

Supramolecular Porphyrin–DABCO Array in Single- and Double-Stranded Polynorbornenes**

Hsien-Wen Wang,^[a] Chih-Hsien Chen,^[a] Tsong-Shin Lim,^[b] Shou-Ling Huang,^[a] and Tien-Yau Luh^{*[a]}

Dedicated to Professor Eiichi Nakamura on the occasion of his 60th birthday

Abstract: Zinc–porphyrin-appended norbornene derivative **6**, the corresponding dimer **7**, coherently aligned single-stranded polynorbornene **5**, and zinc–porphyrin-linked double-stranded polymeric ladderphane **3** have been used for complexation with 1,4-diazabicyclo[2.2.2]octane (DABCO) to generate an array of porphyrin–DABCO supramolecular scaffolds. The stoichiometries of the complex forma-

tion are analyzed in detail by ¹H NMR spectroscopy as well as absorption and emission spectroscopic methods. Bidentate ligand DABCO is found to form with **7**, **5**, and **3** to give 2-to-1 porphyrin–DABCO sandwich structures. Mo-

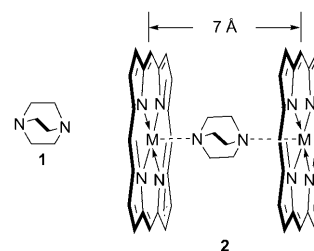
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nomer **6**, on the other hand, forms a 2-to-1 porphyrin–DABCO sandwich structure at high concentration (20 mM), but a 1-to-1 porphyrin–DABCO complex at low concentration (10^{−6} M). Time-resolved fluorescence decays revealed a similar behavior for the 2-to-1 porphyrin–DABCO sandwich structures that are formed from **3**, **5**, and **7**.

Introduction

Numerous systems that have a cofacial alignment of porphyrin derivatives have been designed to mimic the photosynthetic process.^[1–6] This motif provides a unique means to place two porphyrin moieties at a given distance for interchromophoric interactions. Cofacial bisporphyrin dyads,^[2] multiple deck oligoporphyrins,^[3] multiporphyrinic dendrimers,^[4] and porphyrin-appended macromolecules^[5,6] have been extensively examined for through-space interactions. Coordination of imidazole groups from the transmembrane proteins to magnesium ions would bring two porphyrin moieties at the reaction centers into close proximity.^[7] Such an axial coordination to the metalloporphyrin with a donor

ligand offers a powerful platform that leads to supramolecular assemblies.^[8,9] Bidendate ligand 1,4-diazabicyclo[2.2.2]octane (DABCO, **1**) is known to form tight one-to-



two complexes **2** with metalloporphyrins, with K_a values on the order of 10⁵–10⁸ M^{−1}, and the spacing between two porphyrin rings is around 7 Å.^[8] A range of supramolecular systems based on this strategy has been reported.^[9]

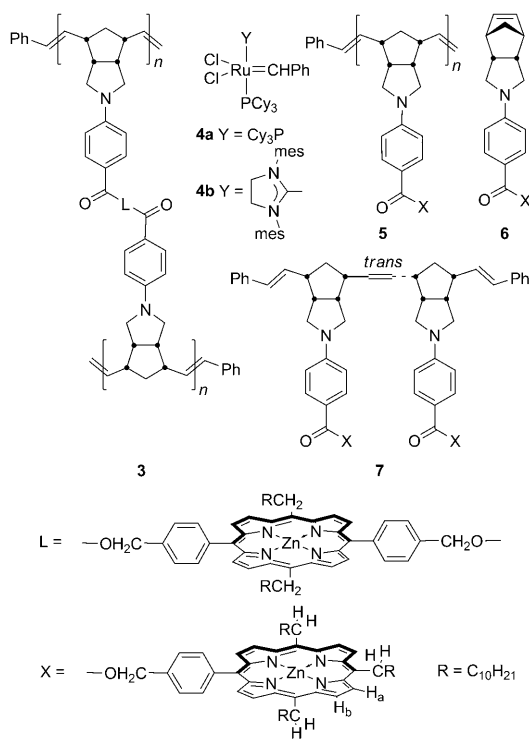
We recently found that isotactic double-stranded polymeric ladderphane **3**, by using porphyrin moieties as linkers, is obtained selectively from the corresponding bisnorbornene monomer by ring-opening metathesis polymerization (ROMP) using the first generation Grubbs catalyst **4a**.^[10] Isotactic polynorbornenes **5**, in which all porphyrin pendants

[a] H.-W. Wang, Dr. C.-H. Chen, S.-L. Huang, Prof. T.-Y. Luh
Department of Chemistry, National Taiwan University
Taipei 106 (Taiwan)
Fax: (+886)2-2364-4971
E-mail: tyluh@ntu.edu.tw

[b] Prof. T.-S. Lim
Department of Physics, Tung Hai University
Taichung 407 (Taiwan)

[**] DABCO = 1,4-diazabicyclo[2.2.2]octane.

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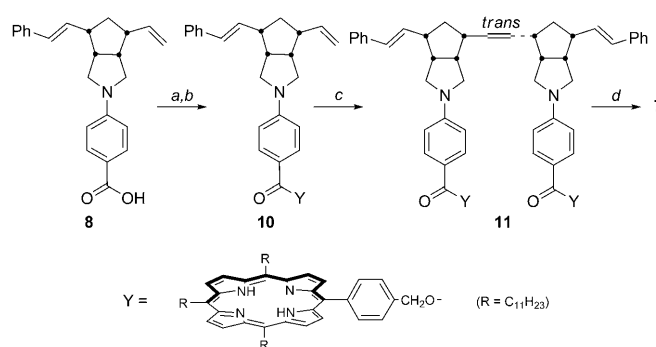


are coherently aligned toward the same direction, are also accessible from **6**.^[6] Strong exciton couplings between these adjacent porphyrins in **3** and **5** may take place as evidenced by the broadening or splitting of the Soret band in the absorption spectra (Figure 1). The average spacing between two adjacent porphyrin rings in these polymers is about 5.5 Å as revealed by the X-ray structure of a monomer^[11] and the scanning tunneling microscopy (STM) images of related double-stranded polymeric ladderphanes.^[10,12] It is envisaged that **1** may insert into the two adjacent porphyrins in these polymers to form a supramolecular porphyrin–DABCO array. In this paper, we wish to report the reactions and photophysical properties of double-stranded polymer **3**, single-stranded polymer **5**, porphyrin-appended monomer **6**, and dimer **7**, with **1**.

Results and Discussion

Synthesis

The synthesis of isotactic double- and single-stranded polynorbornenes **3**, **5**, and monomer **6** were described previously.^[6,10] Isotactic dimer **7** was obtained following our published procedure^[6b] according to Scheme 1.^[9b] Thus, esterification of **8** gave **9** in 81 % yield. Cross-metathesis using the second-generation Grubbs catalyst **4b** (5 mol %) afforded isotactic **10** in 49 % yield after careful chromatographic separation from other stereoisomers. Metalation of **10** with Zn(OAc)₂ furnished 89 % yield of the desired dimer **7** with isotactic stereochemistry.



Scheme 1. Synthesis of **7**: a) (COCl)₂; b) YH (**9**), NEt₃, 4-dimethylaminopyridine (DMAP); c) **4b**; d) Zn(OAc)₂·2H₂O.

Photophysical Properties

The absorption and emission spectra of **3–7** are compared in Figure 1 and the data are summarized in Table 1. It is worth noting that the Soret band of the absorption spectrum of **7** also splits into two peaks owing to the intramolecular exciton coupling between the two porphyrin chromophores. The relative intensity of the shorter wavelength absorption versus the longer wavelength absorption in the Soret band of polymer **5**, however, is higher than that of dimer **7**. Pre-

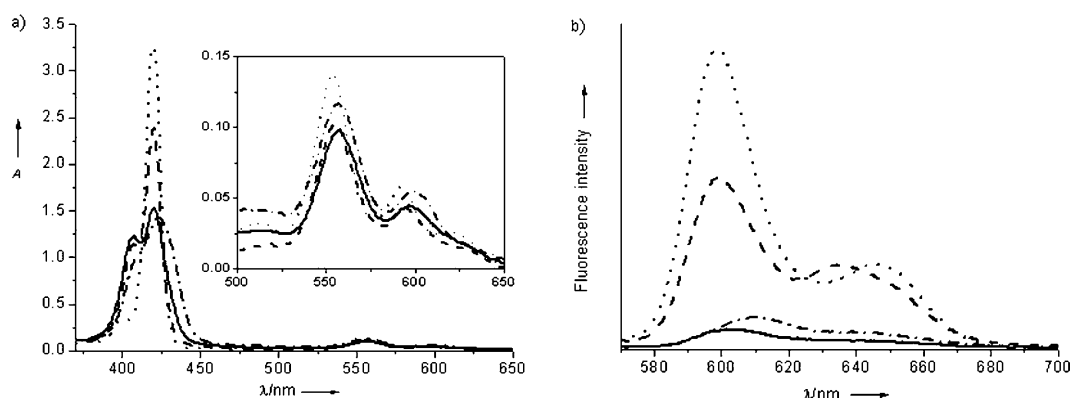


Figure 1. a) Absorption and b) emission spectra of **3** (---), **5** (—), **6** (.....), and **7** (— · —) in CH₂Cl₂.

Table 1. Photophysical properties of **3**, **5**, **6**, and **7** in CH₂Cl₂.

| Compound | <i>M_n</i> (PDI) or molecular weight | Absorption | | Emission | | Lifetime (τ) [ns] |
|----------------|--|--|------------------------------------|--|-------------------------|--------------------------|
| | | Soret band λ_{max} [nm] | Q band λ_{max} [nm] | λ_{max} [nm] ^[a] | Φ_f ^[b] | |
| 3 | 31 000 (1.61) | 422 | 557, 598 | 608 | 0.010 | 1.5 (37 %), 0.2 (63 %) |
| 3 DABCO | — | 425 | 566, 611 | 616 | 0.027 | 2.9 (45 %), 0.4 (55 %) |
| 5 | 17 000 (1.19) | 407, 420 | 557, 596 | 605 | 0.007 | 1.4 (33 %), 0.2 (67 %) |
| 5 DABCO | — | 424 | 569, 611 | 616 | 0.026 | 2.9 (45 %), 0.5 (55 %) |
| 6 | 1177 | 420 | 554, 593 | 600 | 0.036 | 1.4 |
| 6 DABCO | — | 430 | 571, 613 | 631 | 0.033 | 2.0 (21 %), 0.3 (79 %) |
| 7 | 2540 | 407, 420 | 555, 594 | 600 | 0.027 | 1.4 (76 %), 0.3 (24 %) |
| 7 DABCO | — | 424 | 569, 610 | 617 | 0.032 | 2.9 (69 %), 0.3 (31 %) |

[a] Excitation at λ_{max} around 550 nm. [b] The quantum yield for ZnTPP in toluene, used as the reference, is 0.033.

sumably, the presence of multiple modes of interaction between adjacent porphyrin chromophores in **5** might account for this observation.

The fluorescence quantum yields of polymers **3**, **5**, and dimer **7** were significantly reduced in comparison with that of monomer **6**. It is interesting to note that the reduction of quantum yields for polymers **3** and **5** was larger than that for **7**.

Titration with **1**

To elucidate the nature of the complexation between **1** and polymers **3** and **5**, reactions of model monomeric and dimeric porphyrin derivatives **6** and **7** with **1** were examined.

Reactions of **6** with **1**

Zinc-porphyrins are known to exhibit concentration-dependent ¹H NMR spectra on account of the aggregation through π - π interactions.^[13,14] At a concentration of 20 mM (see the Supporting Information), the β protons (H_a and H_b) of the zinc-porphyrin in **6** appear at δ = 9.15 ppm, and the α -methylene protons in the undecyl substituents on the porphyrin ring in **6** at δ = 4.50 ppm. The ¹H NMR spectra in CDCl₃ obtained after different molar ratios^[9g] of **1** were introduced are recorded in Figure 2.

As shown in Figure 2b–d, the peak at δ = −4.88 ppm was assigned to the protons (H_c and H_d) on the complexed DABCO with two zinc-porphyrin rings in **12**.^[8,9] When more than 0.5 equiv of **1** were added, rapid exchange may have taken place

and the signal at δ = −4.88 ppm began to shift to lower field (Figure 2e–h) and became broader.^[8,9] The β protons (H_a and H_b) of the zinc-porphyrin in **6** at δ = 9.15 ppm gradually shifted downfield as the concentration of **1** increased and reached a plateau (δ = 9.25 ppm) when the ratio of [**1**]/[**6**] was 0.5. A further increase in the molar ratio of **1** resulted in a gradual shift to lower field again (e.g., to δ = 9.49 ppm in Figure 2h; see also the Support-

ing Information).^[14] Similar behavior was observed for the α -methylene protons in the undecyl substituents at C¹⁵ on the porphyrin ring. Thus, the signals for these protons shifted from δ = 4.52 to 4.71 ppm. These results indicate that the aggregation between two zinc-porphyrin moieties became less significant as the molar ratios of **1** were increased (up to 0.5 molequiv), thus leading to the formation of two-to-one complex **12**. Further increase in the concentration of **1** would result in one-to-one complex **13**.

The ¹H NMR spectrum of a mixture of **6** and of **1** (1.5 equiv) measured at −60 °C showed two high-field peaks centered at δ = −5.1 and −3.1 ppm (see the Supporting Information).^[14] The former would be the same as that de-

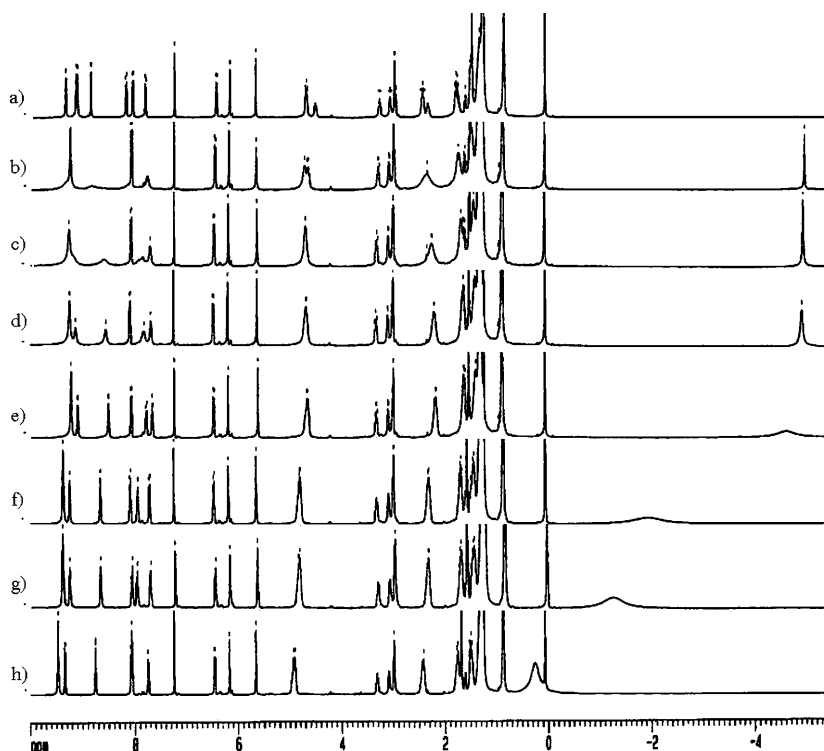
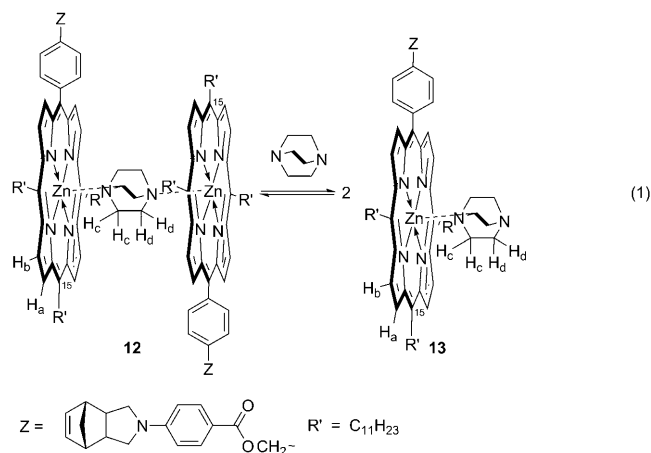


Figure 2. ¹H NMR spectra of **6** (20 mM) with different molar ratios of **1** in CDCl₃ at ambient temperature. Ratio of [**1**]/[**6**]: a) 0, b) 0.2, c) 0.4, d) 0.5, e) 0.6, f) 0.8, g) 1.2, h) 2.0.

scribed above for H_c and H_d in **12**, whereas the latter might be attributed to H_c on the DABCO ligand in one-to-one complex **13** [Eq. (1)].



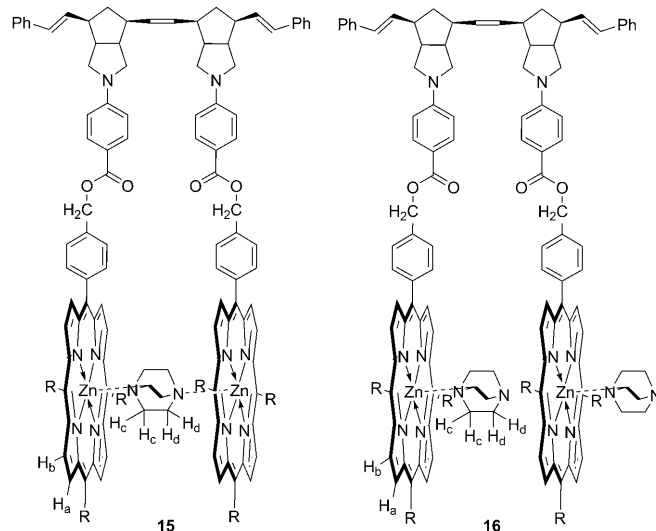
Quinuclidine **14** has only one nitrogen ligand for complexation and therefore can form a one-to-one complex only with a zinc-porphyrin. Indeed, in a controlled titration experiment of **6** with **14**, the β -proton signals (H_a and H_b) appeared at $\delta = 9.5$ ppm when $[14]/[6]$ was 1 (see the Supporting Information).^[14] This observation was similar to that found in one-to-one complex **13** when an excess amount of **1** was introduced.

Titration of monomer **6** in CH_2Cl_2 with incremental amounts of **1** gave a series of UV/Vis spectra with one isosbestic point (Figure 3). The Soret band shifted from 420 to 430 nm and showed a simple isosbestic point at 426 nm. The absorption at 430 nm suggests that one-to-one complex **13** might be formed under these conditions.^[8,9,14] Similar to those reported in the literature,^[9b] no two-to-one complex **12** was observed from the absorption data. The binding con-

stant (K_a) for **13** was $1.3 \times 10^5 M^{-1}$ and the detailed calculations are summarized in the Supporting Information.^[14,15] The emission spectra (Figure 3b) of the mixture of **6** and **1** also behaved similarly to exhibit isosbestic behavior.

Reactions of **7** with **1**

Complexation between dimer **7** with **1** was monitored by 1H NMR spectroscopy (Figure 4) and absorption spectra (Figure 5) in a similar manner as those described above. The two porphyrin moieties in **7** may bind to one molecule of **1** to form a sandwich complex **15**. Beyond this molar ratio, the



signal at $\delta = -4.99$ ppm assigned to the methylene protons (H_c and H_d) of DABCO began to broaden and shift down-field. Again, the low-temperature ($-60^\circ C$) 1H NMR spectrum (see the Supporting Information) of a mixture of **7** and of **1** (1.5 equiv) suggests a rapid equilibrium between **15** (signal for H_c and H_d at $\delta = -5.2$ ppm) and **16** (signal for H_c at $\delta = -3.1$ ppm).^[14] In addition, the signals for the β protons (H_a and H_b) of the zinc-porphyrin in the 1H NMR spectra

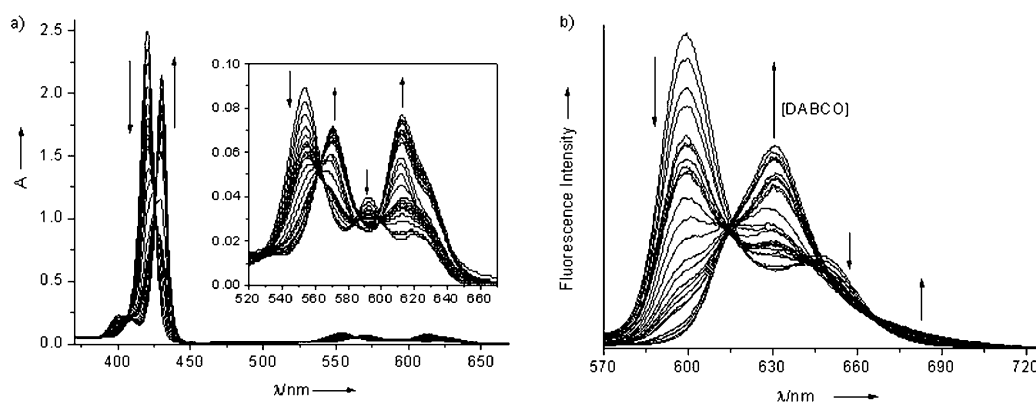


Figure 3. Absorption and emission spectra of **6** ($5 \times 10^{-6} M$) with different molar ratios of **1** in CH_2Cl_2 . Number of equivalents of **1** added per monomer **6**: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0, 5.0, 10.0, 20.0, 30.0.

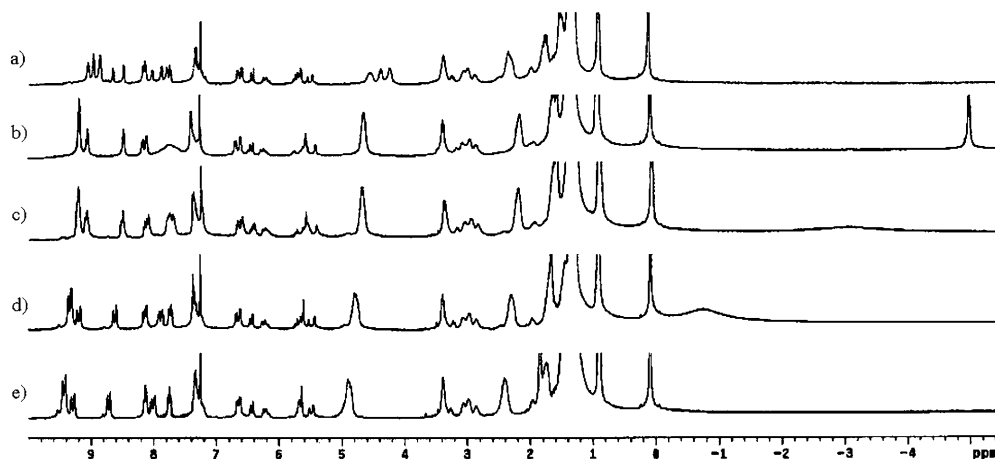


Figure 4. ^1H NMR spectra of **7** (10 mM) with different concentrations of **1** in CDCl_3 at ambient temperature. Ratio of $[\mathbf{1}]/[\mathbf{7}]$: a) 0, b) 1.0, c) 1.5, d) 2.1, e) 5.0.

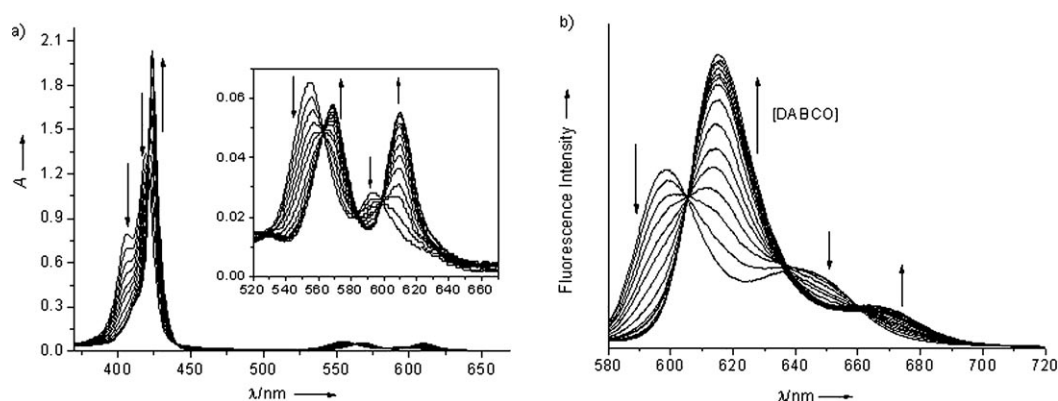


Figure 5. a) Absorption and b) emission spectra of **7** ($2.5 \times 10^{-6} \text{ M}$) with different molar ratios of **1** in CH_2Cl_2 . Number of equivalents of **1** added per **7**: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0, 3.0.

shifted from $\delta = 9.21 \text{ ppm}$ in **7** to a sharp signal at $\delta = 9.41 \text{ ppm}$ in **15**. Presumably, the two porphyrin moieties in **15** would be more separated (from about 5.5 to 7 Å) so that the shielding between the two tethered porphyrin moieties in **7** would become less important. Two DABCO molecules may eventually bind to **7** to form **16** as the molar ratios of **1**

increased and the chemical shift of the β protons (H_a and H_b) appeared at $\delta = 9.65 \text{ ppm}$.

The absorption and emission spectra of the mixture of **7** and **1** shown in Figures 5 and 6 also demonstrated a similar behavior as those described for the reactions of **6**. As the molar fraction of **1** was increased, complex **15** would be

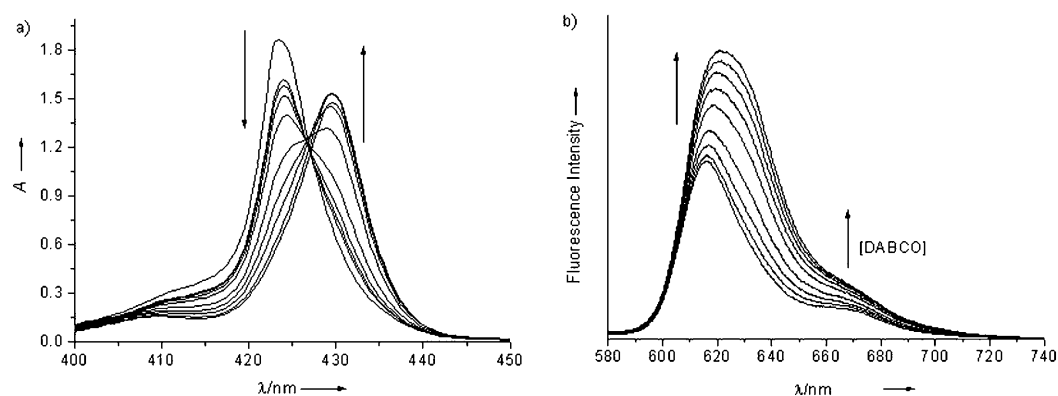


Figure 6. a) Absorption and b) emission spectra of **15** ($2.5 \times 10^{-6} \text{ M}$) with different molar ratios of **1** in CH_2Cl_2 . Number of equivalents of **1** added per **15**: 20, 100, 300, 700, 1700, 5700, 12000, 25000, 60000, 100000.

formed initially as revealed by the appearance of the absorption at 424 nm. When **1** was present in a large excess amount, a new absorption at 430 nm emerged (Figure 6) that could be assigned to the absorption of one-to-one complex **16**^[9] as depicted in the previous section. The equilibrium constants for the formation of **15** from **6** and **16** from **15** were $9.7 \times 10^5 \text{ M}^{-1}$ and 70 M^{-1} , respectively (see the Supporting Information).^[14,15]

The two porphyrin pendants are in close proximity in **7** to accommodate the DABCO ligand in such a way that **15** can readily be formed as a stable complex under these conditions. As shown in Figure 6, a large excess amount of **1** was required for the formation of **16**, and the formation constants for **15** and for **16** differed by several orders of magnitude.

Reactions of **5** with **1**

Single-stranded polynorbornene **5** was treated with **1** in the same manner as those described above, and the ¹H NMR spectra are shown in Figure 7. Since the complex formation

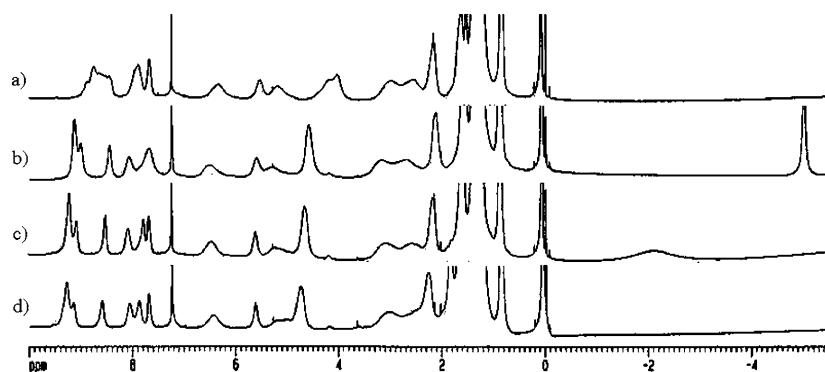
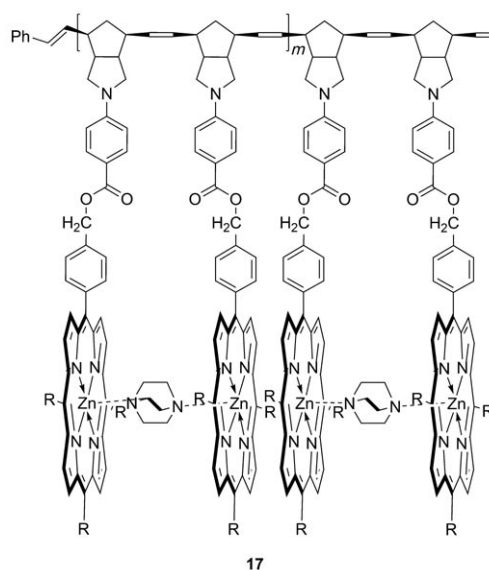


Figure 7. ¹H NMR spectra of **5** (20 mM) with different molar ratios of **1** in CDCl₃ at ambient temperature. Ratio of [**1**]/[**5**]: a) 0, b) 0.5, c) 0.8, d) 2.0.

between **5** and **1** would depend on the number of equivalents of porphyrin pendants in **5**, the concentration of **5** was calculated based on the molecular weight of monomer **6**. The changes in chemical shifts in the ¹H NMR spectra were similar to those described for **6** and **7**. It is particularly noteworthy that the signals for the β protons (H_a and H_b) of the porphyrin moieties in **5** shifted from a broad peak at $\delta = 8.30\text{--}9.20$ ppm to a sharp peak at $\delta = 9.29$ ppm when 3 equiv of **1** were added. In comparison with the chemical shift of the β protons (H_a and H_b) of DABCO dimers **15** and **16**, these results suggest that each of the DABCO molecules may form a complex with a pair of two adjacent porphyrin moieties. The degree of polymerization of **5** was 14. Accordingly, it seems likely that about seven DABCO moieties, on average, may bind with **5** to form an array like **17**.

The low-temperature (-60°C) ¹H NMR spectrum of **5** and of **1** (1.5 equiv) showed two major DABCO signals at $\delta = 2.8$ ppm assigned to the free ligand and at $\delta = -5.1$ ppm for sandwiched DABCO between two adjacent porphyrin



moieties (see the Supporting Information).^[14] The intensity of the peak at $\delta = -3.2$ ppm was negligibly small and suggests that little one-to-one porphyrin–DABCO complex, if any, would be formed in this mixture. These results indicate that **1** can efficiently insert into the single-stranded porphyrin-appended polynorbornene **5** to form a stable array of porphyrin–DABCO complex **17**.

The absorption and fluorescence spectra of **5** with different molar ratios of **1** are shown in Figure 8. It is interesting to

note that absorption profiles were similar to those observed for **7** (Figure 5) and the Soret band shifted from a split pattern at 407 and 420 nm to a single absorption peak at 424 nm, the characteristic absorption for a two-to-one complex. The association constant was $2.8 \times 10^6 \text{ M}^{-1}$, which is about three times larger than that of **7** (see the Supporting Information).^[14]

As mentioned earlier, the distance between two porphyrin rings in a two-to-one porphyrin–DABCO complex is about 7 \AA ,^[8] whereas the spacing occupied by each of the monomeric units in **5** is about 5.5 \AA and all pendants are likely to align coherently towards a similar direction.^[11] As shown in Figure 1, the Soret band of **5** showed strong exciton coupling between the adjacent porphyrin rings and, therefore, the distance between these two adjacent coupling pairs could be shorter than the expected average spacing (5.5 \AA) for **5**. This possibility is illustrated in Figure 9. As such, the distance between one porphyrin moiety of a coupling pair and another porphyrin ring of an adjacent coupling pair would

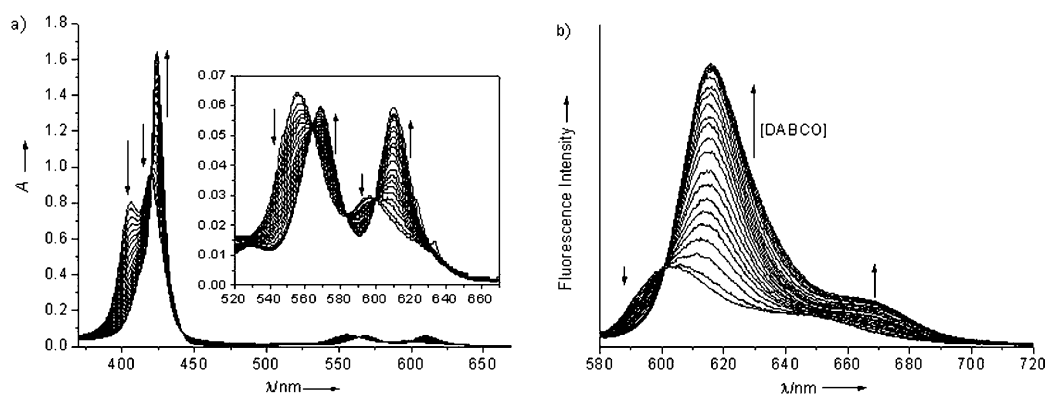


Figure 8. a) Absorption and b) emission spectra of **5** (5×10^{-6} M) with different molar ratios of **1** in CH_2Cl_2 . Ratio of **[1]/[5]**: 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4.

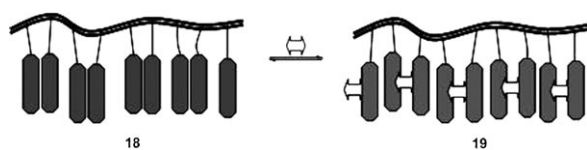


Figure 9. Plausible mode for the insertion of DABCO into **5**.

be somewhat expanded. A structure similar to **18** might be formed. The DABCO molecule would then be able to get into this cavity to form the porphyrin–DABCO array **19**.^[16]

As shown in Figure 7, the chemical shifts of β protons in the ^1H NMR spectra in the **5**–DABCO complex appear in the “normal” region, thus indicating that there would be little shielding between the two adjacent pairs of porphyrin–DABCO conjugates. The appearance of a single Soret band absorption (Figure 8) for this **5**–DABCO conjugate is also consistent with these NMR spectroscopic results, thereby indicating few interactions between adjacent chromophores. A similar observation has been made for related zinc–porphyrin–ligand complexes.^[9e,f] However, the rotation about the C–C bond in the polymeric backbone cannot be ruled out; this may lead to the *syn* conformation of the pendants being converted into the more random *anti* conformation, which might result in no interaction between the adjacent porphyrin–DABCO conjugates. However, as will be discussed in the next section on the DABCO complex with double-stranded polybisnorbornene **3**, a similar behavior (few interactions between the adjacent porphyrin–DABCO pair) was observed while rotation about the polymeric backbone was impossible.

Reactions of **5** with **14**

As described above, each DABCO can coordinate with two porphyrin moieties, whereas monodentate **14** can only form a one-to-one complex with metalloporphyrin. As shown in Figure 10, the peaks at $\delta = -0.58$ and -2.97 ppm were assigned to the methylene protons of the complexed **14** with zinc–porphyrin. When more than 1.0 equiv of **14** was added,

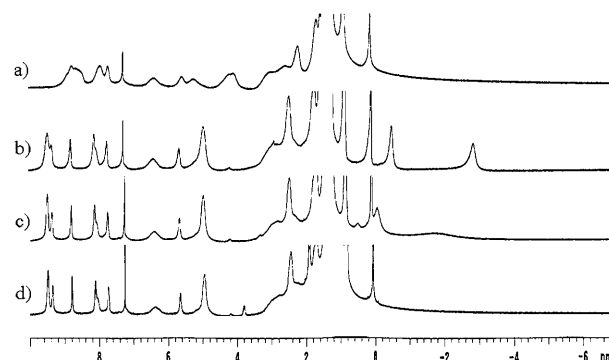


Figure 10. ^1H NMR spectra of **5** (20 mM) with different molar ratios of **14** in CDCl_3 . Ratio of **[14]/[5]**: a) 0, b) 1.0, c) 1.5, d) 5.0.

a rapid exchange could take place and the signal began to shift to lower field (Figure 10). The broad peak of β protons (H_a and H_b) of the zinc–porphyrin in **5** gradually shifted from $\delta = 8.30$ – 9.20 ppm to a sharp peak at $\delta = 9.50$ ppm as the molar ratio of **14** increased and reached a plateau when **[14]/[5]** was 1. This signal ($\delta = 9.50$ ppm) was similar to that of the complex formed from **6** and an excess amount of **1** as described above. The photophysical properties of the mixture of **5** and different molar ratios of **14** are summarized in the Supporting Information.^[14] The equilibrium constant for the formation of **14** with **5** was $1.4 \times 10^5 \text{ M}^{-1}$, which was 20 times smaller than that of the complex formed from **5** and **1**.^[14]

Equilibrium Studies of **1** and **14** with **5**

It is known that the amine ligand can undergo rapid exchange with metalloporphyrin. Different concentrations of **14** were added to a mixture of **5** and of **1** (0.5 equiv) in CDCl_3 (see the Supporting Information). As the amount of **14** was increased, the proton signals for the β protons (H_a and H_b) of the porphyrin moieties in the complex gradually shifted from $\delta = 9.15$ ppm to lower field. When 5 equiv of **14** was added, the proton signals for these β protons (H_a and H_b) appeared at $\delta = 9.41$ ppm. These results indicate that the

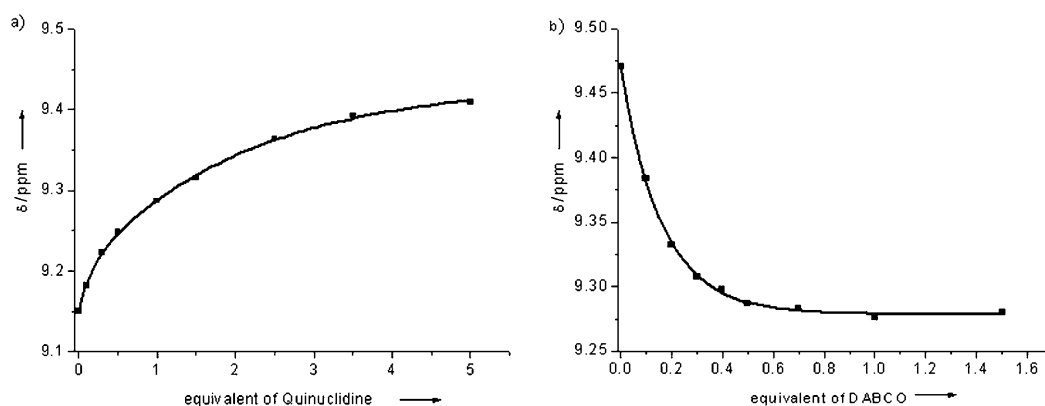


Figure 11. Titration profiles of a) adding **14** to a mixture of **1** and **5** and b) adding **1** to a mixture of **14** and **5**.

complexed DABCO ligand may undergo slow exchange with **14** and the exchange was not complete even with 5 equiv of **14**. The titration profile is shown in Figure 11a. As described above, the difference in formation constants of the complexes with **5** between these two bridgehead nitrogen ligands **1** and **14** was 20-fold in favor of the DABCO ligand. It is not surprising that the exchange was not complete even if **14** was present in excess amounts.

On the contrary, addition of **1** to a solution of **5** and 1 equiv of **14** caused the proton signals for the β protons (H_a and H_b) of the porphyrin moieties to shift from $\delta=9.47$ to 9.29 ppm, and this signal remained constant when 0.5 to 1.5 equiv of **1** were added (see the Supporting Information). The titration profile is shown in Figure 11b. These results suggest that the axial quinuclidine ligands of porphyrins in this mixture may rapidly exchange during the titration process to lead to a two-to-one complex between each pair of adjacent porphyrins and DABCO.

Reactions of **3** with **1**

Treatment of **3** with different molar ratios of **1** similarly afforded the corresponding array of the complex between the porphyrin moieties in **3** and **1**. The concentration of **3** was calculated in a similar manner to that described for **5**. The

1H NMR spectroscopic peaks for **3** were too broad for characterization. However, the high-field absorption at $\delta=-4.97$ ppm owing to the complex formation of **1** with two adjacent porphyrin linkers was clearly observed (see the Supporting Information). Again, at higher molar ratios of **1**, this signal shifted to lower field in a similar manner to those found in **5–7**.

The absorption and fluorescence titration spectra of **3** with different molar ratios of **1** shown in Figure 12 again behaved similarly to those of **5** under similar conditions. Both the absorption and the emission maxima shifted from a shoulder at 410 nm and peak at 422 nm to a single peak at 424 nm as the molar ratios of **1** were increased. These results are consistent with the formation of an array that consisted of a series of the complex formed from two porphyrin linkers with one DABCO, and the binding constant was $3.97 \times 10^6 M^{-1}$.^[14]

Polymer **3** is a rigid double-stranded ladderphane. The polymeric backbone in **3** could not undergo rotation at all. As shown in Figures 1 and 12, the Soret band of **3** is significantly broadened owing to exciton coupling between adjacent chromophores. Accordingly, the formation of the DABCO complex may occur by means of a similar mechanism to that depicted in Figure 9.

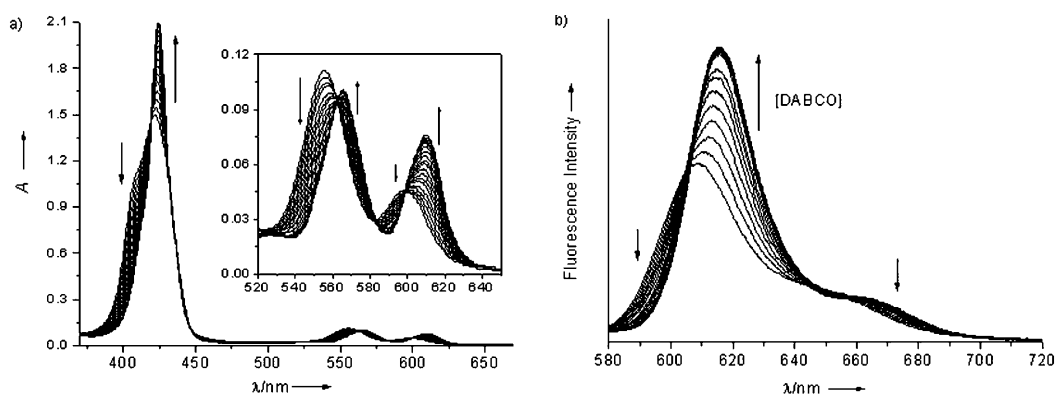


Figure 12. a) Absorption and b) emission spectra of **3** ($5 \times 10^{-6} M$) with different molar ratios of DABCO in CH_2Cl_2 . Ratio of $[1]/[3]$: 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.3, 1.6, 2.0.

Time-Resolved Fluorescence Spectroscopy

Time-resolved fluorescence decays for **3–7** in CH_2Cl_2 were measured (see the Supporting Information) and the results are outlined in Table 1. The lifetimes for DABCO complexes with **3** and **5** were comparable to those of the **7**–DABCO complex. The longer one was assumed from the emission of the two-to-one porphyrin–DABCO complex and the shorter one may arise from self-quenching. The contribution of the shorter lifetimes in the complexes with polymers appeared to be slightly higher than that in the **7**–DABCO complex.

Conclusion

We have demonstrated a new type of supramolecular scaffolds that contain an array of porphyrin–DABCO complexes with both single- and double-stranded polynorbornenes appended or linked with porphyrin moieties **5** and **3**. These supramolecular arrays have been shown to exhibit entirely different photophysical properties from those of the parent polymers. From the structural point of view, the present results have provided additional evidence for the conformation of the single-stranded polynorbornenes **5** in which all porphyrin pendants are coherently aligned towards the same direction. In addition, this observation further illustrates the double-stranded ladderphane nature of **3**. Since the linkers between the porphyrin moieties and the polymeric backbone are somewhat flexible, slight perturbation of the spacing between adjacent porphyrin moieties would enable the accommodation of the DABCO ligands between two neighboring porphyrin rings, thereby leading to the formation of a supramolecular scaffold. The insight of these approaches can pave the way to other opportunities for the use of different kinds of bidentate ligands or the incorporation of other metallomacrocycles in the host polymers.

Experimental Section

General

High-resolution mass spectrometric (HRMS) measurements were obtained with a Jeol-JMS-700 mass spectrometer using the FAB method in a 3-nitrobenzyl alcohol matrix. Gel permeation chromatography (GPC) was performed with a Waters GPC machine using 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 ($7.8 \times 300 \text{ mm}$) were employed for the determination of relative molecular weight using polystyrene as standard (M_n values ranged from 375 to 3.5×10^6). Absorption spectra were measured with a Hitachi U-3310 spectrophotometer and emission spectra with a Hitachi F-4500 fluorescence spectrophotometer. The quantum yield was obtained using zinc tetraphenylporphyrin (ZnTPP) in toluene as the reference ($\Phi = 0.033$).

Compound **10**

Oxalyl chloride (0.53 mL, 6.2 mmol) and DMF (one drop) were added to a solution of **8**^[6a] (0.92 g, 2.56 mmol) in CH_2Cl_2 (30 mL) at 0°C . The mixture was gradually warmed to RT and stirred for 1 h. The solvent was re-

moved in vacuo to give acid chloride, which was used for the next reaction without further purification.

The acid chloride that was prepared from **8** (0.92 g, 2.56 mmol) and oxalyl chloride (0.53 mL, 6.2 mmol) in CH_2Cl_2 (30 mL) were added to a mixture of **9**^[6b] (1.5 g, 1.7 mmol), NEt_3 (3.0 mL), and a trace amount of DMAP in CH_2Cl_2 (30 mL) at 0°C .^[6a] The mixture was stirred at RT for 17 h. Saturated NaHCO_3 was added and the organic layer was separated. The solution in CH_2Cl_2 was washed with water and brine, and dried (MgSO_4). The solvent was removed in vacuo and the residue was subjected to chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2/\text{NEt}_3 = 1:1:0.05$) to give **10** as viscous oil (1.69 g, 81%). $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = -2.65$ (s, 2H), 0.86–0.92 (m, 9H), 1.25–1.42 (m, 36H), 1.50–1.56 (m, 6H), 1.66 (q, $^2J(\text{H,H}) = 12.1 \text{ Hz}$, 1H), 1.77–1.87 (m, 6H), 1.95–2.00 (m, 1H), 2.47–2.59 (m, 6H), 2.83–3.06 (m, 4H), 3.33–3.42 (m, 4H), 4.92–5.01 (m, 6H), 5.07–5.14 (m, 2H), 5.71 (s, 2H), 5.80–5.89 (m, 1H), 6.30 (dd, $^3J(\text{H,H}) = 15.8$, 7.4 Hz, 1H), 6.46 (d, $^3J(\text{H,H}) = 15.8 \text{ Hz}$, 1H), 6.66 (d, $^3J(\text{H,H}) = 8.9 \text{ Hz}$, 2H), 7.22–7.35 (m, 5H), 7.81 (d, $^3J(\text{H,H}) = 8.1 \text{ Hz}$, 2H), 8.13 (d, $^3J(\text{H,H}) = 8.9 \text{ Hz}$, 2H), 8.17 (d, $^3J(\text{H,H}) = 8.1 \text{ Hz}$, 2H), 8.55 (d, $^3J(\text{H,H}) = 4.9 \text{ Hz}$, 2H), 9.38 (d, $^3J(\text{H,H}) = 4.9 \text{ Hz}$, 2H), 9.50 (d, $^3J(\text{H,H}) = 4.9 \text{ Hz}$, 2H), 9.53 ppm (d, $^3J(\text{H,H}) = 4.9 \text{ Hz}$, 2H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 14.1$, 22.68, 22.69, 29.3, 29.4, 29.63, 29.65, 29.71, 29.73, 30.57, 30.65, 31.90, 31.92, 35.2, 35.4, 35.8, 38.7, 38.9, 45.1, 45.8, 46.1, 46.7, 49.5, 49.6, 65.9, 111.8, 115.6, 117.1, 117.5, 119.1, 119.4, 126.0, 126.1, 127.2, 128.6, 130.6, 130.9, 131.6, 134.5, 136.1, 137.3, 138.8, 142.2, 151.2, 167.1 ppm; IR (KBr): $\tilde{\nu} = 3313$, 3025, 2952, 2923, 2852, 1722, 1604, 1522, 1479, 1376, 1270, 1204, 1175, 1164, 1060, 965, 792, 735 cm^{-1} ; MS (FAB): m/z : calcd for $\text{C}_{84}\text{H}_{109}\text{N}_5\text{O}_2$: 1220.7968 [$M^+ + \text{H}$]; found: 1220.8663.

Compound **11**

Under argon, a solution of **10** (1.0 g, 0.82 mmol) and **4b** (34 mg, 0.04 mmol) in CH_2Cl_2 (8 mL) was heated at reflux for 24 h, cooled to RT, and quenched with ethyl vinyl ether (2 mL). Removal of the solvent in vacuo, followed by chromatographic purification (silica gel, hexane/ $\text{CH}_2\text{Cl}_2 = 1:2$) afforded **11** (480 mg, 49%). M.p. $95\text{--}96^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = -2.68$ (s, 1H), -2.65 (s, 1H), 0.86–0.94 (m, 18H), 1.23–1.45 (m, 72H), 1.46–1.59 (m, 12H), 1.71–1.87 (m, 14H), 1.91–1.98 (m, 2H), 2.46–2.61 (m, 12H), 2.73–3.05 (m, 8H), 3.23–3.40 (m, 8H), 4.80–4.91 (m, 12H), 5.43 (m, 1H), 5.48 (m, 1H), 5.70 (s, 2H), 5.72 (s, 2H), 6.18 (dd, $^3J(\text{H,H}) = 7.2$, 15.8, 1H), 6.21 (dd, $^3J(\text{H,H}) = 7.0$, 15.8, 1H), 6.43 (d, $^3J(\text{H,H}) = 15.8$, 1H), 6.45 (d, $^3J(\text{H,H}) = 15.8 \text{ Hz}$, 1H), 6.63 (d, $^3J(\text{H,H}) = 9.0 \text{ Hz}$, 2H), 6.68 (d, $^3J(\text{H,H}) = 9.0 \text{ Hz}$, 2H), 7.22–7.40 (m, 10H), 7.77 (d, $^3J(\text{H,H}) = 7.9 \text{ Hz}$, 2H), 7.81 (d, $^3J(\text{H,H}) = 7.9 \text{ Hz}$, 2H), 8.10 (d, $^3J(\text{H,H}) = 7.9 \text{ Hz}$, 2H), 8.15–8.20 (m, 6H), 8.77 (d, $^3J(\text{H,H}) = 4.8 \text{ Hz}$, 2H), 8.82 (d, $^3J(\text{H,H}) = 4.8 \text{ Hz}$, 2H), 9.28 (d, $^3J(\text{H,H}) = 4.8 \text{ Hz}$, 2H), 9.34 (d, $^3J(\text{H,H}) = 4.8 \text{ Hz}$, 2H), 9.43–9.53 ppm (m, 8H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): $\delta = 14.1$, 22.7, 29.3, 29.4, 29.7, 29.8, 30.5, 30.7, 31.90, 31.92, 35.4, 35.8, 38.7, 38.9, 44.6, 44.8, 45.1, 45.3, 46.3, 46.6, 46.8, 46.9, 49.5, 49.6, 49.7, 65.9, 111.7, 117.2, 117.5, 119.0, 119.1, 119.3, 119.4, 125.9, 126.1, 127.3, 128.57, 128.59, 130.5, 130.6, 130.9, 131.7, 131.85, 131.92, 134.5, 136.09, 136.11, 137.3, 142.1, 142.2, 151.1, 151.2, 167.0 ppm; IR (KBr): $\tilde{\nu} = 3313$, 3025, 2961, 2923, 2852, 1704, 1605, 1479, 1467, 1372, 1271, 1178, 1099, 966, 792, 736 cm^{-1} ; MS (FAB): m/z : calcd for $\text{C}_{166}\text{H}_{214}\text{N}_{10}\text{O}_4$: 2411.6850 [M^+]; found: 2411.6833.

Compound **7**

A mixture of **11** (300 mg, 0.124 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (530 mg, 2.40 mmol) in methanol (15 mL) and CH_2Cl_2 (20 mL) was stirred at RT in the dark for 3 h, and then washed with NaHCO_3 and brine, and dried (Na_2SO_4). The solvent was removed in vacuo to give the residue that was subjected to chromatography on silica gel (hexane/ $\text{CH}_2\text{Cl}_2/\text{NEt}_3 = 1:1:0.05$) to afford **7** (280 mg, 89%). M.p. $104\text{--}105^\circ\text{C}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 0.88\text{--}0.92$ (m, 18H), 1.21–1.68 (m, 86H), 1.68–1.90 (m, 12H), 1.90–2.05 (m, 2H), 2.23–2.48 (m, 12H), 2.80–3.11 (m, 8H), 3.11–3.45 (m, 8H), 4.21–4.31 (m, 4H), 4.31–4.45 (m, 4H), 4.45–4.62 (m, 4H), 5.48 (m, 1H), 5.56 (m, 1H), 5.62–5.79 (m, 4H), 6.18 (dd, $^3J(\text{H,H}) = 7.2$, 15.6, 1H), 6.23 (dd, $^3J(\text{H,H}) = 7.2$, 16.0, 1H), 6.44 (d, $^3J(\text{H,H}) = 16.0 \text{ Hz}$, 2H), 6.61 (d, $^3J(\text{H,H}) = 8.8 \text{ Hz}$, 2H), 6.67 (d, $^3J(\text{H,H}) = 8.8 \text{ Hz}$, 2H), 7.16–7.39 (m, 10H), 7.75 (d, $^3J(\text{H,H}) = 8.0 \text{ Hz}$, 2H), 7.80 (d, 3J

(H,H)=8.0 Hz, 2H), 7.90 (d, $^3J(\text{H,H})=8.0$ Hz, 2H), 8.05 (d, $^3J(\text{H,H})=8.0$ Hz, 2H), 8.14 (d, $^3J(\text{H,H})=9.0$ Hz, 2H), 8.17 (d, $^3J(\text{H,H})=9.0$ Hz, 2H), 8.51 (d, $^3J(\text{H,H})=4.8$ Hz, 2H), 8.68 (d, $^3J(\text{H,H})=4.4$ Hz, 2H), 8.88 (d, $^3J(\text{H,H})=4.8$ Hz, 2H), 8.90 (d, $^3J(\text{H,H})=4.8$ Hz, 2H), 8.99 (d, $^3J(\text{H,H})=4.4$ Hz, 4H), 9.07 ppm (d, $^3J(\text{H,H})=4.8$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): $\delta=14.1, 22.7, 29.4, 29.7, 29.8, 30.7, 31.9, 35.1, 35.3, 38.7, 38.8, 44.5, 44.8, 45.1, 45.3, 46.2, 46.4, 46.7, 46.9, 49.5, 49.6, 49.7, 65.9, 111.7, 117.28, 117.34, 117.9, 118.1, 119.2, 119.35, 119.44, 119.5, 125.9, 126.0, 126.05, 126.07, 127.2, 127.7, 127.8, 127.98, 128.05, 128.1, 128.5, 128.6, 130.5, 130.6, 130.86, 130.90, 131.3, 131.4, 131.6, 134.5, 135.7, 135.8, 137.23, 137.25, 142.7, 142.8, 148.0, 148.1, 148.6, 148.7, 148.8, 149.0, 149.1, 151.05, 151.14, 167.0$ ppm; IR (KBr): $\tilde{\nu}=3123, 3019, 2955, 2922, 2852, 1705, 1605, 1522, 1458, 1375, 1271, 1178, 1097, 1007, 964$ cm^{-1} ; MS (ESI): m/z : calcd for $\text{C}_{166}\text{H}_{210}\text{N}_{10}\text{O}_2\text{Zn}_2$: 2540.2886 [M^+]; found: 2540.5093.

General Procedure for the Titration Experiments

^1H NMR spectroscopy and absorption and emission titrations were performed by adding solutions that contained the ligand (**1** or **14**) to a solution of the zinc porphyrin by using microliter syringes. In all types of titration experiments, the zinc–porphyrin was present in the guest solution at the same concentration as that in the NMR spectroscopy tube or cuvette to avoid dilution effects. ^1H NMR spectroscopic titration experiments were performed by using a constant host concentration (around 20 μM per monomer) and variable guest concentrations at 293 K. UV/Vis and fluorescence titration experiments for the determination of the association constants were performed by using a constant host concentration (around 5×10^{-6} M per monomer) and variable N-containing ligand concentrations. The details for the calculations of the association constants (K_a) are described in the Supporting Information.^[14,15]

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- [16] The alternative possibility that involves the rotation about the carbon–carbon bond(s) in the polymeric backbone of **5** to generate more room for DABCO coordination cannot be ruled out at this stage.

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