Polymeric Materials

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Formation of Discrete Ladders and a Macroporous Xerogel Film by the Zipperlike Dimerization of Meso–Meso-Linked Zinc(II) Porphyrin Arrays with Di(pyrid-3-yl)acetylene**

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Abstract: *Metal porphyrins assemble to form a supramolecular architecture with a characteristic structure and characteristic properties and functions upon complexation with appropriate ligands. However, there are few applications of these assembly processes to the construction of polymeric porphyrin arrays with useful functionalities. In this study, we found that meso–meso-linked Zn^{II} porphyrin arrays underwent zipperlike dimerization upon complexation with di(pyrid-3-yl)acetylene (DPA) in chloroform to form discrete double-stranded porphyrin ladders. Similarly, the assembly of poly(zinc(II) porphyrinylene) with DPA gave a thermoresponsive gel, whose three-dimensional network structure was so strong that a macroporous xerogel film was obtained.*

Supramolecular functional assemblies, such as the photosynthetic antennas LH1 and LH2,[1,2] have inspired extensive studies on the construction of three-dimensional assemblies by the complexation of metal porphyrins with multidentate coordinating ligands.[3] In these assembly processes, structural motifs of the metal porphyrins and coordinating ligands are translated into tertiary structures in the resulting supramolecular assemblies. Reversible and thermodynamic features of these assembly processes have been used for molecular machines, cyclic antenna complexes, and self-sorting assemblies.[4–7] However, the application of these assembly processes of metal porphyrins to the development of polymeric materials with useful properties is rare.

The fabrication of multistranded polymers with a strong rigid linear structure, as opposed to single-stranded polymers, has been a challenging research area in polymer and supramolecular chemistry.[8–17] Polymeric double strands with helical and nonhelical conformations can assemble through attractive noncovalent interactions (Figure 1).

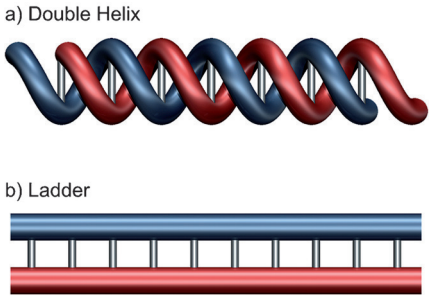

Figure 1. Models of a) helical and b) nonhelical double-stranded architectures.

Although supramolecular helical double strands have been extensively studied because of analogies with DNA, ladder-shaped polymers have attracted little attention.[17,18] However, we expected that such ladder-shaped polymers may have higher stiffness and linearity and lower elasticity owing to their rigid structures. As building blocks of ladder-shaped polymers, meso–meso linked Zn^{II} porphyrin arrays are promising because of their linear shapes and high solubility in common organic solvents.[19]

Anderson and co-workers reported that a series of butadiyne-bridged Zn^{II} porphyrin oligomers formed stable ladder complexes with linear bidentate ligands, such as 1,4-diazabicyclo[2.2.2]octane and 4,4′-bipyridyl.[17] In these ladder complexes, the porphyrin arrays adopt a coplanar conformation to extend π-electronic conjugation in a remarkable manner. Meso–meso-linked porphyrin arrays $\mathbf{ZP}_n$ adopt perpendicular conformations owing to steric repulsion between the pyrrole β hydrogen atoms[20] and are considered to have an intrinsic geometrical impediment to the construction of such supramolecular ladder complexes with linear bidentate nitrogen-based ligands. However, it was thought that di(pyrid-3-yl)acetylene (DPA), a nonlinear bidentate ligand, might form supramolecular ladders with $\mathbf{ZP}_n$ in a 1:2 ratio (Scheme 1). As illustrated schematically in Scheme 1b, simultaneous coordination of two DPA molecules to two $\mathbf{ZP}_2$ arrays might occur without a large decrease in the dihedral angle from 90°. Importantly, this conformational change would lead to increased electronic interaction between the Zn^{II} porphyrins with characteristic UV/Vis absorption-spectral changes.[6a,20]

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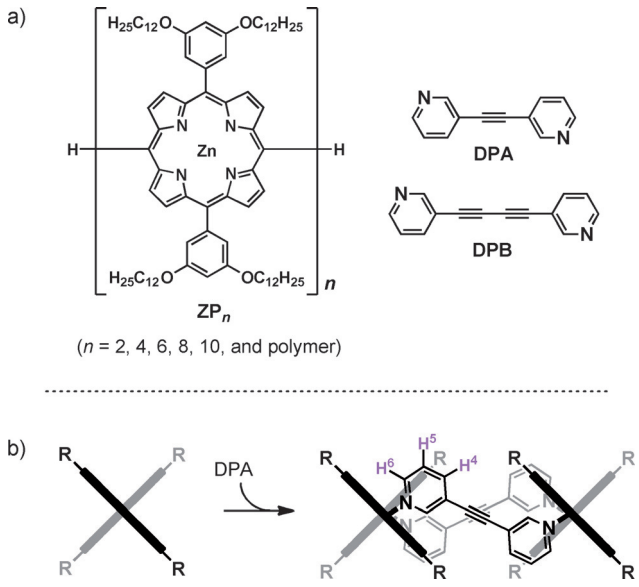
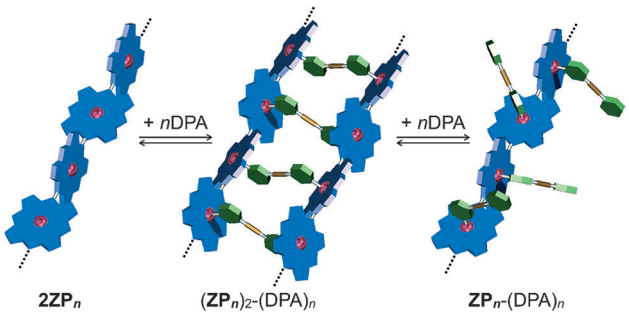


Scheme 1. a) Directly meso–meso-linked multiporphyrin arrays $\mathbf{ZP}_n$ and bidendate ligands. b) Schematic illustration of the formation of a supramolecular ladder complex of $\mathbf{ZP}_n$ and DPA through Zn–N coordination bonds.

Meso–meso-linked porphyrin oligomers $\mathbf{ZP}_n$ ($n = 2$, 4, 6, 8, and 10) and their polymeric congener $\mathbf{ZP}_p$ were prepared by oxidative coupling reactions of a zinc complex of 5,15-bis(3,5-didodecyloxyphenyl)porphyrin (**ZP**) with $AgPF_6$ in $CHCl_3$.[19] The ^{1}H NMR spectrum of $\mathbf{ZP_2}$ in $CDCl_3$ showed a singlet at $\delta = 10.37$ ppm due to the meso hydrogen atoms, four doublets at $\delta = 9.48$, 9.26, 8.80, and 8.07 ppm due to the pyrrolic β hydrogen atoms, and two doublets at $\delta = 7.41$ and 6.79 ppm due to the aromatic hydrogen atoms of the meso aryl substituents (Figure 2b). When an equivalent amount of DPA was added to a solution of $\mathbf{ZP_2}$ in $CDCl_3$ at 293 K, the ^{1}H NMR signals of both $\mathbf{ZP_2}$ and DPA were shifted upfield, and some signals became broadened (see Figure S1 in the Supporting Information), thus indicating the complexation of $\mathbf{ZP_2}$ and DPA.[7] Upon cooling to 223 K, the ^{1}H NMR peaks became sharper with a concurrent increase in the number of peaks (Figure 2b, bottom). A ^{1}H–^{1}H COSY experiment enabled us to assign the peaks of the complex (see Figure S2). Importantly, the pyrrolic β hydrogen atoms were observed in the upfield region as eight separate signals, and the aryl hydrogen atoms of the meso substituents were observed as six separate signals, whereas the meso hydrogen atoms on the porphyrin rings were observed as a singlet at 10.16 ppm, and the signals for the hydrogen atoms of the DPA ligands were observed at 6.45 (H^4), 5.73 (H^5), and 2.75 ppm (H^6). The signal for the hydrogen atom at C2 of DPA was probably shifted into the complex aliphatic region (1.9–0.7 ppm). These observed spectral features indicate the formation of a ladder-shaped complex in which two DPA molecules bind to two molecules of $\mathbf{ZP_2}$ through Zn–N coordination to form a $(\mathbf{ZP_2})_2$–$(DPA)_2$ complex with a slipped-parallel arrangement. On the other hand, the ^{1}H NMR spectrum of a 1:1 mixture of $\mathbf{ZP_2}$ and di(pyrid-3-yl)-1,3-butadiyne (DPB), a longer bidendate pyridyl ligand, showed only broad signals even at 223 K (see Figure S3), thus suggesting a lower thermal stability of the corresponding ladder-shaped complex.

Next, the complexation of higher Zn^{II} porphyrin oligomers with DPA was examined. The ^{1}H NMR spectral pattern of a 1:2 mixture of $\mathbf{ZP_4}$ and DPA in $CDCl_3$ at 273 K, a higher temperature than that used to detect $(\mathbf{ZP_2})_2$–$(DPA)_2$, was similar to that of $(\mathbf{ZP_2})_2$–$(DPA)_2$, thus indicating the formation of a similar discrete ladder complex, $(\mathbf{ZP_4})_2$–$(DPA)_4$. The spectrum featured a singlet at 10.16 ppm due to the meso hydrogen atoms, 16 signals due to the pyrrolic β hydrogen atoms, and 12 signals due to the aryl hydrogen atoms of the meso substituents, together with two sets of highly upfield shifted signals in a 1:1 ratio for the hydrogen atoms of the DPA connectors (Figure 2c; see also Figure S4). The ^{1}H NMR titration of $\mathbf{ZP_4}$ with DPA at 273 K showed that the peaks corresponding to the ladder complex increased at the expense of those of the $\mathbf{ZP_4}$ monomer up to the addition of 2 equivalents of DPA (see Figure S5) but decreased upon the further addition of DPA and were replaced with a new set of peaks, which were assigned to the five-coordinated $\mathbf{ZP_4}$ monomer (Figure 3 and Scheme 2). The overall association constant (K_F) of $[(\mathbf{ZP_4})_2$–$(DPA)_4]/[\mathbf{ZP_4}]^2\,[DPA]^4$ is too large to measure from this titration profile.



Scheme 2. Schematic illustration of the 2:n and 1:n complexation of $\mathbf{ZP}_n$ and DPA.

We then examined diffusion-ordered NMR spectroscopy (DOSY) for a 1:1 mixture of $\mathbf{ZP_4}$ and DPA that was considered to contain the free $\mathbf{ZP_4}$ monomer and the ladder complex in a 1:1 ratio.[21] The DOSY profile showed separate signals for the $\mathbf{ZP_4}$ monomer and the ladder complex, for which diffusion coefficients (D) were calculated of $(2.35 \pm 0.02) \times 10^{-10}$ and $(2.14 \pm 0.04) \times 10^{-10}$ $m^2 s^{-1}$, respectively (see Figure S6). These values allowed us to estimate volumes of the free $\mathbf{ZP_4}$ monomer and the ladder complex of 7.4×10^3 and 9.6×10^3 Å^3, respectively. A similar DOSY experiment revealed the D value of the $\mathbf{ZP_8}$ monomer to be $(2.05 \pm 0.03) \times 10^{-10}$ $m^2 s^{-1}$, which led to an estimation of its molecular volume of 11.0×10^3 Å^3. These results support the hypothesis that the discrete complex formed from $\mathbf{ZP_4}$ and DPA is a $(\mathbf{ZP_4})_2$–$(DPA)_4$ ladder. In analogy with the $\mathbf{ZP_2}$ and $\mathbf{ZP_4}$ systems, the ^{1}H NMR spectrum of a 1:3 mixture of $\mathbf{ZP_6}$ and DPA at 273 K displayed a singlet for the meso hydrogen atoms, 24 signals for the pyrrolic β hydrogen atoms, and three sets of highly upfield shifted signals in a 1:1:1 ratio for the hydrogen atoms of the DPA connectors (Figure 2d; see also

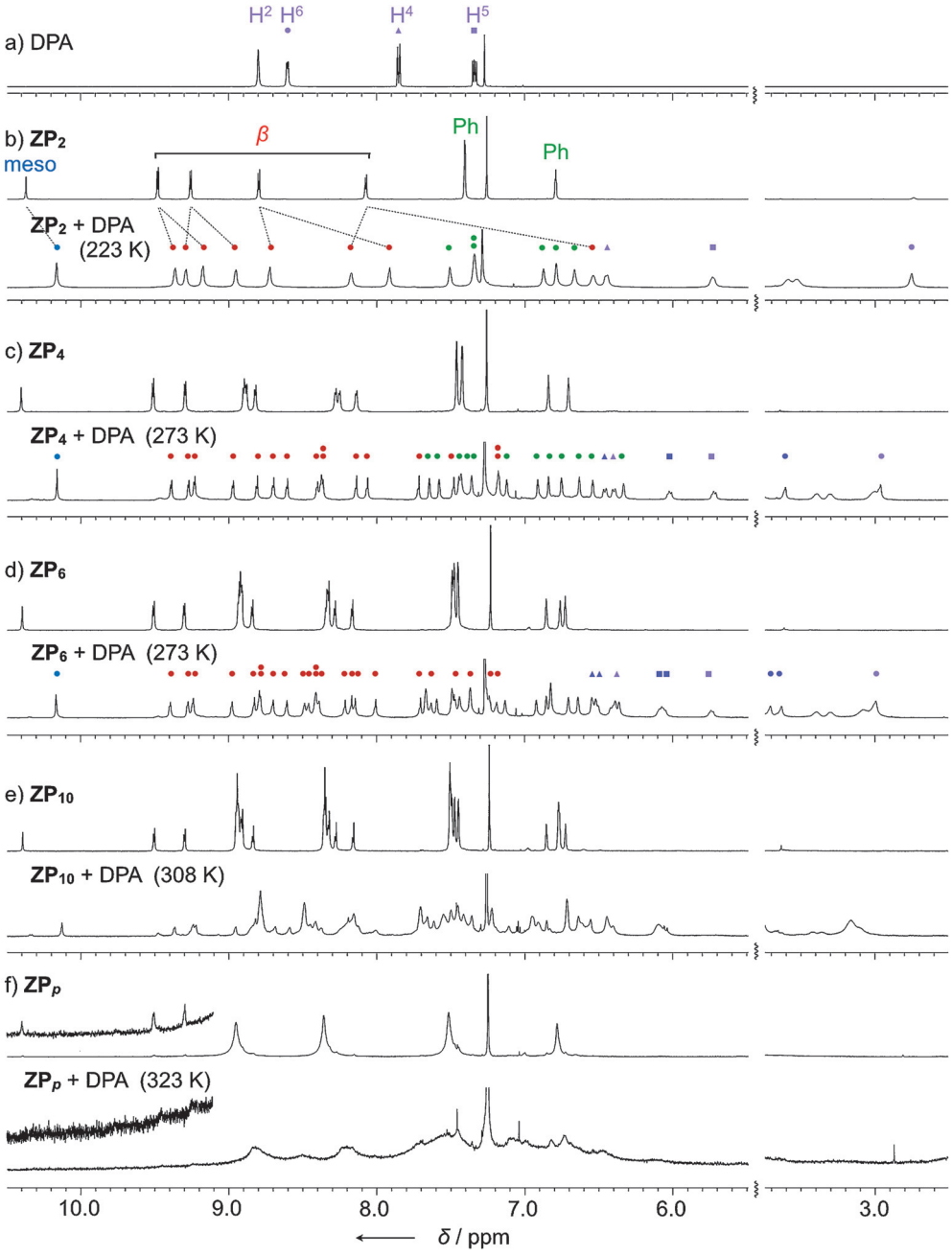


Figure 2. a) ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of DPA. b–f) Changes in the ^{1}H NMR spectra of **ZP$_2$**, **ZP$_4$**, **ZP$_6$**, **ZP$_{10}$**, and **ZP$_p$** upon mixing with DPA (0.5 equiv per monomer unit). [Monomer unit of **ZP$_n$**] = 7.2×10^{-3} M ([**ZP$_2$**] = 3.6×10^{-3} M, [**ZP$_4$**] = 1.8×10^{-3} M, [**ZP$_6$**] = 1.2×10^{-3} M, and [**ZP$_{10}$**] = 7.2×10^{-4} M).

spectra of the complexes of **ZP$_8$** and **ZP$_{10}$** did not change significantly up to 293 and 303 K, respectively.

The meso–meso-linked Zn^{II} porphyrin arrays exhibited characteristic electronic absorption spectra with a split Soret band at 400–550 nm and Q-bands at 550–650 nm (Figure 4a). Under the dilute conditions used for UV/Vis absorption spectral measurement, it was difficult to detect ladder formation from short arrays, such as **ZP$_2$** and **ZP$_4$** (see Figures S9 and S10). It is natural to expect the largest association constant for **ZP$_{10}$**, the longest array in the series, as it has the most coordination sites. When **ZP$_{10}$** was titrated in $CHCl_3$ at 273 K, the absorption spectrum changed with isosbestic points at 422, 510, and 587 nm upon the addition of DPA (0–5 equiv) and underwent secondary spectral changes with isosbectic points at 424, 511, and 590 nm (Figure 4b; see also Figure S11). A plot of ΔAbs at 580 nm shows an inflection point at about 4–5 equivalents of DPA (Figure 4c, black circles). These results indicate the 1:5 association of **ZP$_{10}$** and DPA. A similar inflection point was observed for the complexation of **ZP$_6$** and DPA at approximately 3 equivalents of DPA (Figure 4c, purple circles; see also Figure S12). As a reference experiment, in the titration of **ZP$_{10}$** with pyridine, the Soret band and Q-bands were similarly redshifted upon the addition of an excess amount of DPA (see Figure S13), but the ΔAbs titration curve showed no inflection point (Figure 4c, orange squares). These results, when considered with those of the ^{1}H NMR spectroscopic study, suggest that the initial absorption change may originate from the formation of the ladder complex, and that the later change observed, after the inflection point, is due to the dissociation of the ladder into the monomer complexes (Scheme 2).

Figure S7). In going from **ZP$_2$** to **ZP$_4$** and **ZP$_6$**, the signals for the inner DPA hydrogen atoms were observed at progressively lower chemical shifts. This trend may be ascribed to increased structural rigidity of the ladder complex as the number of the coordinating sites increases. Interestingly, similar ladder-type assemblies were indicated by ^{1}H NMR spectra of a 1:4 mixture of **ZP$_8$** with DPA (see Figure S8) and a 1:5 mixture of **ZP$_{10}$** with DPA (Figure 2e), although these spectra were rather broad. The thermal stability of the complexes increased as the number of porphyrins in the array increased, as indicated by the observation that the ^{1}H NMR

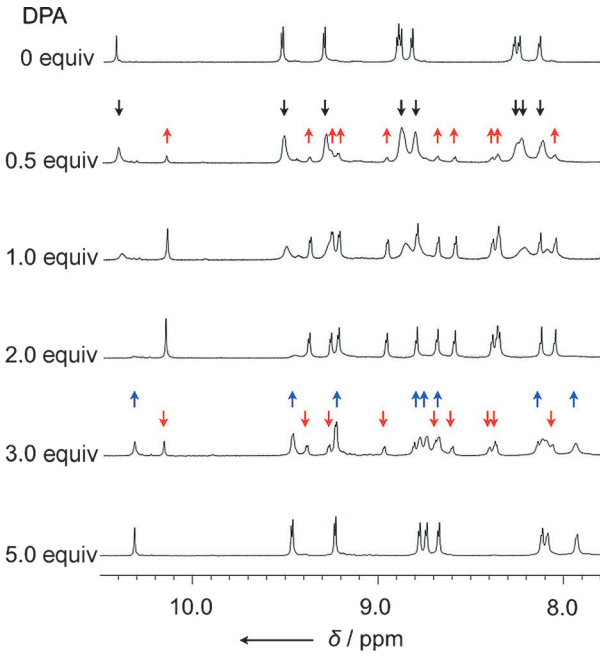


Figure 3. Changes in the ^{1}H NMR spectrum (500 MHz) of $\mathbf{ZP_4}$ upon titration with DPA in $CDCl_3$ at 273 K. $[\mathbf{ZP_4}] = 1.8\times10^{-3}$ M.

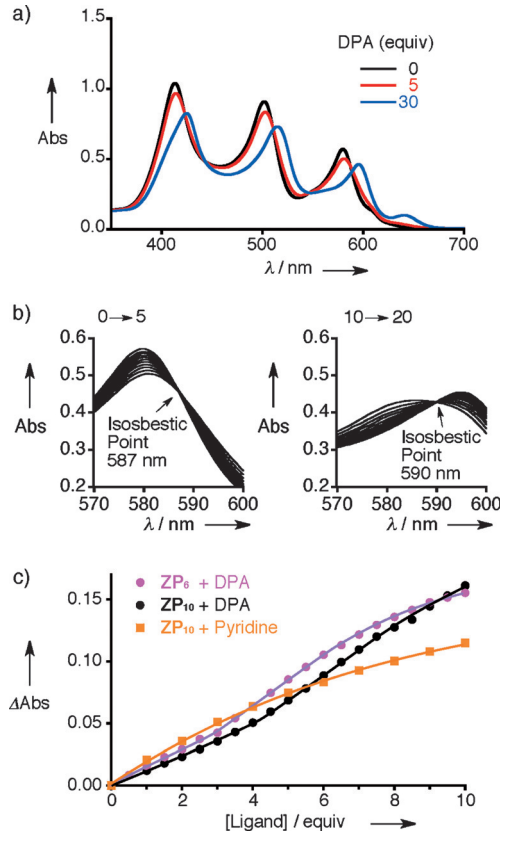


Figure 4. a) Changes in the absorption spectrum of $\mathbf{ZP_{10}}$ upon mixing with DPA (5 and 30 equiv). b) Isosbestic points observed upon the titration of $\mathbf{ZP_{10}}$ with DPA. Left: [DPA]/[$\mathbf{ZP_{10}}$] = 0–5; right: [DPA]/[$\mathbf{ZP_{10}}$] = 10–20. c) Plots of the absorption changes (ΔAbs) of $\mathbf{ZP_{10}}$ and $\mathbf{ZP_6}$ at 580 and 574 nm, respectively, upon titration with DPA or pyridine in $CHCl_3$ at 273 K. [$\mathbf{ZP_{10}}$] = 1.1×10^{-6} M, [$\mathbf{ZP_6}$] = 1.7×10^{-6} M.

It is known that cross-linked polymers, synthesized through radical polymerization or colloidal crystal templating methods, provide macroporous materials (pore size > 50 nm), which are utilized as chromatographic separation media, purification systems, adsorption media, and even synthetic media in combinatorial chemistry.[22,23] However, to the best of our knowledge, no example has been reported of the synthesis of macroporous materials from noncovalently assembled polymers. We took advantage of the high solubility of longer $\mathbf{ZP}_n$ in organic solvents and examined the construction of a supramolecular ladder from a polymeric Zn^{II} porphyrin array. By following our previously reported method,[19c] we prepared the polymeric array $\mathbf{ZP}_p$ with a weight-average molecular weight of $M_w = 5.9\times10^4$ g mol^{-1} and $M_w/M_n = 1.93$, which correspond to a 48 mer (see Figure S14). The ^{1}H NMR spectrum of $\mathbf{ZP}_p$ displayed broad peaks at $\delta = 8.95$ and 8.36 ppm and at $\delta = 7.52$ and 6.78 ppm owing to the pyrrolic β hydrogen atoms and aryl hydrogen atoms, respectively, along with small peaks at $\delta = 10.39$ ppm and at $\delta = 9.51$ and 9.29 ppm owing to the meso hydrogen atoms and pyrrolic β hydrogen atoms of the terminal porphyrin units, respectively. When $\mathbf{ZP}_p$ was mixed with DPA (0.5 equiv with respect to the monomer unit) in $CDCl_3$ at 293 K, the signals due to the pyrrolic hydrogen atoms showed broadening and distinct upfield shifts, and those due to the aryl hydrogen atoms and pyridyl hydrogen atoms also became broadened, thus indicating the formation of a similar ladder polymer. Our failure to detect the signals of the meso hydrogen atoms and pyrrolic β hydrogen atoms may be ascribed to heterogeneous assembly owing to the distribution of $\mathbf{ZP}_p$ with different lengths. In contrast, the ^{1}H NMR spectrum of $\mathbf{ZP}_p$ became sharper with the reappearance of signals for the meso hydrogen atoms and pyrrolic β hydrogen atoms of the terminal porphyrin segments at a higher concentration of DPA, most likely as a result of the dissociation of the dimeric ladder polymers into single-stranded polymer arrays (see Figure S15).

The viscosity of a solution of $\mathbf{ZP}_p$ in $CHCl_3$ increased upon the addition of DPA (0.5 equiv per porphyrin unit) at 293 K (Figure 5). Furthermore, the solution became an organogel upon cooling to 273 K. Scanning electron microscopy (SEM) of $\mathbf{ZP}_p$ deposited on a thin carbon film showed fibrous assemblies (Figure 5c), which became a spongelike macroporous structure with rather regular interpore distances of approximately 10 μm in the presence of DPA (Figure 5d). The appearance of the macroporous structure may be accounted for in terms of the formation of heterogeneous assemblies of $\mathbf{ZP}_p$ with different molecular lengths, which leads to mismatching of the arrays and chain branching of the ladder polymers to form three-dimensional network structures. In an interesting experiment, ^{1}H NMR spectroscopy of a 1:2 mixture of $\mathbf{ZP_2}$ and $\mathbf{ZP_4}$ in the presence of DPA (4 equiv) showed distinguishable sets of ^{1}H NMR signals corresponding to $(\mathbf{ZP_2})_2$–$(DPA)_2$ and $(\mathbf{ZP_4})_2$–$(DPA)_4$ (see Figure S16), thus indicating predominant narcissistic self-sorting after thermodynamic equilibrium has been reached.[25] Hence, it may be considered that the size-distributed long $\mathbf{ZP}_p$ arrays assembled upon the addition of DPA in a kinetically controlled manner to form heterogeneous assemblies, which gave rise to three-dimensional networks.

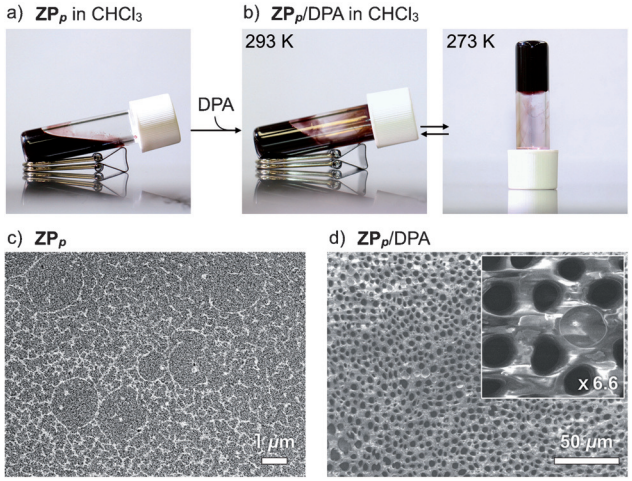


Figure 5. a) Photograph of a solution of **ZP$_p$** in $CHCl_3$. b) Photograph of the solution after the addition of DPA at 293 K and of the organogel formed upon cooling of the sample solution to 273 K. [Monomer unit of **ZP$_p$**] = 1.4×10^{-2} M, [DPA] = 7.2×10^{-3} M. c) Scanning electron micrograph of an air-dried sample of **ZP$_p$**. The sample was prepared from a dilute solution of **ZP$_p$** in $CHCl_3$ and deposited on a specimen grid covered with a thin carbon support film. d) Scanning electron micrograph of a xerogel prepared from a mixture of **ZP$_p$** and DPA in $CHCl_3$.

In summary, meso–meso-linked Zn^{II} porphyrin arrays have been shown to undergo zipperlike dimerization to form discrete porphyrin ladders upon the addition of DPA, despite their orthogonal conformations. Similar assembly of polydiverse **ZP$_p$** led to the formation of a thermoresponsive and a macroporous gel.

Keywords: ladder polymers · macroporous materials · multiporphyrin arrays · supramolecular chemistry · thermoresponsive gels

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