.0 Hz, 1H; CH on norbornene), 1.72–1.85 (m, 6H; CH_2), 2.30–2.38 (m, 2H; CH_2), 2.39–2.49 (m, 4H; CH_2), 3.00–3.04 (m, 4H; H on norbornene), 3.09–3.11 (m, 2H; H on norbornene), 3.30–3.35 (m, 2H; H on norbornene), 4.52 (t, ^3J(H,H)=8.4 Hz 2H; CH_2), 4.71 (t, ^3J(H,H)=7.8 Hz 4H; CH_2), 6.20 (s, 2H; alkenyl H on norbornene), 6.49 (d, ^3J(H,H)=8.8 Hz, 2H; ArH), 7.60 (d, ^3J(H,H)=8.8 Hz, 2H; ArH), 8.19 (d, ^3J(H,H)=8.8 Hz, 2H; ArH), 8.20 (d, ^3J(H,H)=8.8 Hz, 2H; ArH), 8.92 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 9.12 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 9.16 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 9.37 ppm (d, $J=4.8$ Hz, 2H; β-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.3$, 22.8, 29.5, 29.79, 29.83, 29.88, 30.9, 32.0, 35.6, 35.7, 38.97, 39.02, 45.5, 46.8, 50.6, 52.2, 111.1, 115.3, 118.0, 119.8, 119.9, 128.3, 128.5, 131.7, 132.0, 134.9, 135.7, 140.1, 148.4, 149.1, 149.2, 149.4, 150.7, 150.8, 165.6 ppm; IR (KBr): $\tilde{\nu}=3123$, 3060, 2955, 2923, 2852, 1721, 1605, 1527, 1500, 1468, 1380, 1272, 1205, 1175, 1164, 1059, 1008, 788 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{75}H_{97}N_5O_2Zn$: 1163.6934 $[M^+]$; found: 1163.6943.

Compound 1b: In a manner similar to that described above for **1a**, compound **11b** (320 mg, 0.287 mmol) was converted to **1b** (301 mg, 89%). M.p. 68–69°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.89$–0.96 (m, 9H; CH_3), 1.30–1.45 (m, 36H; CH_2), 1.45–1.60 (m, 7H; CH_2; CH on norbornene), 1.64 (d, ^2J(H,H)=8.4 Hz, 1H; CH on norbornene), 1.70–1.85 (m, 6H; CH_2), 2.26–2.28 (m, 2H; CH_2), 2.41–2.43 (m, 4H; CH_2), 2.95–2.99 (m, 4H; H on norbornene), 3.06–3.08 (m, 2H; H on norbornene), 3.24–3.29 (m, 2H; H on norbornene), 4.35–4.39 (m, 2H; CH_2), 4.60–6.64 (m, 4H; CH_2), 5.69 (s, 2H; OCH_2), 6.19 (s, 2H; alkenyl H on norbornene), 6.43 (d, ^3J(H,H)=8.8 Hz, 2H; ArH), 7.84 (d, ^3J(H,H)=8.0 Hz, 2H; ArH), 8.06 (d, ^3J(H,H)=8.8 Hz, 2H; ArH), 8.22 (d, ^3J(H,H)=8.0 Hz, 2H; ArH), 8.88 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 8.98 (d, ^3J(H,H)=4.0 Hz, 2H; β-H), 9.03 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 9.33 ppm (d, ^3J(H,H)=5.2 Hz, 2H; β-H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.6$, 23.1, 29.7, 30.0, 30.1, 31.1, 32.3, 35.7, 39.1, 39.2, 45.6, 46.8, 50.6, 52.3, 65.9, 110.7, 115.9, 118.0, 119.36, 119.43, 125.5, 127.3, 127.9, 128.1, 131.1, 131.3, 134.0, 135.35, 135.41, 142.3, 147.8, 148.4, 148.6, 148.9, 149.9, 166.5 ppm; IR (KBr): $\tilde{\nu}=$ 3063, 2952, 2923, 2852, 1704, 1604, 1523, 1466, 1375, 1271, 1177, 1096, 1008, 788 cm^{-1}; HRMS (ESI): *m*/*z* calcd for $C_{76}H_{99}N_5O_2Zn$: 1177.7090 $[M^+]$; found: 1177.7075.

Compound 1c: In a manner similar to that described for the preparation of **11a**, a mixture of **6b** (500 mg, 0.51 mmol), NEt_3 (1.0 mL), DMAP (trace amount), and **8** (200 mg, 0.77 mmol; freshly prepared from **7**) in CH_2Cl_2 (10 mL) was converted to **1c** (410 mg, 67%). M.p. 65–66°C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.88$–0.93 (m, 9H; CH_3), 1.28–1.46 (m, 36H; CH_2), 1.46–1.66 (m, 8H), 1.77–1.90 (m, 6H; CH_2), 2.31–2.54 (m, 8H), 2.94–2.98 (m, 4H), 3.04–3.07 (m, 2H), 3.18 (t, ^3J(H,H)=7.8 Hz, 2H), 3.24–3.29 (m, 2H), 4.53–4.56 (m, 4H), 4.74 (t, ^3J(H,H)=7.8 Hz, 4H), 6.16 (s, 2H), 6.42 (d, ^3J(H,H)=8.8 Hz, 2H), 7.62 (d, ^3J(H,H)=7.8 Hz, 2H), 7.98 (d, ^3J(H,H)=8.8 Hz, 2H), 8.12 (d, ^3J(H,H)=7.8 Hz, 2H), 8.90 (d, ^3J(H,H)=5.0 Hz, 2H), 9.16 (d, ^3J(H,H)=4.4 Hz, 2H), 9.20 (d, ^3J(H,H)=4.4 Hz, 2H), 9.38 ppm (d, ^3J(H,H)=5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=14.1$, 22.7, 29.4, 29.69, 29.75, 29.77, 30.66, 30.74, 30.80, 31.9, 32.5, 35.0, 35.3, 38.6, 38.8, 45.3, 46.5, 50.4, 52.3, 63.6, 110.9, 116.6, 118.7, 119.3, 119.4, 126.6, 127.8, 128.0, 128.3, 131.2, 131.7, 134.6, 135.7, 140.4, 140.9, 148.0, 148.7, 149.3, 150.4, 167.2 ppm; IR (KBr): $\tilde{\nu}=$ 3120, 3063, 3022, 2952, 2923, 2852, 1704, 1605, 1524, 1467, 1377, 1274, 1179, 1104, 1077, 1008, 788, 769, 713 cm^{-1}; HRMS (FAB): *m*/*z* calcd for $C_{78}H_{103}N_5O_2Zn$: 1205.7403 $[M^++H]$; found: 1205.7410.

Compound 1d: In a manner similar to that described for **1a**, compound **11d** (113 mg, 0.1 mmol) was converted to **1d** (113 mg, 95%). M.p. 200–202°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.94$ (t, ^3J(H,H)=6.6 Hz, 9H; CH_3), 1.36–1.72 (m, 32H), 1.97 (quint., ^3J(H,H)=6.6 Hz, 6H; CH_2), 3.07–3.24 (m, 6H), 3.46–3.51 (m, 2H), 4.23 (t, ^3J(H,H)=6.6 Hz, 6H; OCH_2), 6.35 (s, 2H), 6.78 (d, ^3J(H,H)=8.4 Hz, 2H), 7.25 (d, ^3J(H,H)=8.4 Hz, 6H), 8.01 (d, ^3J(H,H)=8.4 Hz, 2H), 8.10 (d, ^3J(H,H)=8.4 Hz, 6H), 8.94 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 8.95 (s, 4H; β-H), 9.05 ppm (d, $J=4.8$ Hz, 2H; β-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=14.2$, 22.7, 26.3, 29.4, 29.6, 29.7, 31.9, 45.8, 46.7, 51.0, 52.4, 68.4, 110.3, 112.6, 120.4, 120.7, 122.4, 130.0, 131.6, 131.7, 131.8, 132.3, 135.2, 135.4, 135.6, 136.1, 147.1, 150.36, 150.44, 150.5, 151.0, 158.8 ppm; IR (KBr): $\delta=2924$, 2853, 1606, 1573, 1524, 1509, 1489, 1468, 1374, 1338, 1281, 1245, 1173, 996, 796, 724 cm^{-1}; LRMS (MALDI): *m*/*z* (%): 1127.3 (100) $[M^+-Zn-2H]$, 1128.3 (90) $[M^+-Zn-H]$, 1129.3 (88) $[M^+-Zn]$, 1179.4 (20) $[M^+-Zn+CH_3OH+H_2O]$, 1193.3 (18) $[M^+(Zn^{64})]$, 1195.3 (16) $[M^+(^{66}Zn)]$, 1197.3 (14) $[M^+(^{68}Zn)]$; HRMS (MALDI): *m*/*z* calcd for $C_{77}H_{87}N_5O_3{}^{64}Zn$: 1193.6092; found: 1193.6095.

Compound 1e: In a manner similar to that described for **1a**, compound **11e** (500 mg, 0.4 mmol) was converted to **1e** (510 mg, 97%). M.p. 226–228°C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.93$ (t, ^3J(H,H)=6.6 Hz, 9H; CH_3), 1.35–1.63 (m, 32H; CH_2), 1.95 (quint., ^3J(H,H)=6.6 Hz, 6H; CH_2), 2.93–3.05 (m, 6H), 3.20–3.26 (m, 2H), 4.19 (t, ^3J(H,H)=6.6 Hz, 2H; OCH_2), 4.20 (t, ^3J(H,H)=6.6 Hz, 4H; 2×OCH_2), 6.16 (s, 2H), 6.41 (d, ^3J(H,H)=9.0 Hz, 2H), 7.22 (d, ^3J(H,H)=8.4 Hz, 2H), 7.23 (d, $J=8.4$ Hz, 4H), 7.57 (d, $J=8.4$ Hz, 2H), 8.10 (d, ^3J(H,H)=8.4 Hz, 6H), 8.12 (d, ^3J(H,H)=9.0 Hz, 2H), 8.23 (d, ^3J(H,H)=8.4 Hz, 2H), 8.98 (brs, 4H;

β-H), 8.99 (d, ^3J(H,H)=4.8 Hz, 2H; β-H), 9.01 ppm (d, ^3J(H,H)=4.8 Hz, 2H; β-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=14.1, 22.7, 26.2, 29.3, 29.5, 29.7, 31.9, 45.3, 46.6, 50.5, 52.1, 68.3, 110.8, 111.1, 112.6, 115.3, 119.98, 120.04, 120.9, 121.0, 131.1, 131.8, 131.9, 132.0, 132.1, 135.00, 135.04, 135.1, 135.4, 135.8, 139.9, 150.2, 150.48, 150.54, 150.6, 150.8, 151.1, 158.76, 158.78, 165.8 ppm; IR (KBr): $\tilde{\nu}$=2924, 2852, 1722, 1603, 1525, 1509, 1491, 1472, 1379, 1338, 1273, 1245, 1204, 1174, 1060, 998, 797, 720 cm^{-1}; LRMS (MALDI): *m/z* (%): 1313.6 (60) [M^+]; HRMS (MALDI): *m/z* calcd for $C_{84}H_{91}N_5O_5Zn$: 1313.6281 [M^+]); found: 1313.6306; elemental analysis calcd (%) for $C_{84}H_{91}N_5O_5Zn$: C 76.66, H 6.97, N 5.32; found: C 75.86, H 7.32, N 4.93.

Compound 1f: In a manner similar to that described for **1a**, compound **11f** (131 mg, 0.1 mmol) was converted to **1f** (115 mg, 88%). M.p. 199–201 °C; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.94 (t, ^3J(H,H)=6.6 Hz, 9H; CH$_3$), 1.36–1.60 (m, 32H; CH$_2$), 1.96 (quint., ^3J(H,H)=6.6 Hz, 6H; CH$_2$), 2.92–2.98 (m, 4H; H on norbornene), 3.04–3.08 (m, 2H; H on norbornene), 3.21–3.27 (m, 2H; H on norbornene), 4.21 (t, ^3J(H,H)=6.6 Hz, 6H; 3×OCH$_2$), 5.07 (s, 2H; OCH$_2$CO), 6.16 (s, 2H; vinyl-H), 6.36 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 7.24 (d, ^3J(H,H)=8.4 Hz, 6H; ArH), 7.50 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 7.89 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 8.09 (d, ^3J(H,H)=8.4 Hz, 6H; ArH), 8.20 (d, ^3J(H,H)=8.7 Hz, 2H; ArH), 8.91–8.98 ppm (m, 8H; β-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=14.1, 22.7, 26.2, 29.3, 29.5, 31.9, 45.3, 46.6, 50.4, 52.1, 60.8, 68.3, 111.0, 112.6, 114.7, 118.4, 119.4, 119.8, 121.0, 131.6, 131.7, 131.86, 131.92, 132.0, 132.1, 134.96, 135.0, 135.1, 135.4, 135.8, 140.8, 149.9, 150.0, 150.49, 150.52, 150.6, 150.7, 158.8, 166.4, 167.3 ppm; IR (KBr): $\tilde{\nu}$=2926, 2854, 1784, 1712, 1605, 1573, 1525, 1509, 1492, 1473, 1379, 1339, 1282, 1245, 1172, 1105, 998, 797, 720 cm^{-1}; LRMS (MALDI): *m/z* (%): 1371.6 (80) [M^+]; HRMS (MALDI): *m/z* calcd for $C_{86}H_{93}N_5O_7Zn$: 1371.6392 [M^+]; found: 1371.6361.

General procedure for the preparation of polymer 2: A solution of **1** (0.2 mmol) and [Ru(=CHPh)Cl$_2$(Cy$_3$P)$_2$] (8 mg, 0.001 mmol, 5 mol%) in CH$_2$Cl$_2$ (2 mL) was stirred at RT for 2 h Under argon. The mixture was quenched with ethyl vinyl ether (1 mL) and poured into MeOH (10 mL). The resulting solid was collected and redissolved in CH$_2$Cl$_2$ (1 mL) and reprecipitated by adding MeOH (20 mL). This procedure was repeated two to three times and the solid was collected to afford polymer **2**.

Polymer **2a**: Yield 92%; ^{1}H NMR (500 MHz, CDCl$_3$): δ=0.7–0.9 (br, 9H; CH$_3$), 0.9–1.7 (br, 44H; CH$_2$), 1.7–2.2 (br, 6H; CH$_2$), 2.2–2.5 (br, 6H; CH$_2$), 2.5–3.0 (br, 4H), 3.0–3.9 (br, 8H), 4.2–4.7 (br, 2H), 4.9–5.6 (br, 2H), 6.1–6.8 (br, 2H), 7.5–7.8 (br, 2H), 7.8–8.1 (br, 2H), 8.1–8.6 (br, 8H), 8.7–9.0 ppm (br, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=14.1, 22.7, 29.4, 29.8, 30.7, 30.9, 32.0, 34.4, 35.7, 38.7, 44.4, 46.2, 49.6, 111.7, 116.6, 117.3, 118.6, 119.3, 119.9, 126.1, 127.4, 131.0, 132.2, 135.4, 139.8, 148.0, 150.9, 151.3, 165.6 ppm; IR (KBr): $\tilde{\nu}$=3123, 2949, 2923, 2852, 1725, 1606, 1557, 1527, 1500, 1479, 1466, 1379, 1270, 1205, 1177, 1165, 1061, 1009, 963, 825, 788 cm^{-1}; GPC (THF): M_n=18865, M_w=20352, PDI=1.08.

Polymer **2b**: Yield 91%; ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.7–0.9 (br, 9H; CH$_3$), 0.9–1.5 (br, 42H; CH$_2$), 1.5–1.9 (br, 8H; CH$_2$; CH on norbornene), 1.9–2.3 (br, 6H; CH$_2$), 2.3–3.3 (br, 8H; H on norbornene), 3.8–4.5 (br, 8H; CH$_2$), 4.8–5.4 (br, 2H; OCH$_2$), 5.4–5.8 (br, 2H,), 6.1–6.6 (br, 2H; ArH), 7.5–7.7 (br, 2H; ArH), 7.7–8.2 (br, 4H; ArH), 8.2–8.9 ppm (br, 8H; β-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=14.3, 22.8, 29.5, 29.8, 29.9, 30.8, 32.0, 35.0, 38.9, 44.3, 46.3, 49.4, 65.9, 111.4, 117.6, 118.9, 119.2, 125.7, 127.6, 131.3, 134.3, 135.4, 142.5, 147.8, 148.1, 148.5, 150.6, 166.6 ppm; IR (KBr): $\tilde{\nu}$=3123, 2952, 2922, 2852, 1707, 1606, 1522, 1466, 1375, 1271, 1179, 1008, 788 cm^{-1}; GPC (THF): M_n=17136, M_w=20556, PDI=1.19.

Polymer **2c**: Yield 90%; ^{1}H NMR (500 MHz, CDCl$_3$): δ=0.7–0.9 (br, 9H), 0.9–1.6 (br, 44H), 1.6–1.8 (br, 6H), 2.1–2.5 (br, 8H), 2.6–3.3 (br, 8H), 3.9–4.6 (br, 8H), 4.7–5.3 (br, 2H), 6.1–6.5 (br, 2H), 7.4–7.6 (br, 2H), 7.7–8.1 (br, 4H), 8.5–9.1 ppm (br, 8H, β-H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=14.1, 22.7, 29.4, 29.7, 29.8, 30.7, 31.9, 32.4, 35.0, 38.8, 44.3, 46.2, 49.2, 63.7, 111.4, 117.3, 118.3, 119.1, 126.4, 127.8, 131.3, 134.5, 140.2, 140.7, 147.9, 148.4, 148.9, 150.8, 167.0 ppm; IR (KBr): $\tilde{\nu}$=3018, 2952, 2923, 2852, 1705, 1606, 1523, 1466, 1377, 1273, 1180, 1104, 1077, 1007, 964, 788, 768, 707 cm^{-1}; GPC (THF): M_n=15322, M_w=17275, PDI=1.13.

Polymer **2d**: Yield 80%; ^{1}H NMR (500 MHz, CDCl$_3$): δ=0.89 (brs, 9H; CH$_3$), 1.28–2.00 (brm, 38H), 2.20–3.06 (brm, 8H), 3.40–4.23 (brm, 6H, OCH$_2$), 4.80–5.60 (brm, 2H), 6.71–7.28 (brm, 8H), 7.71–8.12 (brm, 8H), 8.67–8.96 ppm (brm, 8H; β-H); ^{13}C NMR (125 MHz, CDCl$_3$): δ=14.1, 22.7, 26.1, 29.3, 29.5, 29.7, 31.8, 44.5, 45.0, 46.2, 50.2 (br), 68.2 (br), 111.4, 112.2, 112.3, 112.5, 120.3, 121.8, 129.5, 131.5, 131.8, 132.1, 135.3, 135.4, 147.4, 150.2, 150.5, 150.7, 158.5 ppm; IR (KBr): $\tilde{\nu}$=3033, 2922, 2852, 1606, 1572, 1524, 1509, 1467, 1365, 1338, 1245, 1172, 1106, 1066, 996 (s), 846 (w), 797 (s), 718 cm^{-1} (w); GPC (THF): M_n=10550, M_w=14550, PDI=1.38.

Polymer **2e**: Yield 92%; ^{1}H NMR (400 MHz, CDCl$_3$): δ=0.85 (brs, 9H; CH$_3$), 1.23–1.98 (m, 38H; CH$_2$), 2.20–3.30 (br, 8H), 3.80–4.25 (br, 6H, OCH$_2$), 5.14 (brs, 2H), 6.34 (brs, 2H), 6.87–7.26 (m, 6H), 7.57 (brs, 2H), 7.85–8.20 (m, 10H), 8.85 ppm (brs, 8H; β-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=14.2, 22.7, 26.1, 29.3, 29.4, 31.8, 39.8, 44.4, 46.8, 49.2, 68.1, 111.6, 112.5, 116.2, 119.8, 120.8, 131.9, 135.3, 140.1, 150.0, 150.4, 151.0, 158.5, 158.7, 165.5 ppm; IR (KBr): $\tilde{\nu}$=2924, 2853, 1725, 1606, 1525, 1509, 1491, 1380, 1339, 1265, 1246, 1205, 1175, 1064, 998, 798, 760, 720 cm^{-1}; elemental analysis calcd (%): C 76.66, H 6.97, N 5.32; found: C 75.37, H 7.14, N 4.90; GPC (THF): M_n=51437, M_w=81295, PDI=1.58.

Polymer **2f**: Yield 92%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.91 (brs, 9H; CH$_3$), 1.32–1.81 (m, 38H; CH$_2$), 2.60–2.98 (m, 8H; H on norbornene), 3.95–4.13 (m, 6H; 3×OCH$_2$), 5.82 (brs, 2H; OCH$_2$CO), 5.19 (brs, 2H; vinyl-H), 6.25 (brs, 2H; ArH), 7.01–7.17 (m, 6H; ArH), 7.37 (brs, 2H; ArH), 7.67 (brs, 2H; ArH), 7.93–8.05 (m, 8H; ArH), 8.85–8.91 ppm (m, 8H; β-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=14.1, 22.7, 26.2, 29.3, 29.4, 31.8, 35.7, 37.4, 39.7, 44.3, 46.2, 49.3, 60.6, 68.2, 111.3, 112.5, 115.3, 119.3, 120.8, 121.0, 126.0, 128.4, 131.6, 131.9, 132.0, 134.96, 135.0, 135.1, 135.3, 135.4, 140.7, 149.9, 150.4, 150.5, 151.1, 158.5, 158.6, 166.0, 167.0 ppm; IR (KBr): $\tilde{\nu}$=2925, 2853, 1745, 1716, 1606, 1524, 1509, 1491, 1378, 1339, 1281, 1245, 1204, 1172, 1105, 998, 798, 798, 767, 719 cm^{-1}; GPC (THF): M_n=9500, M_w=11000, PDI=1.16.

4-Cyclohexyl-4-aza-tricyclo[5.2.1.0^{2,6}]dec-8-ene (12b): Compound **12a**[26] (0.50 g, 2.04 mmol) in THF (20 mL) was added slowly to a slurry of LiAlH$_4$ (0.33 g, 8.68 mmol) in THF (30 mL), and the mixture was refluxed for 4 h. Water (3 mL) and NaOH (10%, 1 mL) were then added and the resulting suspension was filtered. The residue was triturated with THF repeatedly and filtered. The organic solution was dried (MgSO$_4$) and filtered, then the filtrate was evaporated in vacuo to give **12b** as a liquid (0.41 g, 93%). ^{1}H NMR (400 MHz, CDCl$_3$): δ=1.08–1.22 (m, 6H), 1.58–1.78 (m, 2H), 2.79 (s, 2H), 2.88–2.92 (m, 2H), 3.01–3.05 ppm (m, 3H), 6.10 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ=25.2, 26.1, 31.8, 44.7, 46.1, 53.9, 54.4, 63.6, 137.3 ppm; IR (KBr): $\tilde{\nu}$=3059, 2958, 2929, 2853, 2796, 2772, 1636, 1449, 1346, 1136, 878, 799, 733, 714, 689, 465 cm^{-1}; HRMS (FAB): *m/z* calcd for $C_{15}H_{24}N$: 218.1909 [M^++H]; found: 218.1904.

Polymer 13: A solution of **12b** (100 mg, 0.5 mmol) and (Cy$_3$P)$_2$Cl$_2$Ru=CHPh (18 mg, 0.05 equiv) in CH$_2$Cl$_2$ (5 mL) was stirred at RT under argon for 30 min, quenched with ethyl vinyl ether (1 mL), and poured into MeOH (20 mL). The solid was collected and dissolved in CHCl$_3$ (1 mL) and reprecipitated by adding MeOH (20 mL). This procedure was repeated three times and the solid was collected to afford **13** as a grayish solid (81 mg, 81%). ^{1}H NMR (400 MHz, CDCl$_3$): δ=1.21 (br, 2H), 1.40–2.60 (br, 12H), 2.56–5.91 (br, 7H), 5.40 (br, for *cis* double bond, 21%), 5.48 ppm (br, for *trans* double bond, 79%); ^{13}C NMR (100 MHz, CDCl$_3$): δ=25.2, 26.2, 29.8, 32.1, 34.7, 36.3, 40.3, 44.8, 45.0, 45.8, 46.6, 54.4, 63.6, 63.7, 130.4 ppm and residual signals for end groups. IR (KBr): $\tilde{\nu}$=3040, 2926, 2851, 2773, 1632, 1448, 1372, 1135, 969, 890, 691 cm^{-1}; End-group analysis showed that polymer **13** contained 27 repetitive units.

Time-resolved fluorescence experiments: A mode-locked Ti:sapphire laser (wavelength 850 nm, repetition rate 76 MHz, pulse width <200 fs) was passed through an optical parametric amplifier to produce a λ=425 nm pulse laser. The fluorescence of the sample was reflected by a grating (150 g mm^{-1}, BLZ 500 nm) and detected by an optically triggered streak camera (Hamamatsu C5680) with a time resolution of about 0.3 ps. Each 1×10^{-5} M sample was prepared in CH$_2$Cl$_2$ and placed in an ultra-micro cuvet with 1 mm pathlength to maintain simultaneous excitation. The signal was collected twenty times to decrease signal-to-noise ratio [$A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$].

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