Selected Paper

Covalent Linking of Coordination-Organized Slipped Cofacial Porphyrin Dimers

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Coordination-organized porphyrin dimers of 5,15-bis[2-(allyloxycarbonyl)ethyl]- and bis[3-(allyloxy)propyl]-20-(1-methyl-2-imidazolyl)porphyrinatozinc were covalently linked by an intramolecular olefin metathesis reaction in excellent yields (93–98%). It was found that the yields of the intramolecular metathesis reaction depended strongly on the molecular length of the substituent at the 5 and 15 positions. Introducing longer 3-(allyloxycarbonyl)propyl and 4-(allyloxycarbonyl)butyl substituents decreased sharply the yields of the covalent linking reaction to 26% and 16%, respectively. The covalently linked dimers maintained their coordination structures even when dissolved in as polar a solvent as pyridine.

Ultrafast energy, hole, and electron transfers in multi-porphyrin arrays make these materials attractive for possible use as biomimetic materials and for possible applications in nanometer-scale optical and electronic devices.[1] Recently, it was demonstrated that multi-porphyrin systems based on a slipped co-facial dimer of imidazolylporphyrinatozincs[2] exhibited excellent properties as third order non-linear optics materials[3] and light-harvesting antenna complexes.[4] These multi-porphyrins are readily prepared by self-coordination. Special structures, such as large rings,[4] linear oligomers with specific terminal porphyrins,[2b] and vectorial growth on a gold surface[5] were manipulated by self-assembly. These supramolecular systems have many advantages from the viewpoint of organic synthesis. The binding constant of complementary coordination of imidazolyl-to-Zn in chloroform is as large as 10^{10} M^{-1}, but the coordination structure tends to dissociate in the presence of polar solvents, such as methanol or pyridine, and undergoes exchange reactions. These properties enabled re-organization of the structures once formed,[4,5] but at the same time made it difficult to maintain the systems in polar media. With these factors in mind, the linkage of self-assembled structures of porphyrin oligomers and polymers was explored. An effective method of covalently linking self-assembled porphyrin dimers using a ring-closing metathesis reaction[6] is reported.

Results and Discussion

Metathesis Reaction. Olefin metathesis is a powerful method of C–C bond-formation because most functional groups except olefins are inert.[6] In addition, the metathesis reaction proceeds in non-coordinative solvents, such as $CHCl_3$ and CH_2Cl_2, without the presence of any organic base. This reaction was applied to the covalent linkage of self-assembled porphyrin complexes. On the basis of molecular modeling using the Cerius 2 software,[7] it was predicated that two pairs of substituents at the 5,5′ and 15,15′-*meso* positions of complementarily organized porphyrin dimers were close to each other (Fig. 1). Based on this, unsaturated moieties of suitable lengths were introduced at these positions. First, porphyrin dimer **D-5a**, which had 2-(allyloxycarbonyl)ethyl groups at the 5,5′,15,15′-positions, was designed as a precursor for dimer **7a**. An ester moiety was employed for versatile functional transformations such as trans-esterification and hydrolysis. Since **7a** has two internal olefins, all three isomers, (*E*,*E*), (*Z*,*Z*), and (*E*,*Z*), were expected. Structures predicted by molecular mechanics calculations for (*Z*,*Z*)- and (*E*,*E*)-**7a** are shown in Figs. 1(a), (b) and (c), (d), respectively. The size of each ring composed of the 5,5′- or 15,15′-substituents was similar to an 18 membered ring.

The designed porphyrin dimer **5a** was synthesized according to Fig. 2. Porphyrin **2a** was prepared by condensation of dipyrromethane **1a**, 1-methylimidazole-2-carbaldehyde, and octanal in 6% yield. Then, two allyl moieties were introduced into the 5 and 15-positions by trans-esterification under neutral conditions in the presence of the distannoxane catalyst **3**.[8] Treatment of $Zn(OAc)_2$ with **4a** gave the zinc porphyrin complex **5a**, which automatically converted to the complementary dimer **D-5a** in $CHCl_3$. The dimer structure was maintained in $CHCl_3$ even at concentrations below 1 μM.

The key olefin metathesis reaction on **D-5a** was carried out in dilute conditions in $CHCl_3$ (5 mM) in the presence of a 1st generation Grubbs catalyst (10 mol%). The progress of the reaction was monitored by MALDI-TOF mass spectroscopy. In the case of precursor **D-5a**, the dimer structure predominated in $CHCl_3$ solution, with the major peaks in the mass spectra corresponding to monomeric **5a**. As the reaction proceeded, the peak at $m/z = 1497$, corresponding to covalently linked dimer **7a**, appeared and became dominant after 2 h. The crude material was purified by SiO_2 chromatography to give **7a** in excellent yield (95%). Mass spectroscopy of the isolated **7a** indicated the complete formation of two linkages at the 5,5′- and 15,15′-positions. The ^1H NMR spectrum of **7a** showed no signs

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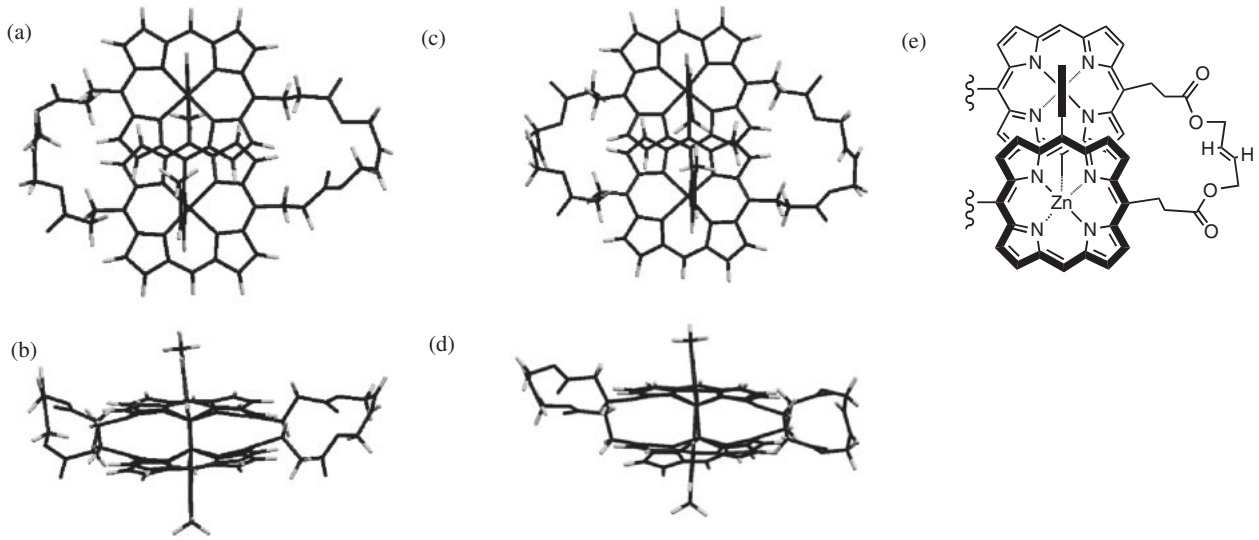

Fig. 1. Molecular modeling using the Cerius2[7] software: (a) top view of (*Z*,*Z*)-**7a**, (b) front view of (*Z*,*Z*)-**7a**, (c) top view of (*E*,*E*)-**7a**, (d) front view of (*E*,*E*)-**7a**, and (e) illustration of (c) using ChemDraw. Heptyl groups are omitted for clarity.

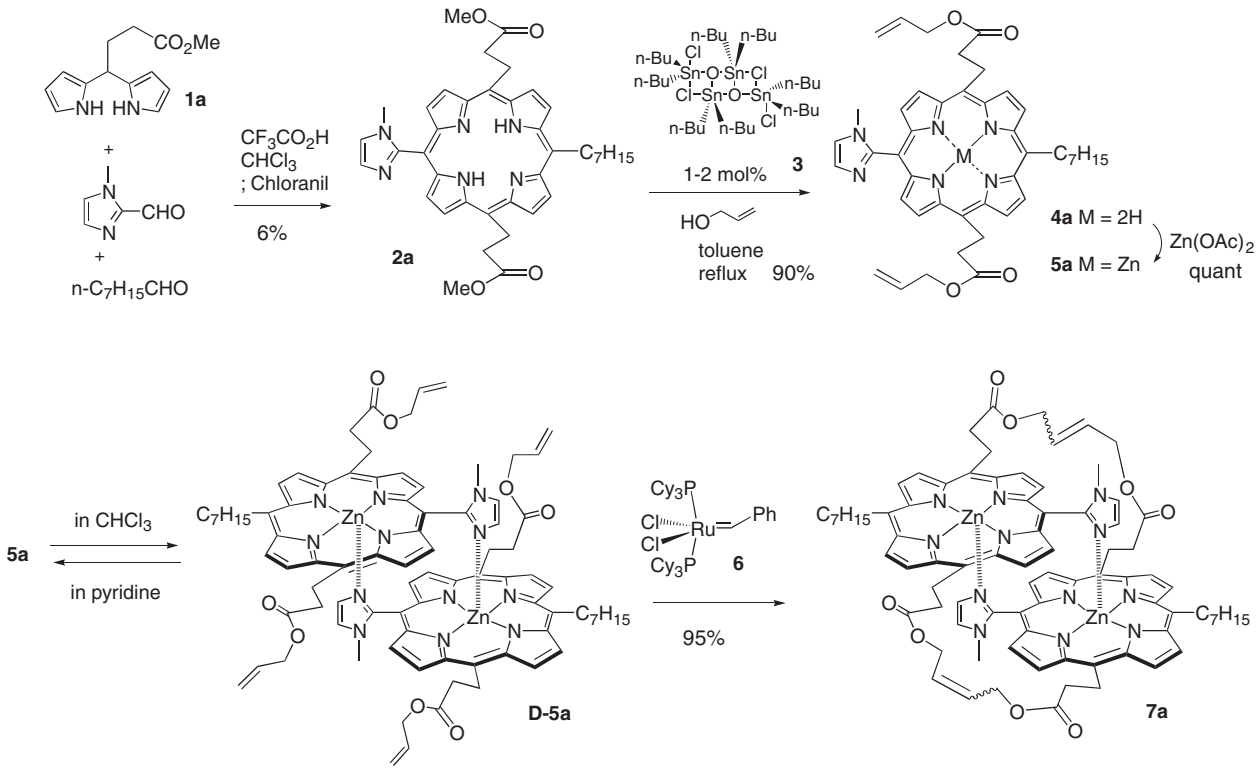

Fig. 2. Synthetic scheme for covalently-linked porphyrin dimer **7a**.

of the terminal olefin, but instead the existence of the *E* and *Z* isomers (with respect to the olefinic moiety). In these isomers, two kinds of peaks were observed for each region of β protons of the porphyrin ring, olefinic and allylic methylenic protons. The ratio of the major and minor peaks was ca. 4:1, although the absolute geometry of each peak could not be determined by NMR. Since formation of the macrocyclic ring (>14 member rings) by ring-closing metathesis generally gave an (*E*)-rich mixture,[9] the major peak observed in the NMR may have corresponded to the (*E*)-form. TLC and GPC analysis of the isolated **7a** gave only a single spot and peak, respectively. This mixture was used for the measurement of electronic spectra described later. The metathesis reaction proceeded smoothly when the concentration of the porphyrin dimer **D-5a** was 2–10 mM, producing **7a** in around 95% yield. However, when the free base porphyrin **4a** was used as the substrate under the same conditions, no dimer was obtained, and almost 100% of **4a** was recovered.

The design of precursor **D-5a** resulted in excellent yields of the covalent linking reaction by olefin metathesis. To examine

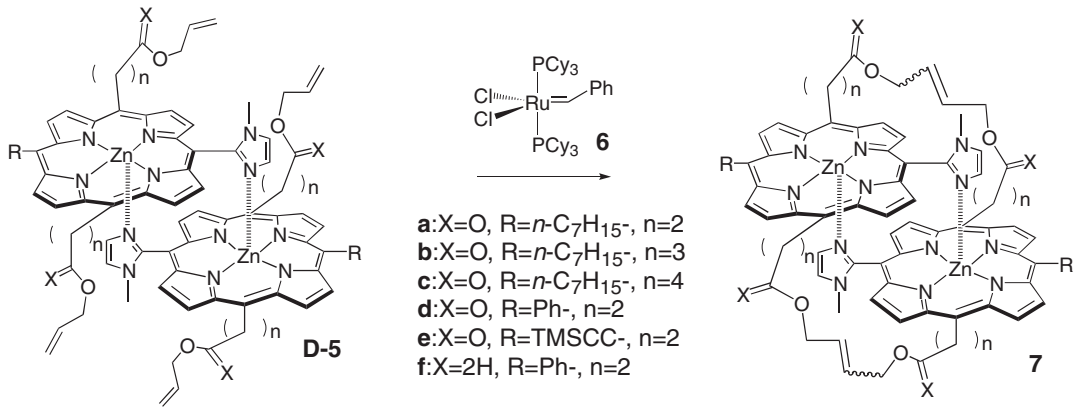

Fig. 3. Ring-closing metathesis of **D-5**.

Table 1. Covalent Linkage of Porphyrin Dimer **D-5** Shown in Fig. 3 by Ring-Closing Metathesis

Run	Substrate	Product	X	R	*n*	Cat. /mol%	Time /h	Temp /°C	Yield /%[a)]
1	**D-5a**	**7a**	O	*n*-C_7H_{15}–	2	10	2	25	95%
2	**D-5b**	**7b**	O	*n*-C_7H_{15}–	3	50[b)]	36	0[b)]	26%[c)]
3	**D-5c**	**7c**	O	*n*-C_7H_{15}–	4	50[b)]	36	0[b)]	16%[c)]
4	**D-5d**	**7d**	O	Ph–	2	10	2	25	95%
5	**D-5e**	**7e**	O	TMSCC–	2	10	2	25	93%
6	**D-5f**	**7f**	2H	Ph–	2	10	2	25	98%

a) Isolated yield. b) Rate of conversion was very slow under standard conditions (cat.: 10 mol%, temp.: 25 °C). c) No starting material was recovered.

the scope and the limitations of the metathesis reaction, precursors **D-5b**–**D-5f** were also prepared. In porphyrin dimers **D-5b** and **D-5c**, 3-(allyloxycarbonyl)propyl and 4-(allyloxycarbonyl)butyl groups were introduced instead of the 2-(allyloxycarbonyl)ethyl group to evaluate the ideal length of the side chain. In **D-5d** and **D-5e**, phenyl and trimethylsilylethynyl groups were introduced at the 10-meso position. A 3-(allyloxy)propyl group was also introduced in dimer **D-5f**. These porphyrin dimers **D-5b**–**D-5f** were prepared by a similar method as that of **D-5a** (Fig. 2). The results of the olefin metathesis reactions are summarized in Fig. 3 and Table 1.

When the reactions of **D-5b** and **D-5c** were carried out in the presence of 10 mol% Grubbs catalyst at room temperature, the conversion was very slow. Covalently linked compounds **7b** and **7c** were obtained by the addition of 50 mol% Grubbs catalyst at 0 °C in 26% and 16% yields, respectively. This was accompanied by the formation of significant amounts of the oligomeric species (Runs 2 and 3). Longer substituent groups appeared to decrease the reactivity of the metathesis reaction. On the other hand, **D-5d** and **D-5e**, which contain 2-(allyloxycarbonyl)ethyl groups, gave the corresponding products, **7d** and **7e**, in good yields of 95% and 93%, respectively. Dimer **D-5f**, which had an ether-type unsaturated 3-(allyloxy)propyl group, gave **7f** in 98% yield. These results indicate that the length of the side chain at the 5 and 15-positions is critical, and that 2-(allyloxycarbonyl)ethyl and 3-(allyloxy)propyl groups give the best results. The substituent groups at the 10-position can be freely selected. Generally, yields of ring-closing metathesis are heavily influenced by the size of ring to be produced. Five to seven membered rings were obtained naturally in good yields, whereas larger membered rings usually were obtained only in moderate or low yields.[10] The excellent yields obtained in the cases of **5a** and **5d**–**5f** suggests that the two olefinic moieties at the 5,5′- and 15,15′-positions were brought sufficiently close together by coordination to favor the metathesis reaction.

UV–Vis Spectra. The UV–vis spectra (2.6 μM solution) before and after the ring-closing metathesis (**D-5a** and **7a**) were compared in chloroform and pyridine (Fig. 4). As was reported previously,[2] the complementarily coordinated dimer, like **D-5a**, was very stable even in a highly diluted chloroform solution ($<10^{-9}$ M). It gave characteristically split Soret bands, which arise from blue and red shifts by face-to-face and head-to-tail interactions of the transition moments, respectively. However, the dimer **D-5a** was completely dissociated into **5a** in pyridine by competitive coordination (Fig. 4(A)). After the metathesis, however, the UV–vis spectra of **7a** in chloroform and in pyridine were almost identical, showing characteristically split Soret bands (Fig. 4(B)). The intramolecular coordination of imidazolyl to Zn was, therefore, maintained even in as highly coordinating a solvent as pyridine (2.4×10^6-fold excess). At the same time, the spectra of **D-5a** and **7a** in $CHCl_3$ were also identical, suggesting that none of the electronic states of the porphyrins were perturbed and, therefore, no strain was induced by the covalent linking.

Conclusion

Coordination-organized porphyrin pairs were successfully linked covalently by template-assisted ring-closing metathesis reactions in excellent yields. The resulting pairs retained their coordination structures even in highly coordinating solvents

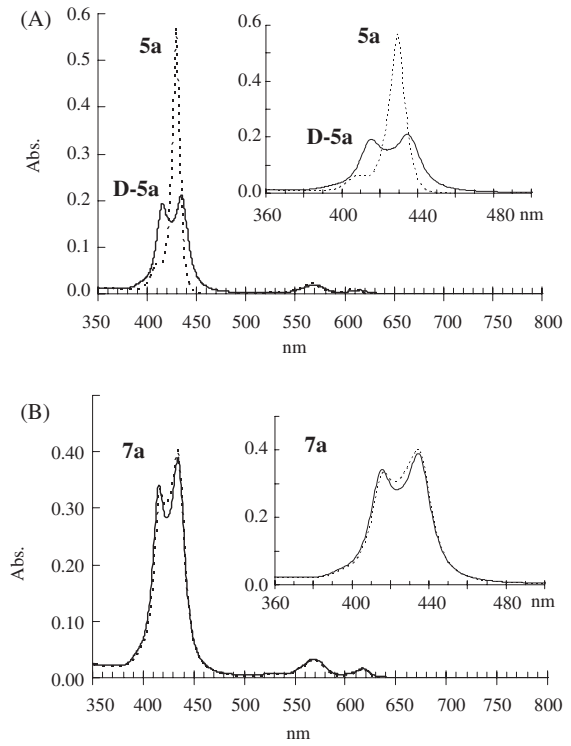

Fig. 4. UV–vis spectra of (A) **5a** (2.6 μM as monomer unit) and (B) **7a** (2.6 μM as dimer) in chloroform (solid line) and pyridine (dotted line). Inset: enlarged spectra.

such as pyridine. The excellent yields of the linked products may be applied to systems of porphyrin oligomers and polymers composed of multiple complementary dimer units. In particular, we may now use this method for stabilization of macroring systems and immobilization of meso–meso linked porphyrin oligomers on a gold surface.

Experimental

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL ECP-600 (600 MHz NMR) or a EX-270 (270 MHz) spectrometer using TMS (0 ppm) or the residual resonance (7.26 ppm (^{1}H) or 77.0 ppm (^{13}C) for $CHCl_3$) of the solvent as the internal standard. UV–vis spectra were obtained from a Shimadzu UV-3100PC instrument. Fluorescence spectra were obtained with a Hitachi F-4500 spectrometer. MALDI-TOF mass spectra were measured with a Perseptive Biosystems Voyager DE-STR apparatus. Dithranol purchased from SIGMA was used as a matrix in the MALDI-TOF mass spectrometric measurements. Chromatography was performed using silica gel 60 N (KANTO chemical Co., 63–210 μm). Thin-layer chromatography was performed on Merck silica gel 60F254 plates. All chemicals obtained from commercial sources were used without further purification.

Synthesis of Dipyrromethane. ***meso*-[2-(Methoxycarbony)-ethyl]dipyrromethane 1a:** Methyl 4-hydroxybutanoate;[11] γ-Butyrolactone (5 g, 58 mmol) and triethylamine (48 mL, 348 mmol) were dissolved in MeOH (100 mL) and stirred for 12 h at rt. Triethylamine and methanol were evaporated to give a mixture of methyl 4-hydroxybutanoate and γ-butyrolactone (total 6.4 g, molar ratio 3:1 determined by ^{1}H NMR). The mixture was directly used for the next step without purification. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.36 (t, $J = 6.75$ Hz, 0.65H, lactone), 3.68 (s, 3H, OMe, propanol), 3.66 (t, $J = 5.94$ Hz, 2H, CH_2O, propanol), 2.67 (brs, 1H, OH, propanol), 2.53–2.43 (m, 2.65H, $CH_2C(O)$, propanol + lactone), 2.30–2.24 (m, 0.65H, CH_2, lactone), 1.94–1.84 (m, 2H, CH_2, propanol).

Methyl 4-oxobutanoate;[11] A solution of oxalyl chloride (5 mL, 58.7 mmol) in $CHCl_3$ (200 mL) was cooled at −60 °C. DMSO (8.3 mL, 117 mmol) was added to the solution, and then a crude mixture of methyl 4-hydroxybutanoate and γ-butyrolactone (6.4 g) was added to the mixture. The mixture was stirred for 15 min at −60 °C. Et_3N (37 mL, 267 mmol) was then added to the mixture, followed by stirring at rt for 10 h. Water (80 mL) was then added to the mixture, followed by extraction with $CHCl_3$. The organic layer was washed with 0.1 M HCl, saturated $NaHCO_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under reduced pressure to give a mixture of methyl 4-oxobutanoate and γ-butyrolactone (total 4.38 g, molar ratio 2.4:1 determined by ^{1}H NMR) as a yellow oil. The mixture was directly used for the next step without further purification. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.81 (s, 1H, CHO, oxobutanoate), 4.35 (t, $J = 7.0$ Hz, 0.9H, lactone), 3.70 (s, 3H, OMe, oxobutanoate), 2.81 (t, $J = 6.2$ Hz, 2H, oxobutanoate), 2.64 (t, $J = 6.2$ Hz, 2H, oxobutanoate), 2.50 (t, $J = 7.5$ Hz, 0.9H, lactone), 2.30–2.24 (m, 0.9H, lactone).

Trifluoroacetic acid (0.29 mL, 3.7 mmol) was added to a mixture of crude 4-oxobutanoate (4.3 g, 28.8 mmol for net aldehyde) and pyrrole (103 mL, 1.48 mol) in deoxygenated $CHCl_3$. After stirring for 12 h at rt, the mixture was diluted with $CHCl_3$ and washed with 0.1 M NaOH solution and water. The organic layer was dried over Na_2SO_4, followed by the evaporation of $CHCl_3$ under reduced pressure. Excess pyrrole was then recovered by distillation under reduced pressure. The brown residue was purified by SiO_2 column chromatography (EtOAc/hexane 1/2) to give dipyrromethane **1a** (3.92 g, 3 steps 27%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.76 (brs, 2H, NH), 6.59–6.55 (m, 2H, pyrrole β), 6.14–6.09 (m, 2H, pyrrole α), 6.06–6.02 (m, 2H, pyrrole α), 3.97 (t, $J = 7.3$ Hz, 1H, CH), 3.62 (s, 3H, OMe), 2.32–2.17 (m, 4H, CH_2). ^{13}C NMR (67.7 MHz, $CDCl_3$) δ 173.78, 132.26, 117.27, 107.93, 105.74, 51.59, 36.89, 31.93, 29.53. mp 49 ± 1 °C. Anal: calcd for $C_{13}H_{16}N_2O_2$; C, 67.22; H, 6.94; N, 12.06%; found C, 67.09; H, 6.85; N, 11.88%.

***meso*-[3-(Methoxycarbonyl)propyl]dipyrromethane 1b:** Dipyrromethane **1b** (1.1 g, 50%) was synthesized from methyl 5-oxopentanoate[11] (1.1 g, 8.5 mmol) and pyrrole in a similar manner as for the preparation of **1a**. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.94 (brs, 2H, NH), 6.66 (s, 2H, pyrrole CH_β), 6.145 (s, 2H, pyrrole CH_α), 6.065 (s, 2H, pyrrole CH_α), 4.12 (t, $J = 7.3$ Hz, 1H, CH), 3.66 (s, 3H, OMe), 2.33 (t, $J = 7.3$ Hz, 2H, $CH_2C(O)$), 2.02–1.97 (m, 2H, CH_2), 1.69–1.62 (m, 2H, CH_2).

***meso*-[4-(Methoxycarbonyl)butyl]dipyrromethane 1c:** Dipyrromethane **1c** (5.9 g, 46%) was synthesized from methyl 6-oxohexanoate[11] (7.5 g, 52 mmol) and pyrrole in a similar manner as for the preparation of **1a**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (brs, 2H, NH), 6.64 (s, 2H, pyrrole CH_β), 6.14 (s, 2H, pyrrole CH_α), 6.05 (s, 2H, pyrrole CH_α), 3.99 (t, $J = 7.32$ Hz, 1H, CH), 3.65 (s, 3H, OMe), 2.29 (t, $J = 6.0$ Hz, 2H, $CH_2C(O)$), 1.99–1.93 (m, 2H, CH_2), 1.68–1.62 (m, 2H, CH_2), 1.37–1.31 (m, 2H, CH_2).

***meso*-(3-Allyloxypropyl)dipyrromethane 1d:** Dipyrromethane **1d** (4.26 g, 40%) was synthesized from 4-allyloxybutanal[12] (5.6 g, 43.6 mmol) and pyrrole in a similar manner as for the preparation of **1a**. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.76 (brs, 2H, NH), 6.60–6.50 (m, 2H, pyrrole H_5), 6.14–6.10 (m, 2H, pyrrole H_4), 6.05–6.01 (m, 2H, pyrrole H_3), 5.90 (ddt, $J = 17.3$, 10.4, 5.4 Hz, 1H, C<u>H</u>=CH_2), 5.25 (ddt, $J = 17.3$, 3.5, 1.6 Hz, 1H, CH=C<u>H</u>$_2$), 5.15 (ddt, $J = 10.4$, 4.3, 1.6 Hz, 1H, CH=C<u>H</u>$_2$), 3.96 (t, $J = 7.8$

Hz, 1H, CH), 3.93 (dt, J = 5.4, 1.6 Hz, 2H, C$\underline{H_2}$–CH=CH_2), 3.42 (t, J = 6.21 Hz, 2H), 2.05–1.94 (m, 2H, CH_2), 1.63–1.52 (m, 2H, CH_2). ^{13}C NMR (67.70 MHz, $CDCl_3$) δ 134.76, 133.24, 116.94, 116.75, 107.84, 105.45, 71.76, 70.13, 37.36, 31.35, 27.66. mp < 25 °C. Anal: calcd for $C_{15}H_{20}N_2O$; C, 73.74; H, 8.25; N, 11.47%, found C, 73.52; H, 8.32; N, 11.21%.

Synthesis of Porphyrin. 5,15-Bis[2-(methoxycarbonyl)ethyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrin (2a): A 2 L round-bottom flask was charged with 2-formyl-1-methylimidazole (240 mg, 2.2 mmol), octanal (280 mg, 2.2 mmol), *meso*-[2-(methoxycarbonyl)ethyl]dipyrromethane **1a** (1 g, 4.3 mmol), and chloroform (1 L). After bubbling with a N_2 stream for 5 min, trifluoroacetic acid (TFA) (1.2 mL, 8.6 mmol) was added to the mixture, and the mixture was stirred at rt in the dark for 4 h. *p*-Chloranil (1.6 g, 6.5 mmol) was then added, and the reaction mixture was again stirred for 10 h. A saturated $NaHCO_3$ solution was added to the mixture, and the mixture was then extracted with $CHCl_3$. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was loaded on a silica gel column and eluted with $CHCl_3$/acetone (10:1) to give **2a** (82 mg, 6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.56 (d, J = 4.2 Hz, 2H, Porβ), 9.51 (d, J = 4.2 Hz, 2H, Porβ), 9.44 (d, J = 4.2 Hz, 2H, Porβ), 8.74 (d, J = 4.2 Hz, 2H, Porβ), 7.67 (br.s, 1H, imidazole CH), 7.45 (br.s, 1H, Im CH), 5.30–5.23 (m, 4H, ester $\beta$$CH_2$), 5.00–4.98 (m, 2H, heptyl-C_1), 3.75 (s, 6H, COO$\underline{Me}$), 3.52–3.45 (m, 4H, ester $\alpha$$CH_2$), 3.38 (s, 3H, NCH_3), 2.55–2.45 (m, 2H, heptyl-C_2), 1.80–1.78 (m, 2H, heptyl-C_3), 1.54–1.52 (m, 2H, heptyl-C_4), 1.36–1.34 (m, 4H, heptyl-C_5, C_6), 0.91 (t, J = 7 Hz, 3H, heptyl-C_7), −2.71 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2 (C=O), 148.7 (Im N=C–N), 128.5 (imidazole ring), 132–126 (br, 4 carbons (Porβ)), 122.1 (Im CH), 121.5 (*meso*), 116.9 (*meso*), 104.0 (*meso*), 52.0 (COO$\underline{Me}$), 41.8 (ester α), 39.1 (heptyl-C_1), 36.1 (heptyl-C_2), 34.6 (NCH_3), 32.0 (heptyl-C_5), 30.7 (heptyl-C_3), 30.5 (ester β), 29.6 (heptyl-C_4), 22.8 (heptyl-C_6), 14.2 (heptyl-C_7). The other 4 carbons (Porα) could not be observed by broadening; UV–vis ($CHCl_3$): 418 (Abs.; 1.3949), 516 (0.0856), 551 (0.0366), 594 (0.0260), 652 (0.0188) nm; Fluorescence (Ex = 418 nm, $CHCl_3$): 620, 723 nm; MALDI-TOF Mass of $C_{39}H_{44}N_6O_4$ Calcd: 660.3; Found: 661.9 (M + H)$^+$.

5,15-Bis[3-(methoxycarbonyl)propyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrin (2b): In a similar manner as for the preparation of **2a**, porphyrin **2b** was synthesized by condensation of 2-formyl-1-methylimidazole (440 mg, 4.0 mmol), octanal (512 mg, 4 mmol), and *meso*-[3-(methoxycarbonyl)propyl]dipyrromethane **1b** (2 g, 8.1 mmol) in the presence of TFA (2.3 mL, 16.3 mmol) in $CHCl_3$ (1 L) followed by oxidation with *p*-chloranil (3 g, 12.2 mmol). Purification was performed using a silica gel column ($CHCl_3$/acetone (10:1)) to give **2b** (300 mg, 10%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.34 (m, 6H, Porβ), 8.67 (m, 2H, Porβ), 7.62 (br.s, 1H, Im CH), 7.31 (br.s, 1H, Im CH), 4.76–4.74 (m, 6H, heptyl-C_1, ester γ), 3.73 (s, 6H, COO$\underline{Me}$), 3.32 (s, 3H, NCH_3), 2.71–2.67 (m, 4H, ester β), 2.62–2.58 (m, 4H, ester α), 2.42–2.38 (m, 2H, heptyl-C_2), 1.72–1.68 (m, 2H, heptyl-C_3), 1.48–1.42 (m, 2H, heptyl-C_4), 1.33–1.30 (m, 4H, heptyl-C_5, C_6), 0.89 (t, J = 7 Hz, 3H, heptyl-C_7), −2.86 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1 (C=O), 148.9 (Im N=C–N), 128.2 (Im CH), 132–126 (br, 4 carbons (Porβ)), 121.7 (Im CH), 121.5 (*meso*), 118.2 (*meso*), 103.4 (*meso*), 51.8 (COO$\underline{Me}$), 39.1 (heptyl-C_2), 35.9 (heptyl-C_1), 34.5 (NCH_3), 34.3 (ester γ), 34.0 (ester β), 32.8 (ester α), 32.0 (heptyl-C_5), 30.7 (heptyl-C_3), 29.5 (heptyl-C_4), 22.8 (heptyl-C_6), 14.3 (heptyl-C_7). The other 4 carbons (Porα) could not be observed by broadening; UV–vis ($CHCl_3$): 417 (Abs.; 0.4774), 518 (0.0225), 552 (0.0095), 593 (0.0070), 650 (0.0050) nm; Fluorescence (Ex = 417 nm, $CHCl_3$): 654, 721 nm; MALDI-TOF Mass of $C_{41}H_{48}N_6O_4$ Calcd: 688.3; Found: 689.1 (M + H)$^+$.

5,15-Bis[4-(methoxycarbonyl)butyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrin (2c): In a similar manner as for the preparation of **2a**, porphyrin **2c** was synthesized by condensation of 2-formyl-1-methylimidazole (440 mg, 4.0 mmol), octanal (512 mg, 4 mmol), and *meso*-[4-(methoxycarbonyl)butyl]dipyrromethane **1c** (2 g, 8.1 mmol) in the presence of TFA (2.3 mL, 16.3 mmol) in $CHCl_3$ (1 L) followed by oxidation with *p*-chloranil (3 g, 12.2 mmol). Purification was performed using a silica gel column ($CHCl_3$/acetone (10:1)) to give **2c** (202 mg, 7%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (d, J = 4.4 Hz, 2H, Porβ), 9.43 (d, J = 4.4 Hz, 2H, Porβ), 9.37 (d, J = 4.4 Hz, 2H, Porβ), 8.72 (d, J = 4.4 Hz, 2H, Porβ), 7.67 (br.s, 1H, Im CH), 7.44 (br.s, 1H, Im CH), 4.97 (t, J = 7 Hz, 2H, heptyl-C_1), 4.91 (t, J = 7 Hz, 4H, ester δ), 3.66 (s, 6H, COO$\underline{Me}$), 3.37 (s, 3H, NCH_3), 2.52–2.50 (m, 2H, heptyl-C_2), 2.49–2.45 (m, 8H, ester β, γ), 2.10 (m, 4H, ester α), 1.81 (m, 2H, heptyl-C_3), 1.54 (m, 2H, heptyl-C_4), 1.36–1.34 (m, 4H, heptyl-C_5, C_6), 0.90 (t, J = 7 Hz, 3H, heptyl-C_7), −2.79 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.1 (C=O), 148.9 (Im N=C–N), 128.4 (Im CH), 132–126 (br, 4 carbons (Porβ)), 121.7 (Im CH), 121.4 (*meso*), 118.9 (*meso*), 103.4 (*meso*), 51.7 (COO$\underline{Me}$), 39.1 (heptyl-C_2), 37.8 (ester γ), 36.1 (NCH_3), 34.9 (ester δ), 34.5 (heptyl-C_1), 34.1 (ester β), 32.0 (heptyl-C_5), 30.7 (heptyl-C_3), 29.5 (heptyl-C_4), 25.8 (ester α), 22.8 (heptyl-C_6), 14.2 (heptyl-C_7). The other 4 carbons (Porα) could not be observed by broadening; UV–vis ($CHCl_3$): 418 (Abs.; 0.2271), 518 (0.0100), 555 (0.0042), 591 (0.0031), 649 (0.0021) nm; Fluorescence (Ex = 418 nm, $CHCl_3$): 651, 716 nm; MALDI-TOF Mass of $C_{43}H_{52}N_6O_4$ Calcd: 716.4; Found: 717.3 (M + H)$^+$.

5,15-Bis[2-(methoxycarbonyl)ethyl]-20-(1-methyl-2-imidazolyl)-10-phenylporphyrin (2d): In a similar manner as for the preparation of **2a**, porphyrin **2d** was synthesized by condensation of 2-formyl-1-methylimidazole (220 mg, 2 mmol), benzaldehyde (0.2 mL, 2 mmol), and *meso*-[2-(methoxycarbonyl)ethyl]dipyrromethane **1a** (1.03 g, 4 mmol) in the presence of TFA (0.9 mL, 6 mmol) in $CHCl_3$ (1 L) followed by oxidation with *p*-chloranil (1.5 g, 6 mmol). Purification was performed using a silica gel column ($CHCl_3$/acetone (20:1)) to give **2d** (73 mg, 6%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (d, J = 4.2 Hz, 2H, Porβ), 9.43 (d, J = 4.2 Hz, 2H, Porβ), 8.89 (d, J = 4.2 Hz, 2H, Porβ), 8.81 (d, J = 4.2 Hz, 2H, Porβ), 8.22 (d, J = 7 Hz, 1H, Ph), 8.10 (d, J = 7 Hz, 1H, Ph), 7.82–7.74 (m, 3H, Ph), 7.68 (s, 1H, Im CH), 7.48 (s, 1H, Im CH), 5.32 (t, J = 7.4 Hz, 4H, ester β), 3.75 (s, 6H, COO$\underline{Me}$), 3.50 (t, J = 7.4 Hz, 4H, ester α), 3.40 (s, 3H, NCH_3), −2.73 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.1 (C=O), 148.7 (Im N=C–N), 144.2–149.5 (br, 4 carbons (Porα)), 142.3 (Ph), 134.4 (Ph), 132.7 (Porβ), 131.1 (Porβ), 128.9 (Porβ), 128.5 (C; Ph), 128.0 (Im CH), 127.4 (Porβ), 126.73 (Ph), 126.66 (Ph), 121.5 (Im CH), 121.3 (*meso*), 117.5 (*meso*), 104.8 (*meso*), 52.0 (COO$\underline{Me}$), 41.8 (ester α), 34.6 (NCH_3), 30.4 (ester β); UV–vis ($CHCl_3$): 417 (Abs.; 1.9670), 515 (0.1159), 548 (0.0415), 590 (0.0384), 647 (0.0224) nm; Fluorescence (Ex = 417 nm, $CHCl_3$): 652, 717 nm; MALDI-TOF Mass of $C_{38}H_{34}N_6O_4$ Calcd: 638.26; Found: 639.8 (M + H)$^+$.

5,15-Bis[2-(methoxycarbonyl)ethyl]-20-(1-methyl-2-imidazolyl)-10-(trimethylsilylethynyl)porphyrin (2e): In a similar manner as for the preparation of **2a**, porphyrin **2e** was synthesized by condensation of 2-formyl-1-methylimidazole (1.1 g, 10 mmol), 3-trimethylsilylpropynal (0.632 g, 5 mmol), and *meso*-[2-(methoxy-

carbonyl)ethyl]dipyrromethane **1a** (2.32 g, 10 mmol) in the presence of TFA (1.16 mL, 15 mmol) in $CHCl_3$ (1 L) followed by oxidation with *p*-chloranil (3.68 g, 15 mmol). Purification was performed using a silica gel column ($CHCl_3$/MeOH (9:1)) to give **2e** (208 mg, 6.3%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.70 (d, J = 4.2 Hz, 2H, Porβ), 9.41 (d, J = 4.2 Hz, 2H, Porβ), 9.34 (d, J = 4.2 Hz, 2H, Porβ), 8.71 (d, J = 4.2 Hz, 2H, Porβ), 7.70 (br.s, 1H, Im CH), 7.46 (br.s, 1H, Im CH), 5.19–5.17 (m, 4H, ester β), 3.7 (s, 6H, COO<u>Me</u>), 3.43 (t, J = 7.2 Hz, 4H, ester α), 3.33 (s, 3H, NCH_3), 0.67 (s, 9H, TMS), −2.78 (s, 2H, inner proton); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0 (C=O), 148.4 (Im N=C–N), 147–144 (br, 4 carbons (Porα)), 131.9 (Porβ), 131.2 (Porβ), 128.4 (Porβ), 128.3 (Im CH), 128.2 (Porβ), 121.7 (Im CH), 118.3 (*meso*), 107.1 (TMS–C≡<u>C</u>–), 106.4 (*meso*), 102.5 (*meso*), 100.1 (TMS–<u>C</u>≡C–), 52.0 (COO<u>Me</u>), 41.7 (ester α), 34.6 (NCH_3), 30.2 (ester β), 0.4 (TMS); UV–vis (nm, $CHCl_3$): 427 (Abs.; 2.3982), 527 (0.1086), 566 (0.1405), 608 (0.0553), 665 (0.0651); Fluorescence (Ex = 427 nm, $CHCl_3$): 668, 740 nm; MALDI-TOF Mass of $C_{37}H_{38}N_6O_4Si$ Calcd: 658.2; Found: 659.2 $(M + H)^+$.

5,15-Bis(3-allyloxypropyl)-20-(1-methyl-2-imidazolyl)-10-phenylporphyrin (4f): In a similar manner as for the preparation of **2a**, porphyrin **4f** was synthesized by condensation of 2-formyl-1-methylimidazole (0.23 g, 2.1 mmol), benzaldehyde (0.22 g, 2.1 mmol), and *meso*-(3-allyloxypropyl)dipyrromethane **1d** (0.96 g, 3.9 mmol) in the presence of TFA (0.9 mL, 5.3 mmol) in $CHCl_3$ (1 L) followed by oxidation with *p*-chloranil (1.6 g, 6.5 mmol). Purification was performed using a silica gel column ($CHCl_3$/acetone (9:1)) to give **4f** (90 mg, 6.5%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.54 (d, J = 4.8 Hz, 2H, Porβ), 9.48 (d, J = 4.8 Hz, 2H, Porβ), 8.87 (d, J = 4.8 Hz, 2H, Porβ), 8.79 (d, J = 4.8 Hz, 2H, Porβ), 8.25 (d, J = 5.3 Hz, 1H, *o*-Ph), 7.84–7.68 (m, 3H, *m*- and *p*-Ph), 7.68 (d, J = 1.0 Hz, 1H, Im), 7.48 (d, J = 1.0 Hz, 1H, Im), 6.16–6.00 (m, 2H, C<u>H</u>=CH$_2$), 5.42 (d, J = 17.3 Hz, 2H, CH=C<u>H</u>$_2$), 5.26 (d, J = 10.2 Hz, 2H, CH=C<u>H</u>$_2$), 5.11 (t, J = 7.3 Hz, 4H, Por-C<u>H</u>$_2$), 4.07 (d, J = 5.4 Hz, 4H, C<u>H</u>$_2$–CH=CH$_2$), 3.66 (t, J = 5.8 Hz, 4H, CH$_2$–O–), 3.40 (s, 3H, N–Me), 2.85–2.74 (m, 4H, –CH$_2$–C<u>H</u>$_2$–CH$_2$), −2.66 (s, 2H, NH).

5,15-Bis[2-(allyloxycarbonyl)ethyl)-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrin (4a): A mixture of porphyrin **2a** (100 mg, 0.15 mmol) and allyl alchol (0.2 mL, 3 mmol) was refluxed in toluene (3 mL) in the presence of distannoxane catalyst **3** (1 mg, 2 μmol). The reaction was monitored by MALDI-TOF mass spectra. Normally, the transesterification was completed within 4 h. The mixture was cooled to rt, and water was added to the mixture. The mixture was then extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was loaded on a silica gel column and eluted with $CHCl_3$/MeOH (10:1) to give **4a** (90 mg, 90%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.51 (d, J = 4 Hz, 2H, Porβ), 9.47 (d, J = 4 Hz, 2H, Porβ), 9.41 (d, J = 4 Hz, 2H, Porβ), 8.73 (d, J = 4 Hz, 2H, Porβ), 7.68 (s, 1H, Im CH), 7.45 (s, 1H, Im CH), 5.92 (ddt, J = 5.9, 11.0, 17.4 Hz, 2H, C<u>H</u>=CH$_2$), 5.32 (d, J = 17.4 Hz, 2H, CH=C<u>H</u>$_2$), 5.26 (t, J = 7 Hz, 4H, ester β), 5.21 (d, J = 11.0 Hz, 2H, CH=C<u>H</u>$_2$), 4.93 (t, J = 7 Hz, 2H, heptyl-C$_1$), 4.68 (d, J = 5.9 Hz, 4H, –OCH$_2$), 3.50 (t, J = 7 Hz, 4H, ester α), 3.34 (s, 3H, NCH_3), 2.49 (m, 2H, heptyl-C$_2$), 1.78 (m, 2H, heptyl-C$_3$), 1.53–1.51 (m, 2H, heptyl-C$_4$), 1.35–1.34 (m, 4H, heptyl-C$_5$, C$_6$), 0.92–0.89 (m, 3H, heptyl-C$_7$), −2.81 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.4 (C=O), 148.7 (Im N=C–N), 132.2 (<u>C</u>H=CH$_2$), 128.3 (Im CH), 129.5–126.3 (br, 4 Porβ), 122.1 (Im CH), 121.6 (*meso*), 118.6 (CH=<u>C</u>H$_2$), 116.9 (*meso*), 103.8 (*meso*), 65.6 (–OCH$_2$), 41.9 (ester α), 39.1 (heptyl-C$_1$), 36.0 (heptyl-C$_2$), 34.6 (NCH_3), 32.0 (heptyl-C$_5$), 30.7 (ester β), 30.4 (heptyl-C$_3$), 29.4 (heptyl-C$_4$), 22.8 (heptyl-C$_6$), 14.2 (heptyl-C$_7$). The other 4 carbons (Porα) could not be observed by broadening; UV ($CHCl_3$): 417 (Abs.; 0.1438), 517 (0.0100), 553 (0.0051), 589 (0.0035), 647 (0.0024) nm; Fluorescence (Ex = 417 nm, $CHCl_3$) : 655, 722 nm; MALDI-TOF Mass of $C_{43}H_{48}N_6O_4$ Calcd: 712.37; Found: 713.6 $(M + H)^+$.

5,15-Bis[3-(allyloxycarbonyl)propyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrin (4b): In a similar manner as for the preparation of **4a**, the transesterification of **2b** (116 mg, 1.7 mmol) was carried out to give **4d** (110 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.52 (m, 2H, Porβ), 9.50 (m, 2H, Porβ), 9.34 (m, 2H, Porβ), 8.63 (m, 2H, Porβ), 7.69 (s, 1H, Im CH), 7.46 (s, 1H, Im CH), 6.00 (ddt, J = 5.9, 11.0, 17.4 Hz, 2H, C<u>H</u>=CH$_2$), 5.34 (d, J = 17.4 Hz, 2H, CH=C<u>H</u>$_2$), 5.26 (t, J = 7 Hz, 4H, ester β), 5.25 (d, J = 11.0 Hz, 2H, CH=C<u>H</u>$_2$), 4.98 (t, J = 7 Hz, 2H, heptyl-C$_1$), 4.89–4.86 (m, 4H, ester γ), 4.57 (dd, J = 5.9 Hz, 4H, –OCH$_2$), 3.31 (s, 3H, NCH_3), 2.88–2.77 (m, 4 H, ester β), 2.76–2.65 (m, 4H, ester α), 2.52 (m, 2H, heptyl-C$_2$), 1.68 (m, 2H, heptyl-C$_3$), 1.57–1.51 (m, 2H, heptyl-C$_4$), 1.39–1.34 (m, 4H, heptyl-C$_5$, C$_6$), 0.91 (t, J = 7 Hz, 3H, heptyl-C$_7$), −2.87 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3 (C=O), 148.6 (Im N=C–N), 132.3 (allyl β), 127.8 (Im CH), 132–127 (br, 4 carbons (Porβ), 121.9 (Im CH), 121.6 (*meso*), 118.6 (CH=<u>C</u>H$_2$), 118.3 (*meso*), 102.6 (*meso*), 65.4 (–O<u>C</u>H$_2$), 39.1 (heptyl-C$_2$), 36.1 (heptyl-C$_1$), 34.6 (NCH_3), 34.3 (ester γ), 34.2 (ester α), 32.7 (ester β), 32.0 (heptyl-C$_5$), 30.7 (heptyl-C$_3$), 29.4 (heptyl-C$_4$), 22.8 (heptyl-C$_6$), 14.2 (heptyl-C$_7$). The other 4 carbons (Porα) could not be observed by broadening; UV (nm, $CHCl_3$): 417 (Abs.; 0.5504), 518 (0.0168), 552 (0.0039), 593 (0.0028), 649 (0.0029); Fluorescence (Ex = 417 nm, $CHCl_3$): 654, 721 nm; MALDI-TOF Mass of $C_{45}H_{52}N_6O_4$ Calcd: 740.4; Found: 741.7 $(M + H)^+$.

5,15-Bis[4-(allyloxycarbonyl)butyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrin (4c): In a similar manner as for the preparation of **4a**, the transesterification of **2c** (116 mg, 1.7 mmol) was carried out to give **4c** (151 mg, 78%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (d, J = 4 Hz, 2H, Porβ), 9.41 (d, J = 4 Hz, 2H, Porβ), 9.36 (d, J = 4 Hz, 2H, Porβ), 8.70 (d, J = 4 Hz, 2H, Porβ), 7.66 (s, 1H, imidazole ring), 7.43 (s, 1H, imidazole ring), 5.88 (ddt, J = 4.4, 11.0, 16.8 Hz, 2H, C<u>H</u>=CH$_2$), 5.30 (d, J = 16.8 Hz, 2H, CH=C<u>H</u>$_2$), 5.17 (d, J = 11.0 Hz, 2H, CH=C<u>H</u>$_2$), 4.94 (t, J = 7 Hz, 2H, heptyl-C$_1$), 4.89 (t, J = 7 Hz, 4H, ester δ), 4.58 (d, J = 4.4 Hz, 4H, –OCH$_2$), 3.34 (s, 3H, NCH_3), 2.52–2.46 (m, 10H, heptyl-C$_2$, ester β, γ), 2.14–2.08 (m, 4H, ester α), 1.80 (m, 2H, heptyl-C$_3$), 1.53–1.51 (m, 2H, heptyl-C$_4$), 1.35–1.34 (m, 4H, heptyl-C$_5$, C$_6$), 0.92–0.89 (m, 3H, heptyl-C$_7$), −2.70 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.3 (C=O), 148.9 (Im N=C–N), 132.3 (<u>C</u>H=CH$_2$), 128.3 (Im CH), 132–127 (br.s, 4 carbons (Porβ), 122.8 (Im CH), 121.4 (*meso*), 118.9 (*meso*), 118.6 (CH=<u>C</u>H$_2$), 103.3 (*meso*), 65.2 (–OCH$_2$), 39.1 (CH$_2$), 37.7 (CH$_2$), 36.1 (CH$_2$), 34.9 (CH$_2$), 34.6 (NCH_3), 34.2 (CH$_2$), 32.0 (CH$_2$), 30.7 (CH$_2$), 29.4 (CH$_2$), 25.8 (CH$_2$), 22.8 (CH$_2$), 14.2 (CH$_3$). The other 4 carbons (Porα) could not be observed by broadening; UV–vis (nm, $CHCl_3$): 418 (Abs.; 1.0357), 517 (0.0439), 552 (0.0179), 594 (0.0118), 651 (0.0103); Fluorescence (Ex = 418 nm, $CHCl_3$): 655, 722 nm; MALDI-TOF Mass of $C_{47}H_{56}N_6O_4$ Calcd: 768.44; Found: 769.9 $(M + H)^+$.

5,15-Bis[2-(allyloxycarbonyl)ethyl]-10-phenyl-20-(1-methyl-2-imidazolyl)porphyrin (4d): In a similar manner as for the preparation of **4a**, the transesterification of **2d** (60 mg, 94 μmol) was carried out to give **4d** (55 mg, 85%). ^{1}H NMR (600 MHz,

$CDCl_3$) δ 9.50 (d, $J = 4.8$ Hz, 2H, Porβ), 9.44 (d, $J = 4.8$ Hz, 2H, Porβ), 8.89 (d, $J = 4.8$ Hz, 2H, Porβ), 8.81 (d, $J = 4.8$ Hz, 2H, Porβ), 8.21 (d, $J = 7$ Hz, 1H, Ph), 8.11 (d, $J = 7$ Hz, 1H, Ph), 7.82–7.73 (m, 3H, Ph), 7.68 (s, 1H, Im CH), 7.47 (s, 1H, Im CH), 5.90 (ddt, $J = 6$, 10, 16 Hz, 4H, C$\underline{H}$=CH_2), 5.32 (d, $J =$ 16 Hz, 2H, CH=C$\underline{H_2}$), 5.30 (t, $J = 8$ Hz, 4H, ester β), 5.19 (d, $J =$ 10 Hz, 2H, CH=C$\underline{H_2}$), 4.69 (d, $J = 6$ Hz, 4H, –OCH_2), 3.53 (t, $J =$ 8 Hz, 4H, ester α), 3.39 (s, 3H, NCH_3), −2.73 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2 (C=O), 148.6 (Im N=C–N), 149.2–144.4 (4 carbons (Porα)), 142.2 (Ph), 134.3 (Ph), 132.7 (Porβ), 132.1 (C$\underline{H}$=CH_2), 131.1 (Porβ), 128.9 (Porβ), 128.5 (Ph), 128.0 (Im CH), 127.5 (Porβ), 126.7 (Ph), 126.6 (Ph), 121.5 (Im CH), 121.2 (*meso*), 118.5 (CH=C$\underline{H_2}$), 117.4 (*meso*), 104.8 (*meso*), 65.6 (–OCH_2), 41.9 (ester β), 34.6 (NCH_3), 30.4 (ester α); UV–vis (nm, $CHCl_3$): 417 (Abs.; 2.0850), 515 (0.1201), 549 (0.0424), 590 (0.0392), 647 (0.0230); Fluorescence (Ex = 417 nm, $CHCl_3$): 652, 718 nm; MALDI-TOF Mass of $C_{42}H_{38}N_6O_4$ Calcd: 690.30; Found: 691.2 $(M + H)^+$.

5,15-Bis[2-(allyloxycarbonyl)ethyl]-20-(1-methyl-2-imidazolyl)-10-(trimethylsilylethynyl)porphyrin (4e): In a similar manner as for the preparation of **4a**, the transesterification of **2e** (70 mg, 0.1 mmol) was carried out to give **4e** (62 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.71 (d, $J = 4.2$ Hz, 2H, Porβ), 9.44 (d, $J = 4.2$ Hz, 2H, Porβ), 9.39 (d, $J = 4.2$ Hz, 2H, Porβ), 8.74 (d, $J = 4.2$ Hz, 2H, Porβ), 7.68 (s, 1H, Im CH), 7.45 (s, 1H, Im CH), 5.89 (ddt, $J = 6$, 11, 19 Hz, 2H, C$\underline{H}$=CH_2), 5.30 (d, $J = 19$ Hz, 2H, CH=C$\underline{H_2}$), 5.24 (t, $J = 8$ Hz, 2H, ester β), 5.19 (d, $J = 11$ Hz, 2H, CH=C$\underline{H_2}$), 4.67 (d, $J = 6$ Hz, 4H, –OCH_2–), 3.48 (t, $J = 7$ Hz, 4H, ester α), 3.35 (s, 3H, NCH_3), 0.66 (s, 9H, TMS), −2.67 (s, 2H, NH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3 (C=O), 148.5 (Im N=C–N), 148.2–144.5 (4 carbons (Porα)), 132.1 (C$\underline{H}$=CH_2), 131.8 (Porβ), 131.3 (Porβ), 128.5 (Porβ), 128.4 (Im CH), 128.3 (Porβ), 121.6 (Im CH), 118.6 (CH=C$\underline{H_2}$), 118.3 (*meso*), 107.1 (TMS–C≡C–), 106.7 (*meso*), 102.5 (*meso*), 100.1 (TMS–C≡C–), 65.6 (–OCH_2–), 41.8 (ester α), 34.5 (NCH_3), 30.2 (ester β), 0.44 (TMS); UV–vis (nm, $CHCl_3$): 427 (Abs.; 2.3423), 527 (0.1030), 565 (0.1344), 607 (0.0452), 665 (0.0633); Fluorescence (Ex = 427 nm, $CHCl_3$): 668, 740 nm; MALDI-TOF Mass of $C_{41}H_{42}N_6O_4Si$ Calcd: 710.3; Found: 711.0 $(M + H)^+$.

Synthesis of Zinc Complex. 5,15-Bis[2-(allyloxycarbonyl)-ethyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrinatozinc (5a): A saturated solution of zinc acetate in MeOH (5 mL) was added to a solution of **4a** (80 mg, 0.12 mmol) in $CHCl_3$ (15 mL). After stirring for 1 h at rt, the mixture was diluted with $CHCl_3$ and washed with water. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure to give **5a** (88 mg, quant). **D-5a**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73 (d, $J = 4$, 2 Hz, 2H, Porβ), 9.66 (d, $J = 4.2$ Hz, 2H, Porβ), 8.87 (d, $J = 4.2$ Hz, 2H, Porβ_3), 6.07 (ddt, $J = 5.9$, 10.8, 16.2 Hz, 4H, CH=CH_2), 5.47 (d, $J = 16.2$ Hz, 2H, CH=C$\underline{H_2}$), 5.46 (d, $J =$ 1.8 Hz, 1H, Im H_4), 5.50–5.40 (m, 4H, ester β), 5.40 (d, $J = 4.2$ Hz, 2H, Porβ_4), 5.32 (dd, $J = 1.8$, 10.2 Hz, 2H, CH=C$\underline{H_2}$), 5.25 (t, $J = 7$ Hz, 2H, heptyl-C_1), 4.88 (dd, $J = 13.8$, 5.9 Hz, 2H, –OCH_2), 4.82 (dd, $J = 13.8$, 5.9 Hz, 2H, –OCH_2), 3.86–3.80 (m, 2H, ester α), 3.75–3.64 (m, 2H, ester α), 2.75 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_2), 2.00 (t.t, $J = 7$, 7 Hz, 2H, hepty-C_3), 1.97 (d, $J =$ 1.8 Hz, 1H, Im H_5), 1.67 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_4), 1.64 (s, 3H, NCH_3), 1.48–1.43 (m, 4H, heptyl-C_5, C_6), 0.98 (t, $J = 7$ Hz, 3H, heptyl-C_7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9 (C=O), 150.1 (Porα), 149.5 (Porα), 149.2 (Porα), 148.6 (Porα), 146.1 (Im N=C–N), 132.6 (C$\underline{H}$=CH_2), 129.5 (Porβ_2), 128.9 (Porβ_3), 128.3 (Porβ_1), 127.2 (Porβ_4), 122.8 (Im CH), 121.6 (*meso*), 118.4 (Im CH), 117.8 (CH=C$\underline{H_2}$), 116.8 (*meso*), 95.8 (*meso*), 65.5 (–OCH_2), 42.7 (ester α), 39.8 (heptyl-C_2), 36.3 (heptyl-C_1), 32.7 (NCH_3), 32.2 (heptyl-C_3), 30.9 (ester β), 29.7 (heptyl-C_4), 22.9 (heptyl-C_6), 14.3 (heptyl-C_7); **D-5a**: UV–vis ($CHCl_3$): 416 (Abs.; 0.1052), 434 (0.1165), 568 (0.0104), 616 (0.0044) nm; **5a (monomer)**: UV–vis (pyridine): 426, 566, 610 nm; Fluorescence (Ex = 416 nm, $CHCl_3$) : 619, 673 nm; MALDI-TOF Mass of $C_{43}H_{46}N_6O_4Zn$ Calcd: 774.3; Found: 775.4 $(M + H)^+$.

5,15-Bis[3-(allyloxycarbonyl)propyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrinatozinc (5b): In a similar manner as for the preparation of **5a**, the introduction of zinc ion into **4b** (75.4 mg, 102 μmol) was carried out to give **5b** (82 mg, quant). **D-5b**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.72 (d, $J = 4$ Hz, 2H, Porβ), 9.66 (d, $J = 4$ Hz, 2H, Porβ), 8.92 (d, $J = 4$ Hz, 2H, Porβ_3), 6.09 (m, 2H, C$\underline{H}$=CH_2), 5.47 (s, 1H, Im H_5), 5.46 (d, $J = 16.2$ Hz, 2H, CH=C$\underline{H_2}$), 5.32 (d, $J = 10.8$ Hz, 2H, CH=C$\underline{H_2}$), 5.31 (d, $J = 4$ Hz, 2H, Porβ_4), 5.28–5.23 (m, 4H, heptyl-C_1), 5.14–4.98 (m, 4H, ester γ), 4.83 (d, $J = 6$ Hz, 4H, –OCH_2), 3.27–3.23 (m, 2H, ester β), 3.10–3.00 (m, 4H, ester β,α), 2.98–2.94 (m, 2H, ester α), 2.76 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_2), 2.01 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_3), 1.98 (d, $J = 2$ Hz, 1H, Im H_4), 1.70–1.66 (m, 2H, heptyl-C_4), 1.64 (s, 3H, NCH_3), 1.49–1.41 (m, 4H, heptyl-C_5, C_6), 0.99 (t, $J = 7$ Hz, 3H, heptyl-C_7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.8 (C=O), 150.4 (Porα), 149.5 (Porα), 149.2 (Porα), 148.4 (Porα), 146.3 (Im N=C–N), 132.6 (C$\underline{H}$=CH_2), 129.3 (Porβ_3), 129.1 (Porβ_2), 128.4 (Porβ_1), 127.0 (Porβ_4), 122.3 (*meso*), 121.6 (Im CH), 118.5 (CH=C$\underline{H_2}$), 118.0 (Im CH), 117.6 (*meso*), 95.5 (*meso*), 65.4 (–OCH_2), 39.7 (heptyl-C_2), 36.3 (heptyl-C_1), 35.0 (ester γ), 34.9 (ester α), 33.5 (ester β), 32.6 (NCH_3), 32.2 (heptyl-C_5), 31.0 (heptyl-C_3), 29.7 (heptyl-C_4), 22.9 (heptyl-C_6), 14.3 (heptyl-C_7); UV–vis ($CHCl_3$): 416 (Abs.; 0.0726), 434 (0.0840), 568 (0.0014), 618 (−0.0008) nm; Fluorescence (Ex = 416 nm, $CHCl_3$): 621, 674 nm; MALDI-TOF Mass of $C_{45}H_{50}N_6O_4Zn$ Calcd: 802.32; Found: 803.62 $(M + H)^+$.

5,15-Bis[4-(allyloxycarbonyl)butyl]-10-heptyl-20-(1-methyl-2-imidazolyl)porphyrinatozinc (5c): In a similar manner as for the preparation of **5a**, the introduction of zinc ion into **4c** (105 mg, 137 μmol) was carried out to give **5c** (113 mg, quant). **D-5c**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.71 (d, $J = 4$ Hz, 2H, Porβ), 9.60 (d, $J = 4$ Hz, 2H, Porβ), 8.82 (d, $J = 4$ Hz, 2H, Porβ_3), 5.96 (ddt, $J = 5$, 11, 16 Hz, 2H, C$\underline{H}$=CH_2), 5.43 (s, 1H, Im H_5), 5.32 (d, $J = 4$ Hz, 2H, Porβ_4), 5.25 (dd, $J = 16$ Hz, 2H, CH=C$\underline{H_2}$), 5.20 (dd, $J = 11$ Hz, 2H, CH=C$\underline{H_2}$), 5.27–5.20 (m, 4H, heptyl-C_1), 5.14–5.00 (m, 4H, ester δ), 4.67 (d, $J = 5$ Hz, 4H, –OCH_2), 2.90 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_2), 2.77–2.73 (m, 8H, ester α,γ), 2.55–2.33 (m, 4H, ester β), 2.00 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_3), 1.98 (d, $J = 1.8$ Hz, 1H, Im H_4), 1.69 (t.t, $J = 7$, 7 Hz, 2H, heptyl-C_4), 1.62 (s, 3H, NCH_3), 1.48–1.43 (m, 4H, heptyl-C_5, C_6), 0.99 (t, $J = 7$ Hz, 3H, heptyl-C_7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.6 (C=O), 150.4 (Porα), 149.4 (Porα), 149.0 (Porα), 148.4 (Porα), 146.2 (Im N=C–N), 132.5 (C$\underline{H}$=CH_2), 129.1 (Porβ_1), 129.0 (Porβ_3), 128.3 (Porβ_2), 127.0 (Porβ_4), 122.3 (*meso*), 121.6 (Im CH), 118.8 (*meso*), 118.3 (CH=C$\underline{H_2}$), 117.7 (Im CH), 95.5 (*meso*), 65.2 (–OCH_2), 39.8 (ester α), 38.6 (heptyl-C_2), 36.4 (ester δ), 35.6 (heptyl-C_1), 34.7 (ester γ), 32.7 (NCH_3), 32.2 (heptyl-C_5), 31.0 (heptyl-C_3), 29.7 (heptyl-C_4), 26.7 (ester β), 22.9 (heptyl-C_6), 14.3 (heptyl-C_7); UV–vis ($CHCl_3$): 415 (Abs.; 0.6215), 435 (0.7064), 531 (0.0085), 568 (0.0544), 618 (0.0294) nm; Fluorescence (Ex = 415 nm, $CHCl_3$): 622, 677 nm; MALDI-TOF Mass of $C_{47}H_{54}N_6O_4Zn$ Calcd: 830.35; Found: 831.32 $(M + H)^+$.

5,15-Bis[2-(allyloxycarbonyl)ethyl]-20-(1-methyl-2-imidazolyl)-10-phenylporphyrinatozinc (5d): In a similar manner as for the preparation of **5a**, the introduction of zinc ion into **4d** (530 mg, 43 μmol) was carried out to give **5d** (33 mg, quant). **D-5d**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61 (d, $J = 4.2$ Hz, 2H, Porβ_2), 9.06 (d, $J = 4.2$ Hz, 2H, Porβ_1), 8.94 (d, $J = 4.2$ Hz, 2H, Porβ_3), 8.67 (d, $J = 6.6$ Hz, 1H, Ph), 8.13 (d, $J = 7.8$ Hz, 1H, Ph), 7.94 (dd, $J = 7.8$, 8.4 Hz, 1H, Ph), 7.87 (t, $J = 8.4$ Hz, 1H, Ph), 7.77 (dd, $J = 6.6$, 8.4 Hz, 1H, Ph), 6.06 (ddt, $J = 6$, 10.2, 16.2 Hz, 2H, C$\underline{H}$=CH$_2$), 5.53 (d, $J = 2$ Hz, 1H, Im H$_5$), 5.51–5.46 (m, 4H, ester β), 5.47 (d, $J = 4.2$ Hz, 2H, Porβ_4), 5.46 (dd, $J = 1.8$, 16.2 Hz, 2H, CH=C$\underline{H}_2$), 5.31 (dd, $J = 1.8$, 10.2 Hz, 2H, CH=C$\underline{H}_2$), 4.87 (ddt, $J = 1.2$, 6, 12 Hz, 2H, –OCH$_2$), 4.84 (ddt, $J = 1.2$, 6, 12 Hz, 2H, –OCH$_2$), 3.88–3.81 (m, 2H, ester α), 3.75–3.68 (m, 2H, ester α), 2.13 (d, $J = 2$ Hz, 1H, Im H$_4$), 1.67 (s, 3H, NCH$_3$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8 (C=O), 150.7 (Porα), 149.6 (Porα), 149.5 (Porα), 148.3 (Porα), 146.0 (Im N=C–N), 134.8 (Ph), 134.7 (Ph), 132.7 (Porβ_2), 132.5 (C$\underline{H}$=CH$_2$), 128.9 (Porβ_1), 128.1 (Porβ_3), 127.6 (Porβ_4), 127.4 (Ph), 126.5 (Ph), 126.3 (Ph), 122.0 (*meso*), 121.5 (Im CH), 118.4 (Im CH), 118.0 (CH=C$\underline{H}_2$), 117.5 (*meso*), 96.4 (*meso*), 65.6 (–OCH$_2$), 42.7 (ester α), 32.7 (NCH$_3$), 30.9 (ester β); UV–vis ($CHCl_3$): 413 (Abs.; 0.1400), 435 (0.1510), 565 (0.0198), 616 (0.0107) nm; Fluorescence (Ex = 413 nm, $CHCl_3$): 619, 674 nm; MALDI-TOF Mass of $C_{42}H_{36}N_6O_4Zn$ Calcd: 752.21; Found: 753.4 $(M + H)^+$.

5,15-Bis[2-(allyloxycarbonyl)ethyl]-20-(1-methyl-2-imidazolyl)-10-(trimethylsilylethynyl)porphyrinatozinc (5e): In a similar manner as for the preparation of **5a**, the introduction of zinc ion into **4e** (50 mg, 70 μmol) was carried out to give **5e** (54 mg, quant). **D-5e**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.92 (d, $J = 4.2$ Hz, 2H, Porβ_2), 9.65 (d, $J = 4.2$ Hz, 2H, Porβ_1), 8.86 (d, $J = 4.2$ Hz, 2H, Porβ_3), 6.06 (ddt, $J = 6$, 10.8, 16.2 Hz, 2H, C$\underline{H}$=CH$_2$), 5.48 (d, $J = 16.2$ Hz, 2H, CH=C$\underline{H}_2$), 5.45 (d, $J = 4.2$ Hz, 2H, Porβ_4), 5.44 (d, $J = 2$ Hz, 1H, Im CH), 5.31 (d, $J = 10.8$ Hz, 2H, CH=C$\underline{H}_2$), 4.86 (dd, $J = 6$, 12.6 Hz, 2H, –OCH$_2$), 4.80 (dd, $J = 6$, 12.6 Hz, 2H, –OCH$_2$), 3.85–3.77 (m, 2H, ester β), 3.73–3.67 (m, 2H, ester β), 2.02 (d, $J = 2$ Hz, 1H, Im CH), 1.66 (s, 3H, NCH$_3$), 0.74 (s, 9H, TMS); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.7 (C=O), 152.0 (Porα), 150.5 (Porα), 150.0 (Porα), 147.8 (Porα), 145.5 (Im N=C–N), 132.5 (C$\underline{H}$=CH$_2$), 131.9 (Porβ_2), 129.3 (Porβ_3), 128.8 (Porβ_1), 127.9 (Porβ_4), 121.9 (Im CH), 118.5 (*meso*), 118.4 (Im CH), 118.2 (CH=C$\underline{H}_2$), 109.2 (*meso*), 100.4 (TMS–C≡C–), 99.9 (TMS–C≡C–), 98.7 (*meso*), 65.6 (–OCH$_2$), 42.7 (ester β), 32.7 (NCH$_3$), 30.9 (ester α), 0.7 (TMS); UV–vis ($CHCl_3$): 426 (Abs.; 0.7554), 445 (1.2834), 579 (0.0830), 637 (0.1747) nm; Fluorescence (Ex = 426 nm, $CHCl_3$): 640, 698 nm; MALDI-TOF Mass of $C_{41}H_{40}N_6O_4SiZn$ Calcd: 772.22; Found: 773.6 $(M + H)^+$.

5,15-Bis(3-allyloxypropyl)-20-(1-methyl-2-imidazolyl)-10-phenylporphyrinatozinc (5f): In a similar manner as for the preparation of **5a**, the introduction of zinc ion into **4f** (90 mg, 136 μmol) was carried out to give **5f** (99 mg, quant). **D-5f**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.63 (d, $J = 4.8$ Hz, 2H, Porβ_1), 9.03 (d, $J = 4.8$ Hz, 2H, Porβ_2), 8.95 (d, $J = 4.8$ Hz, 2H, Porβ_3), 8.68 (d, $J = 7.4$ Hz, 1H, *o*-Ph), 8.16 (d, $J = 7.3$ Hz, 1H, *o*-Ph), 7.98–7.72 (m, 3H, *m*- and *p*-Ph), 6.18 (ddt, $J = 17.3$, 10.4, 5.4 Hz, 2H, C$\underline{H}$=CH$_2$), 5.52 (ddt, $J = 17.3$, 3.5, 1.6 Hz, 2H, CH=C$\underline{H}_2$), 5.50 (d, $J = 1.7$ Hz, 1H, Im H$_5$), 5.41 (d, $J = 4.8$ Hz, 2H, Porβ_4), 5.33 (ddt, $J = 10.4$, 4.3, 1.6 Hz, 2H, CH=C$\underline{H}_2$), 5.28–5.14 (m, 4H, Por αCH$_2$), 4.23 (dt, $J = 5.4$, 1.6 Hz, 4H, C$\underline{H}_2$–CH=CH$_2$), 4.00–3.85 (m, 4H, –CH$_2$O), 3.16–2.90 (m, 4H, CH$_2$), 2.14 (d, $J = 1.7$ Hz, 1H, Im H$_4$), 1.66 (s, 3H, N–Me). UV–vis (PhCN): 415 (Abs.; 0.47), 439 (0.49), 523 (0.051), 566 (0.056), 620 (0.056) nm; MALDI-TOF Mass of $C_{42}H_{40}N_6O_2Zn$ Calcd: 726.3; Found: 727.3 [$(M + H)^+$, 100 (relative intensity)], 1452.2 [$(M_2 + H)^+$, 60].

Covalently Linked Dimer 7a: A mixture of **D-5a** (80 mg, 0.11 mmol as **5a**) and Grubbs catalyst **6** (8 mg, 10 μmol) was stirred in $CHCl_3$ (15 mL) at rt. The time course of the reaction progress was monitored by MALDI-TOF mass spectra. (Normally, convergent peaks corresponding to the desired product were observed after 2–3 h.) Water was added to the mixture, and the mixture was extracted with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was loaded on a silica gel column and eluted with $CHCl_3$/acetone (9:1) to give the covalently linked dimer **7a** (73 mg, 95%). Split signals due to isomers with respect to two olefin moieties were observed in a ca. 1:4 ratio. Asterisk (*) and prime (′) indicate signals of major and minor isomers, respectively. No mark indicates that peaks of both isomers are overlapped. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_2), 9.75* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_2), 9.67′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_1), 9.63* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5; Porβ_1), 8.91′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_3), 8.89* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_3), 6.47–6.45* (*trans*; m, $J = 1.2$ Hz, 4H × 4/5, CH=CH), 6.40′ (*cis*; t, $J = 6.0$ Hz, 4H × 1/5, CH=CH), 5.50–5.42 (*trans* & *cis*; m, 4H, ester β), 5.43*′ (*trans* & *cis*; s, 2H, Im H$_5$), 5.39* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_4), 5.33′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_4), 5.29–5.22 (*trans* & *cis*; m, 4H, heptyl-C$_1$), 5.20′ (*cis*; dd, $J = 6.0$, 12 Hz, 2H × 1/5, CH=CH), 5.10′ (*cis*; dd, $J = 6.0$, 12 Hz, 2H × 1/5, O–CH$_2$), 5.06* (*trans*; d, $J = 10.2$ Hz, 2H × 4/5, O–CH$_2$), 5.00* (*trans*; d, $J = 10.2$ Hz, 2H × 4/5, O–CH$_2$), 4.14–4.05′ (*cis*; m, 4H × 1/5, ester α), 3.85–3.79′ (*cis*; m, 4H × 1/5, ester α), 3.92–3.80* (*trans*; m, 4H × 4/5, ester α), 3.74–3.60* (*trans*; m, 4H × 4/5, ester α), 2.77–2.70 (*trans* & *cis*; m, 4H, heptyl-C$_2$), 2.03–1.97 (*trans* & *cis*; m, 4H, heptyl-C$_3$), 1.94 (*trans* & *cis*; s, 2H, Im H$_4$), 1.69–1.65 (*trans* & *cis*; m, 4H, heptyl-C$_4$), 1.64 (*trans* & *cis*; s, 6H, NCH$_3$), 1.48–1.43 (*trans* & *cis*; m, 8H, heptyl-C$_5$, C$_6$), 0.99 (*trans* & *cis*; t, $J = 7.2$ Hz, 6H, heptyl-C$_7$); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9′ (C=O; *cis*), 172.5* (C=O; *trans*), 150.0* (Porα; *trans*), 149.9′ (Porα; *cis*), 149.63′ (Porα; *cis*), 149.60* (Porα; *trans*), 149.0* (Porα; *trans*), 148.9′ (Porα; *cis*), 148.4* (Porα; *trans*), 148.3′ (Porα; *cis*), 146.0′ (Im N=C–N; *cis*), 145.9* (Im N=C–N; *trans*), 130.8* (CH=CH; *trans*), 129.8′ (CH=CH; *cis*), 129.6 (Porβ_2), 128.7′ (Porβ_3; *cis*), 128.6* (Porβ_3; *trans*), 128.2 (Porβ_1), 127.37 & 127.32 (Porβ_4), 122.8* (*meso*; *trans*), 122.7′ (*meso*; *cis*), 121.65 & 121.61 (imidazole ring), 117.90 & 117.86 (imidazole ring), 116.8′ (*meso*; *cis*), 116.7* (*meso*; *trans*), 96.0*′ (*meso*), 63.4* (–OCH$_2$; *trans*), 58.9′ (–OCH$_2$; *cis*), 43.2 (ester α), 39.8 (heptyl-C$_2$), 36.3 (heptyl-C$_1$), 32.7 (NCH$_3$), 32.2 (heptyl-C$_5$), 31.4 (ester β), 30.9 (heptyl-C$_3$), 29.6 (heptyl-C$_4$), 22.9 (heptyl-C$_6$), 14.3 (heptyl-C$_7$); UV–vis (nm, $CHCl_3$): 416 (Abs.; 2.0287), 435 (2.2464), 570 (0.2089), 617 (0.0799), (nm, pyridine): 417 (Abs.; 0.7124), 436 (0.8064), 570 (0.712), 617 (0.0301), (nm, MeOH/$CHCl_3$ = 100/1): 416 (Abs.; 0.1009), 431 (0.1135), 566 (0.0100), 615 (0.0045); Fluorescence (Ex = 416 nm, $CHCl_3$): 620, 673 nm; MALDI-TOF Mass of $C_{82}H_{84}N_{12}O_8Zn_2$ Calcd: 1492.5; Found: 1493.3 $(M + H)^+$.

Covalently Linked Dimer 7b: A mixture of **D-5b** (82 mg, 102 μmol as **5b**) and Grubbs catalyst **6** (42 mg, 51 μmol) was stirred in $CHCl_3$ (20 mL) at 0 °C. After 36 h, water was added to the mixture,

followed by extraction with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was loaded on a silica gel column and eluted with $CHCl_3$/acetone (9:1) to give the covalently linked dimer **7b** (41 mg, 26%). Small peaks due to inseparable impurities were observed in the ^{1}H NMR spectra. Split signals due to isomers with respect to two olefin moieties were observed in a ca. 1:3 ratio. Asterisk (*) and prime (′) indicate signals of major and minor isomers, respectively. No mark indicates that peaks of both isomers are overlapped. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.73′ (*cis*; d, $J = 4$ Hz, 4H × 1/4; Porβ_2), 9.71* (*trans*; d, $J = 4$ Hz, 4H × 3/4, Porβ_2), 9.59–9.54 (*trans* & *cis*; d, $J = 4$ Hz, Porβ_1), 8.92′ (*cis*; d, $J = 4$ Hz, 4H × 1/4, Porβ_3), 8.90* (*trans*; d, $J = 4$ Hz, 4H × 3/4, Porβ_3), 6.23–6.17* (*trans*; m, 4H × 3/4, CH=CH), 5.93–5.87′ (*cis*; m, 4H × 1/4, CH=CH), 5.42 (*trans* & *cis*; s, 2H, Im H_5), 5.39* (*trans*; d, $J = 4$ Hz, 4H × 3/4, Porβ_4), 5.35′ (*cis*; d, $J = 4$ Hz, 4H × 1/4, Porβ_4), 5.27–5.22 (*trans* & *cis*; m, 4H, heptyl-C_1), 5.16–5.07 (*trans* & *cis*; m, 8H, ester γ), 5.02–4.85′ (*cis*; m, 8H × 1/4, –OCH_2), 4.87–4.69* (*trans*; m, 8H × 3/4, –OCH_2), 3.12–2.98 (*trans* & *cis*; m, 8H, ester β), 2.94–2.91 (*trans* & *cis*; m, 4H, ester α), 2.86–2.82 (*trans* & *cis*; m, 4H, ester α), 2.77–2.70 (*trans* & *cis*; m, 4H, heptyl-C_2), 2.03–1.98 (*trans* & *cis*; m, 4H, heptyl-C_3), 1.97 (*trans* & *cis*; s, 2H, Im H_4), 1.71–1.66 (*trans* & *cis*; m, 4H, heptyl-C_4), 1.62 (*trans* & *cis*; s, 6H, NCH_3), 1.48–1.42 (*trans* & *cis*; m, 8H, heptyl-C_5, C_6), 0.99 (*trans* & *cis*; t, $J = 7$ Hz, 6H, heptyl-C_7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7′ (C=O; *cis*), 173.6* (C=O; *trans*), 150.4* (Porα; *trans*), 149.9′ (Porα; *cis*), 149.7′ (Porα; *cis*), 149.6* (Porα; *trans*), 149.0 (Porα), 148.7 (Porα), 146.2 (Im N=C–N), 129.5′ (Porβ_3; *cis*), 129.3* (Porβ_3; *trans*), 129.0 (Porβ_2), 128.4′ (CH=CH; *cis*), 128.3* (CH=CH; *trans*), 128.1 (Porβ_2), 127.3* (Porβ_4; *trans*), 127.0′ (Porβ_4; *cis*), 122.4 (*meso*), 121.7 (Im CH), 118.5′ (*meso*; *cis*), 118.1* (*meso*; *trans*), 118.0 (Im CH), 117.7 (*meso*), 95.4 (*meso*), 63.6* (–OCH_2; *trans*), 60.0′ (–OCH_2; *cis*), 39.7 (heptyl-C_2), 36.3 (heptyl-C_1), 35.2 (ester γ), 35.1* (ester β; *trans*), 34.8′ (ester β; *cis*), 33.7′ (ester α; *cis*), 33.4* (ester α; *trans*), 32.7 (heptyl-C_5), 32.2 (NCH_3), 31.0 (heptyl-C_3), 29.7 (heptyl-C_4), 22.9 (heptyl-C_6), 14.3 (heptyl-C_7); UV–vis ($CHCl_3$): 416 (Abs.; 0.2307), 434 (0.2680), 568 (0.0221), 617 (0.0112), (pyridine): 417 (Abs.; 0.6572), 434 (0.8115), 568 (0.0661), 617 (0.0341) nm; Fluorescence (Ex = 416 nm, $CHCl_3$): 620, 678 nm; MALDI-TOF Mass of $C_{86}H_{92}N_{12}O_8Zn_2$ Calcd: 1548.5; Found: 1549.5 $(M + H)^+$.

Covalently Linked Dimer 7c: A mixture of **D-5c** (105 mg, 126 μmol as **5c**) and Grubbs catalyst **6** (52 mg, 63 μmol) was stirred in $CHCl_3$ (20 mL) at 0 °C. After 36 h, water was added to the mixture, followed by extraction with $CHCl_3$. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was loaded on a silica gel column and eluted with $CHCl_3$/acetone (10:1) to give the covalently linked dimer **7c** (33 mg, 16%). Split signals due to isomers with respect to two olefin moieties were observed in a ca. 1:2 ratio. Asterisk (*) and prime (′) indicate signals of major and minor isomers, respectively. No mark indicates that peaks of both isomers are overlapped. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.72 (*trans* & *cis*; d, $J = 4.2$ Hz, 4H, Porβ_2), 9.60 (*trans* & *cis*; d, $J = 4$ Hz, 4H, Porβ_1), 8.86′ (*cis*; d, $J = 4$ Hz, 4H × 1/3, Porβ_3), 8.82* (*trans*; d, $J = 4$ Hz, 4H × 2/3, Porβ_3), 6.06–6.04* (*trans*; m, $J = 1.2$ Hz, 4H × 2/3, CH=CH), 5.93′ (*cis*; t, $J = 6.0$ Hz, 4H × 1/3, CH=CH), 5.46 (*trans* & *cis*; s, 2H, Im CH), 5.35* (*trans*; d, $J = 4$ Hz, 4H × 2/3, Porβ_4), 5.30′ (*cis*; d, $J = 4$ Hz, 4H × 1/3, Porβ_4), 5.29–5.22 (*trans* & *cis*; m, 4H, heptyl-C_1), 5.15–4.95 (*trans* & *cis*; m, 8H, ester δ), 4.92–4.87′ (*cis*; m, 8H × 1/3, –OCH_2), 4.79–4.77′ (*cis*; m, 8H × 1/3, –OCH_2), 4.73–4.67* (*trans*; m, 8H × 2/3, –OCH_2), 2.93–2.90 (*trans* & *cis*; m, 8H, ester α), 2.77–2.72 (*trans* & *cis*; m, 4H, heptyl-C_2), 2.71–2.65 (*trans* & *cis*; m, 8H, ester γ), 2.45–2.32 (*trans* & *cis*; m, 8H, ester β), 2.03–1.99 (*trans* & *cis*; m, 4H, heptyl-C_3), 1.98 (*trans* & *cis*; s, 2H, Im CH), 1.72–1.67 (*trans* & *cis*; m, 4H, heptyl-C_4), 1.54 (*trans* & *cis*; s, 6H, NCH_3), 1.48–1.43 (*trans* & *cis*; m, 8H, heptyl-C_5, C_6), 0.99 (*trans* & *cis*; t, $J = 7$ Hz, 6H, heptyl-C_7); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5′ (C=O; *cis*), 173.4* (C=O; *trans*), 150.4* (Porα; *trans*), 150.3′ (Porα; *cis*), 149.3* (Porα; *trans*), 149.2′ (Porα; *cis*,), 149.1′ (Porα; *cis*), 149.0* (Porα; *trans*), 148.4′ (Porα; *cis*), 148.3* (Porα; *trans*), 146.2 (imidazole), 129.0′ (Porβ_3; *cis*), 128.9* (Porβ_3; *trans*), 128.7′ (CH=CH; *cis*), 128.4* (CH=CH; *trans*), 128.3 (Porβ_2), 127.0 (Porβ_4), 122.4 (*meso*), 121.6 (imidazole ring), 118.8′ (*meso*; *cis*), 118.6* (*meso*; *trans*), 117.7 (imidazole ring), 95.6 and 95.5 (*meso*), 63.3* (–OCH_2; *trans*), 60.3′ (–OCH_2; *cis*), 39.8 (heptyl-C_2), 38.8′ (ester α; *cis*), 38.4* (ester α; *trans*), 36.3 (hepyl-C_1), 35.6′ (ester δ; *cis*), 35.5* (ester δ; *trans*), 35.1* (ester γ; *trans*), 34.9′ (ester γ; *cis*), 32.6 (NCH_3), 32.2 (heptyl-C_5), 31.0 (heptyl-C_3), 29.6 (heptyl-C_4), 26.7* (ester β, *trans*), 26.5′ (ester β; *cis*), 22.9 (heptyl-C_6), 14.3 (heptyl-C_7); UV–vis ($CHCl_3$): 416 (Abs.; 0.0771), 435 (0.0849), 570 (0.0071), 617 (0.0025), (pyridine): 417 (Abs.; 0.3506), 435 (0.4257), 569 (0.0339), 619 (0.0195), ($MeOH/CHCl_3 = 100/1$): 412 (Abs.; 0.0737), 430 (0.0816), 565 (0.0073), 615 (0.0043) nm; Fluorescence (Ex = 416 nm, $CHCl_3$): 620, 674 nm; MALDI-TOF Mass of $C_{90}H_{100}N_{12}O_8Zn_2$ Calcd: 1604.6; Found: 1605.5 $(M + H)^+$.

Covalently Linked Dimer 7d: In a similar manner as for the preparation of **7a**, the covalent linking of **D-5d** (30 mg, 40 μmol) was carried out to give **7d** (28 mg, 95%). Split signals due to isomers with respect to two olefin moieties were observed in a ca. 1:4 ratio. Asterisk (*) and prime (′) indicate signals of major and minor isomers, respectively. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.61′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_2), 9.58* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_2), 9.07 (*trans* & *cis*; d, $J = 4.2$ Hz, 4H, Porβ_1), 8.99′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_3), 8.97* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_3), 8.74–8.65 (*trans* & *cis*; br, 2H, Ph), 8.15–8.01 (*trans* & *cis*; br, 2H, Ph), 7.95 (*trans* & *cis*; br.t, $J = 7.8$ Hz, 2H, Ph), 7.87 (*trans* & *cis*; br.t, $J = 8.4$ Hz, 2H, Ph), 7.77 (*trans* & *cis*; br.t, $J = 7.8$ Hz, 2H, Ph), 6.47* (*trans*; br.s, 4H × 4/5, CH=CH), 6.40′ (*cis*; t, $J = 6.0$ Hz, 4H × 1/5, CH=CH), 5.58–5.42 (*trans* & *cis*; m, 8H, ester β), 5.48 (*trans* & *cis*; br, 2H, Im H_5), 5.47* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_4), 5.39′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_4), 5.19′ (*cis*; dd, $J = 6.0$, 12 Hz, 4H × 1/5, –OCH_2), 5.10′ (*cis*; dd, $J = 6.0$, 12 Hz, 4H × 1/5, –OCH_2), 5.06* (*trans*; d, $J = 10.2$ Hz, 4H × 4/5, –OCH_2), 5.00* (*trans*; d, $J = 10.2$ Hz, 4H × 4/5, –OCH_2), 4.15–4.05′ (*cis*; m, 4H × 1/5, ester α), 3.90–3.87′ (*cis*; m, 4H × 1/5, ester α), 3.95–3.80* (*trans*; m, 4H × 4/5, ester α), 3.78–3.65* (*trans*; m, 4H × 4/5, ester α), 2.10 (*trans* & *cis*; br, 2H, Im H_4), 1.68 (*trans* & *cis*; s, 6H, NCH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.9′ (C=O; *cis*), 172.4* (C=O; *trans*), 150.6 (Porα), 149.6 (Porα), 149.5 (Porα), 148.0 (Porα), 143.8 (Im N=C–N), 134.7 (Ph), 134.6 (Ph), 132.8 (Porβ_1), 129.8 (Porβ_3), 128.8′ (CH=CH; *cis*), 128.7* (CH=CH; *trans*), 128.0 (Porβ_2), 127.5 (Porβ_4), 127.4 (Ph), 126.6 (Ph), 126.2 (Ph), 121.5 (Im CH), 118.0 (Im CH), 117.3 (*meso*), 63.4* (–OCH_2; *trans*), 58.9′ (–OCH_2; *cis*), 43.2 (ester α), 32.7 (NCH_3), 31.4 (ester β); UV–vis ($CHCl_3$): 413 (Abs.; 0.0722), 436 (0.0739), 565 (0.0124), 617 (0.079) nm; Fluorescence (Ex = 413 nm, $CHCl_3$): 620, 676 nm; MALDI-TOF Mass of $C_{80}H_{64}N_{12}O_8Zn_2$ Calcd: 1448.36; Found: 1449.47 $(M + H)^+$.

Covalently Linked Dimer 7e: In a similar manner as for the preparation of **7a**, the covalent linking of **D-5e** (40 mg, 52 μmol) was carried out to give **7e** (36 mg, 93%). Split signals due to isomers with respect to two olefin moieties were observed in a ca. 1:4 ratio. Asterisk (*) and prime (′) indicate signals of major and minor isomers, respectively. ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.933′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_2), 9.928* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_2), 9.65′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_1), 9.62* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_1), 8.90′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_3), 8.89* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_3), 6.47–6.45* (*trans*; dd, $J = 2.0$ Hz, 4H × 4/5, CH=CH), 6.40′ (*cis*; br.t, $J = 6.0$ Hz, 4H × 1/5, CH=CH), 5.41–5.40 (*trans* & *cis*; m, 8H, ester β), 5.44* (*trans*; d, $J = 4.2$ Hz, 4H × 4/5, Porβ_4), 5.42 (*trans* & *cis*; s, 2H, Im H_5), 5.37′ (*cis*; d, $J = 4.2$ Hz, 4H × 1/5, Porβ_4), 5.20′ (*cis*; dd, $J = 6.0$, 12 Hz, 4H × 1/5, –OCH_2), 5.10′ (*cis*; dd, $J = 6.0$, 12 Hz, 4H × 1/5, –OCH_2), 5.07* (*trans*; d, $J = 10.2$ Hz, 4H × 4/5, –OCH_2), 5.00* (*trans*; d, $J = 10.2$ Hz, 4H × 4/5, –OCH_2), 4.10–4.02′ (*cis*; m, 4H × 1/5, ester α), 3.82–3.75′ (*cis*; m, 4H × 1/5, ester α), 3.89–3.80* (*trans*; m, 4H × 4/5, ester α), 3.73–3.60* (*trans*; m, 4H × 4/5, ester α), 2.00 (*trans* & *cis*; br, 2H, Im H_4), 1.68 (*trans* & *cis*; s, 6H, NCH_3), 0.74 (*trans* & *cis*; s, 18H, TMS); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8′ (C=O; *cis*), 172.3* (C=O; *trans*), 152.3′ (Porα; *cis*), 152.1* (Porα; *trans*), 150.4* (Porα; *trans*), 150.3′ (Porα; *cis*), 149.9′ (Porα; *cis*), 149.8* (Porα; *trans*), 147.6* (Porα; *trans*), 147.5′ (Porα; *cis*), 145.4 (Im N=C–N), 132.0 (Porβ_1), 130.8* (CH=CH; *trans*), 129.8′ (CH=CH; *cis*), 129.0 (Porβ_2), 128.6* (Porβ_3; *trans*), 128.5′ (Porβ_3; *cis*), 127.8 (Porβ_4), 121.9 (Im CH), 118.2 (Im CH), 109.0 (*meso*), 100.6 (*meso*), 99.9* (*meso*; *trans*), 99.8′ (*meso*; *cis*), 98.8 (*meso*), 63.4* (–OCH_2; *trans*), 59.0′ (–OCH_2; *cis*), 43.2 (ester α), 32.8 (NCH_3), 31.4 (ester β), 29.8 (TMS–C≡C–), 0.7 (TMS); UV–vis ($CHCl_3$): 425 (Abs.; 0.0930), 445 (01505), 579 (0.0153), 637 (0.0253) nm; Fluorescence (Ex = 425 nm, $CHCl_3$): 640, 698 nm; MALDI-TOF Mass of $C_{78}H_{72}N_{12}O_8Si_2Zn_2$ Calcd: 1488.4; Found: 1489.1 $(M + H)^+$.

Covalently Linked Dimer 7f: In a similar manner as for the preparation of **7a**, the covalent linking of **D-5f** (20 mg, 28 μmol) was carried out to give **7f** (20 mg, quant). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.58–9.52 (m, $J = 4.3$, others Hz, 2H, Porβ_1), 9.09 (d, $J = 4.3$ Hz, 2H × 1/8, Porβ_2), 9.06 (d, $J = 4.3$ Hz, 2H × 6/8, Porβ_2), 9.03–8.99 (m, 2H, Porβ_3 + 2H × 1/8, Porβ_2), 8.73–8.67 (m, 1H, *o*-Ph), 8.12 (d, $J = 7.2$ Hz, 1H × 1/4, *o*-Ph), 8.09 (d, $J = 6.6$ Hz, 1H × 3/4, *o*-Ph), 7.94 (t, $J = 7.2$ Hz, 1H, *m*-Ph), 7.85 (t, $J = 7.2$ Hz, 1H, *m*-Ph), 7.78–7.72 (m, 1H, *p*-Ph), 6.44 (m, 2H × 7/8, CH=CH), 6.10 (m, 2H × 1/8, CH=CH), 5.51 (d, $J = 1.1$ Hz, 1H × 1/4, Im H_4), 5.50 (d, $J = 1.1$ Hz, 1H × 3/4, Im H_5), 5.47 (d, $J = 4.3$ Hz, 2H × 1/4, Porβ_4), 5.44 (d, $J = 4.3$ Hz, 2H × 3/4, Porβ_4), 5.43–5.36 (m, 2H × 3/4, αCH_2), 5.25–5.17 (m, 2H × 1/4, αCH_2), 5.16–5.07 (m, 2H, αCH_2), 4.67 (m, 4H × 1/8, –C<u>H$_2$</u>–CH=CH–), 4.46–4.38 (m, 4H × 7/8, –C<u>H$_2$</u>–CH=CH–), 4.19 (m, 4H, –CH_2–O–), 3.17–3.08 (m, 2H, –CH_2–), 3.06–2.95 (m, 2H, –CH_2–), 2.13 (d, $J = 1.1$ Hz, 1H × 1/4, Im H_4), 2.11 (d, $J = 1.1$ Hz, 1H × 3/4, Im-H_4), 1.70 (s, 3H × 3/4, NMe), 1.68 (s, 3H × 1/4, NMe); UV–vis ($CHCl_3$): 414 (Abs.; 0.69), 438 (0.74), 529 (0.012), 567 (0.059), 619 (0.034) nm; MALDI-TOF Mass of $C_{80}H_{72}N_{12}O_4Zn_2$ Calcd (max. peak): 1396.3; Found: 1398.5 $(M + H)^+$.

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