

FOCUS REVIEW

Strapped porphyrin-based polymeric systems

Kazunori Sugiyasu, Soichiro Ogi and Masayuki Takeuchi

Inspired by functional systems in nature, chemists have created a number of intriguing and useful molecular systems from porphyrins and their metal complexes. Of the synthetic porphyrin derivatives developed to date, strapped porphyrins are unique because they have three-dimensional architectures based on a built-in two-dimensional porphyrin molecule. Consequently, the structures of strapped porphyrins can be customized through detailed molecular design, thereby allowing the synthesis of sophisticated molecular systems. Herein, we describe strapped porphyrin-based polymeric systems. In particular, we focus on molecular design concepts that are established in combination with photophysical, electronic and mechanical properties of polymeric materials.

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INTRODUCTION

Porphyrins and their derivatives have important roles in nature and have served as models for chemists to design functional molecular systems. Examples of natural porphyrin-based systems include the photosynthetic reaction center and heme proteins. By mimicking the principles that underpin these systems (that is, by taking a biomimetic approach), various photofunctional systems, catalysts and sensors have been developed. This area of research has witnessed extensive developments,^{1,2} and a complete review of the background is beyond the scope of this paper.

From a molecular design perspective, strapped porphyrins (including those categorized as basket-handle porphyrins) are attractive building blocks because of their unique structures.^{3–5} Strapped porphyrins are reminiscent of the tertiary structure of heme proteins in that the porphyrin molecule (that is, the coenzyme) is encapsulated within a three-dimensional (3D) framework (that is, the apoenzyme) (see Figure 1a). In fact, a number of strapped porphyrin derivatives have been developed in the field of biomimetic chemistry for the purpose of realizing artificial enzymes. These studies have suggested that not only the electronic characteristics of the porphyrins and their metal complexes but also their spatial molecular designs, including the ‘apoenzyme’ framework, are of significance for achieving sophisticated functionalities. For example, the selectivity, reactivity and stability of metalloporphyrin-based catalysts have been significantly improved by designing them such that they possess a 3D architecture, thereby optimizing the cooperative action between the porphyrin molecule and the strap moieties.^{3–5} Considering these successful examples, we envisaged that strapped porphyrins would also have significant applicability in the fields of polymer chemistry and materials science, leading to the synthesis of novel functional materials.

In this review, we focus on strapped porphyrin-based polymeric systems. Before discussing various examples of such systems, it would be helpful to discuss the prototypical strapped porphyrin molecule shown in Figure 1b. The ‘strap’ confers unique structural characteristics to the porphyrin molecule: (1) the front and back sides of the porphyrin plane can be distinguished; (2) the π -surface is shielded, and thus, π – π stacking is prevented; (3) the rotational motion of the *meso*-phenyl groups is fixed, thereby allowing directional functionalization; (4) the cavity formed by the porphyrin molecule and the strap can be used for guest binding; (5) the direction of metal coordination and/or π – π stacking can be defined (it corresponds to the side opposite to the strap moiety); (6) functionalization on the strap is possible; and (7) chirality arises even in the absence of chiral groups if the porphyrin plane is prochiral.^{3–5} The examples that are discussed below have exploited these unique structural features of strapped porphyrins in polymeric systems.

Rowan and co-workers⁶ attempted to extend the concept of artificial enzymes to polymeric systems. They synthesized a strapped manganese(III) porphyrin complex (SP1) through which a polybutadiene strand was threaded; that is to say, they synthesized polyrotaxane (Figure 2a). The structure of this complex is unique in that a catalyst is topologically linked to the substrate, which resembles a biological enzyme such as DNA polymerase. The translational motion of SP1 along the polybutadiene chain accompanies the catalytic oxidation of the double bonds to epoxides, functioning very similar to the biological ‘processive’ enzymes. Swager and co-workers⁷ reported a doubly strapped porphyrin-based thiophene monomer that could be electrochemically polymerized on electrodes (SP2 in Figure 2b). The hydrogen-bonding donors of the amide groups that converge into the cavities were capable of binding fluoride anions, upon which the electrochemical responses, such as conductivity, were

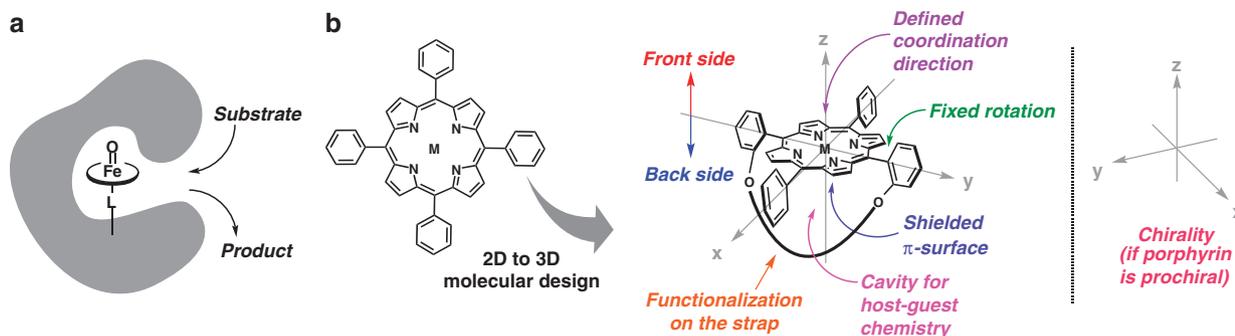


Figure 1 (a) Diagrammatic sketch of a heme enzyme (cytochrome *P450*), which has served as a model for designing an artificial enzyme. (b) Designing a three-dimensional (3D) strapped porphyrin from a two-dimensional (2D) porphyrin molecule. The concept conveys the unique structural features exhibited by the porphyrin molecule.

altered. Accordingly, SP2 was found to function as a highly sensitive fluoride-ion sensor. Weiss and co-workers⁸ synthesized a phenanthroline-strapped porphyrin (SP3) that bore an imidazole anchor at the *meso* position (Figure 2c). The imidazole anchor was strongly bound to the strap through hydrogen bonds and metal–ligand coordination, yielding a supramolecular coordination polymer. Such a porphyrin array could find use in molecular electronics because it allows for both electronic and photonic conduction. Takeuchi *et al.*⁹ reported a strapped porphyrin-based conjugated polymer, SP4, that adopted a helical conformation owing to the angle defined by the strap (Figure 2d). This helical polymer was able to twine around amine-functionalized polymers via metal–ligand coordination. Interestingly, the polymer complex further assembled into a highly ordered structure. This new approach can be expected to lead to the development of anisotropic functional materials. In addition, the same polymer was found to perturb the crystallization process of C_{60} molecules.¹⁰ In the presence of SP4, C_{60} formed microspheres consisting of nanoplates exhibiting face-centered cubic C_{60} crystal packing. It was hypothesized that SP4 weakly interacted with the C_{60} molecules through π – π interactions and influenced their crystallization pathway. This process is analogous to biomineralization—crystal growth in which polymer additives dictate the crystal structures—and might be useful for creating new crystalline organic materials. Osuka and co-workers¹¹ reported doubly strapped and triply linked porphyrin tapes up to dodecamer in structure (the tetramer is shown as SP5 in Figure 2e). Despite the vastness of the π -conjugated systems, intermolecular electronic communication (that is, π – π stacking) was suppressed to some extent. Therefore, SP5 can be expected to serve as an ‘insulated’ molecular wire.¹²

Considering the above-described examples, it can be expected that the 3D architectures of strapped porphyrins can also be exploited to develop advanced polymeric and supramolecular materials. In this focus review, we would like to present an update on some of the strapped porphyrin-based polymeric systems that we have recently developed with a particular focus on the molecular design concepts. The polymeric systems described herein are (1) photofunctional polymers, (2) conducting polymers (CPs) and (3) supramolecular polymers.

STRAPPED PORPHYRIN-BASED PHOTOFUNCTIONAL POLYMERS

The photophysical properties and functions of porphyrin arrays strongly depend on how the porphyrin molecules are arranged with respect to one another within the system, as interpreted based on the exciton coupling theory.¹³ Indeed, the initial photosynthetic systems

found in nature demonstrate how energy and electrons can be transferred directionally and efficiently within well-defined chromophore arrays. To program the molecular arrangements, unique polymer structures, such as dendrimers, cyclic, ladder and helical polymers, can be used as scaffolds. Control over the density, angle and handedness of the porphyrin molecules, as well as the intermolecular distance, achieved along the polymer backbone has led to the realization of functionalities such as light-harvesting ability, efficient energy migration and charge separation, and circularly polarized luminescence. Similarly, the unique 3D architecture of strapped porphyrins could lead to the development of novel photofunctional materials.

We designed doubly strapped porphyrins (SP6¹⁴ and SP7¹⁵ in Figures 3 and 4, respectively) bearing π -conjugated molecules that were hanging on the straps. In these doubly strapped porphyrins, efficient fluorescence resonance energy transfer (FRET) occurs from the π -conjugated molecules (donors) to the porphyrins (acceptors). The donors and acceptors are connected in a conjunction mode that resembles a ‘universal joint’ (Figures 3a and 4a). The uniqueness of this molecular design stems from the fact that the angle between the transition dipoles of the donor and the acceptor has a significant impact on FRET efficiency.¹⁶ For instance, according to FRET theory, an orthogonal alignment excludes the possibility of FRET. Thus, the fluorescence properties of these molecules are synchronized with the molecular orientation that is defined by the universal joint framework. We expect that such molecular design concepts can aid in the development of new polymeric systems that can link molecular-level functionality and human-scale dynamics by taking advantage of the mechanical properties of polymeric materials (for example, their ability to stretch, bend and twist). It should be noteworthy that such mechanoresponsive polymeric systems have attracted much attention recently because they will allow for the exploitation of mechanical forces in synthetic organic chemistry.^{17,18}

The relationship between the FRET efficiency and the angle between the donor and acceptor dipoles was determined from absorption and steady-state fluorescence spectra, as well as from fluorescence lifetime and quantum yield measurements, which were performed on the basis of FRET theory. As shown in Figure 3b, if the polymer main chain is extended from a random conformation, the donor dipoles should be oriented orthogonally to the acceptor dipole, and in principle, the FRET efficiency should decrease to 0.

A polymeric matrix can most likely be used to control the conformation of the polymer SP6. Through preliminary experiments, we confirmed that the photophysical characteristics of SP6 were preserved in the polymer matrix (the polymers used were polystyrene

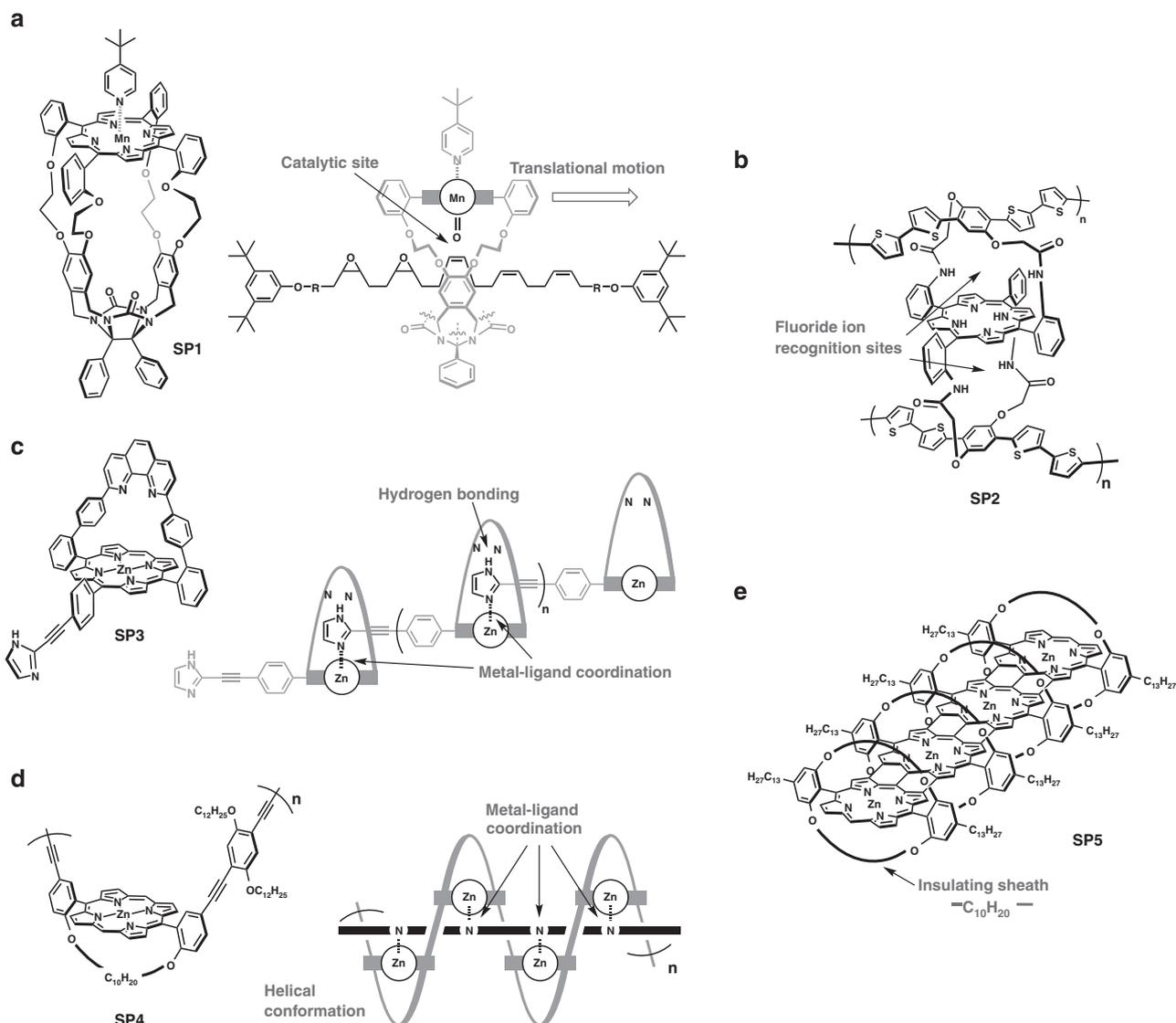


Figure 2 Strapped porphyrin-based polymeric systems reported by (a) Rowan and co-workers⁶ (b) Swager and co-workers⁷ (c) Weiss and co-workers⁸ (d) Takeuchi *et al.*⁹ and Zhang and Takeuchi¹⁰ and (e) Osuka *et al.*¹¹ A full color version of this figure is available at *Polymer Journal* online.

(PS), poly(methyl methacrylate) and polyethylene glycol, among others), and consequently, the composite materials could be processed using the spin-coating and electrospinning methods (Figure 3c). We are exploring methods to control the FRET efficiency of SP6 by applying mechanical perturbations to the polymer composite, and we will report our results in due course.¹⁴ In addition to this approach, we also used an elastomeric material as the polymer matrix for a similar purpose, as discussed below.

SP7 is also based on the universal joint structure, similar to SP6; however, in the case of SP7, two olefin groups are installed at both ends (Figure 4a).¹⁵ Accordingly, SP7 can be incorporated into a polydimethylsiloxane (PDMS) network through a hydrosilylation reaction using Karstedt's catalyst (Figure 4b). The as-obtained PDMS film, in which SP7 was covalently incorporated, was stretchable by approximately 100%. When unstretched, the PDMS film exhibited fluorescence only from the porphyrin molecule. This observation was indicative of quantitative FRET (>99%) from the donor molecules to the porphyrin molecule. Interestingly, the fluorescence from the

quenched donor recovered upon stretching the film (Figure 4c), which suggests that the FRET efficiency was *decreased* by the macroscopic mechanical force. Because the I_D/I_A ratio is a function of the FRET efficiency, we were able to calculate the change in the FRET efficiency (ΔE) induced upon elongation; elongations of 30% and 60% induced ΔE of 5.6% and 13.1%, respectively. A theoretical analysis suggested that the ΔE of SP7 was not because of the change in the donor-acceptor distance but rather because of the change in the relative orientation of the emission transition dipole of the donor with respect to the absorption transition dipole of the acceptor. In fact, the results of anisotropic absorption spectral measurements indicated that the transition dipoles of the donor and the acceptor become orthogonally aligned upon stretching, as expected from the molecular design. We believe that the universal joint structure of doubly strapped porphyrins, when combined with polymeric systems, should result in a unique framework that can translate macroscopic mechanical forces into molecular conformations, thereby allowing for the control over the molecular functionality.

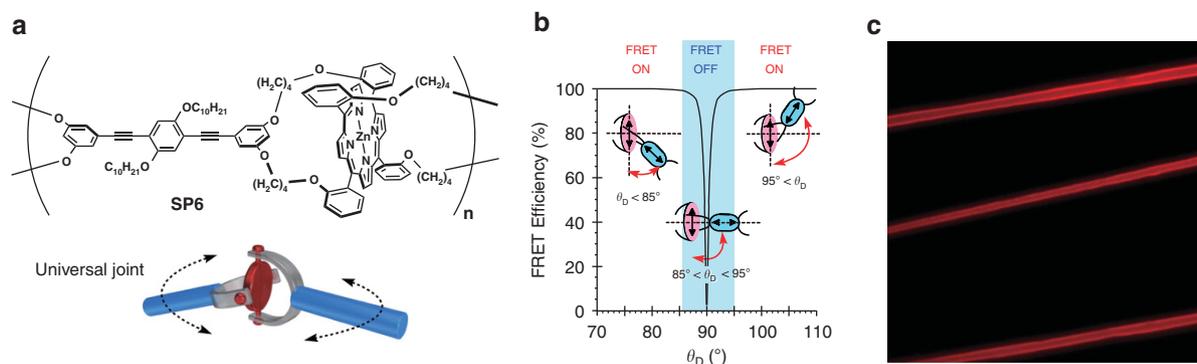


Figure 3 (a) Structure of the strapped porphyrin-based alternating copolymer SP6, whose repeating unit resembles the so-called universal joint (see diagrammatic sketch). (b) Relationship between the fluorescence resonance energy transfer (FRET) efficiency and the angle between the transition dipoles of the oligo(phenylene ethynylene) and porphyrin molecules; the relationship was determined based on the results of photophysical measurements. (c) Electrospun fibers of SP6/polyethylene glycol composites with a diameter of approximately 2.5 μm .

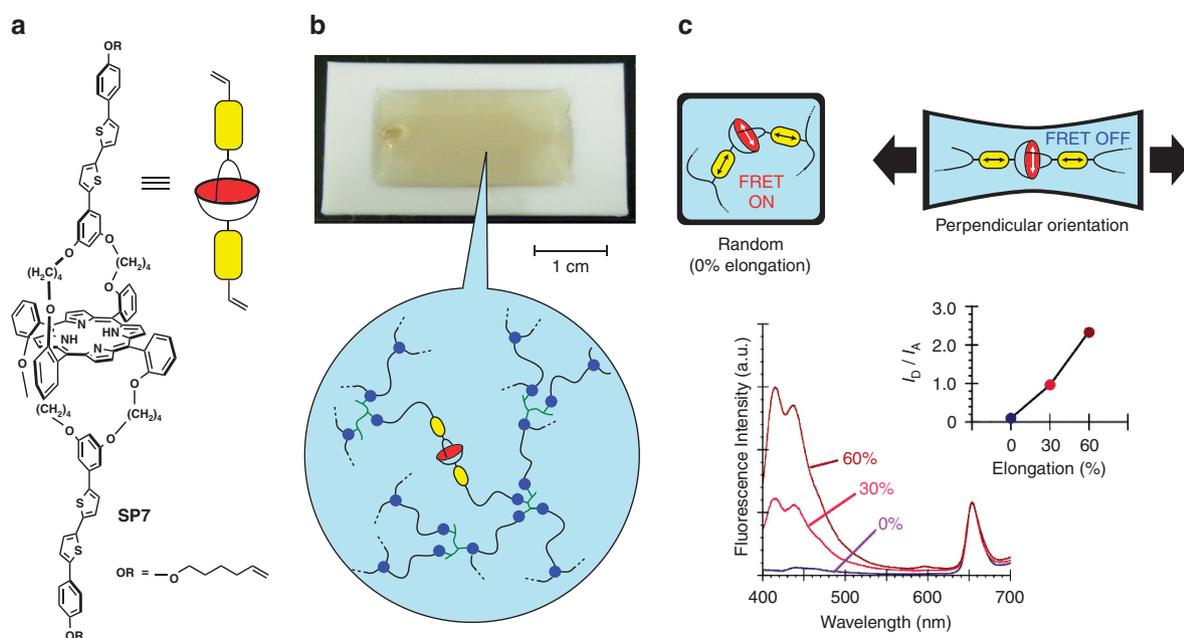


Figure 4 (a) Structure of SP7, which consists of a donor–acceptor pair and olefin termini. (b) Photograph of an elastomeric film in which SP7 crosslinks the polydimethylsiloxane (PDMS) network (see diagrammatic sketch). (c) Fluorescence spectral changes of the PDMS film measured upon stretching of the film.

STRAPPED PORPHYRIN-BASED CONJUGATED POLYMERS

Conjugated polymers (CPs) are promising alternatives to inorganic semiconducting materials for next-generation electronic devices owing to their designability and because of the various advantages originating from their organic nature (that is, their high flexibility, processability and light weight).¹⁹ The functionalization of CPs with photo- and electroactive molecules can lead to advanced materials that can be used in applications such as photovoltaics and sensors. In many instances, this concept has been demonstrated by appending π -conjugated molecules, including porphyrins, onto the backbones of CPs, given the attractive photophysical and redox characteristics of these π -conjugated systems.¹⁹ However, the appended π -conjugated molecules, as well as the CPs themselves, tend to aggregate, which may cause deterioration in the performance of the resulting polymeric systems. To address this issue, we proposed a new molecular design concept, in which porphyrins and CPs are integrated synergistically

with respect to their electronic functions while being spatially arranged such that they do not undergo aggregation.²⁰

SP8 is a doubly strapped porphyrin molecule from which four bithiophene molecules divergently protrude (Figure 5a). The bithiophene arms can be oxidatively coupled through electrochemistry to yield a quaterthiophene backbone (Figure 5b); accordingly, SP8 results in a CP network crosslinked by the doubly strapped porphyrin molecule (Figure 5c). The double straps fix the rotational motion of the *meso*-phenyl groups, which define the direction of the oxidative coupling reaction (see the arrows in Figure 5a). In addition, the double straps encapsulate the porphyrin molecule, preventing it from forming aggregates.

The results of fluorescence spectral measurements using control compounds revealed that efficient FRET occurs from the quaterthiophene moieties to the porphyrin molecule, indicating effective electronic communication between them. In addition, the absorption

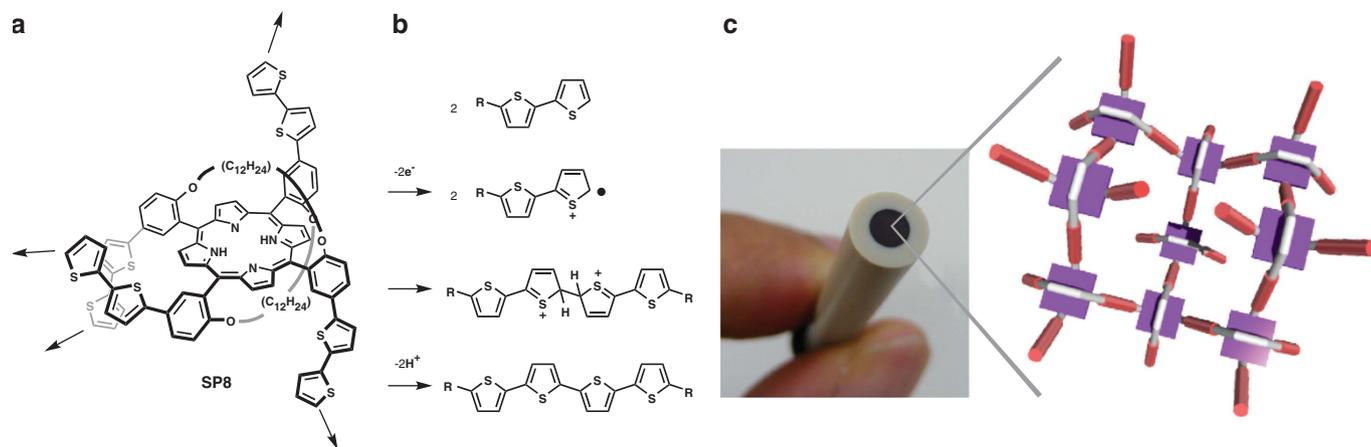


Figure 5 (a) The electrochemically polymerizable doubly strapped porphyrin monomer SP8. (b) Electrochemical oxidative coupling between bithiophenes. (c) Photograph of a polymeric film prepared on a platinum electrode through the electrochemical polymerization of SP8; the diagrammatic sketch shows the plausible structure of the polymeric network.

spectrum of SP8 in its film form was sharper than that of tetraphenylporphyrin (no straps present), which implied that the double strap prevented the porphyrin molecule from forming a π - π stack. These results confirmed the aforementioned molecular design concept. Furthermore, the fluorescence intensity of SP8 in film form was twofold greater than that of the unstrapped porphyrin film. This result indicates that the nonradiative deactivation of the excited state of the porphyrin is suppressed owing to the ‘encapsulation’ by the double strap. We can therefore assert that polymeric SP8 is a light-harvesting system that should allow for efficient utilization of the harvested energy. We believe that such a CP material based on the detailed molecular design would find use in various photoelectronic applications, including in photovoltaics and as a photocatalyst.

STRAPPED PORPHYRIN-BASED SUPRAMOLECULAR POLYMERS

Supramolecular polymers are a new type of polymer in which the monomeric units are brought together by reversible and highly directional non-covalent interactions, such as hydrogen bonding, coordination bonding and π - π stacking. Therefore, supramolecular polymers are endowed with novel functionalities and properties that originate from their dynamic behavior and highly ordered molecular organization.^{21–23} One-dimensional stacking arrays of π -conjugated molecules should find widespread application in material science and nanotechnology because of their unique photophysical and electronic properties. However, compared with conventional covalent polymer chemistry, the supramolecular polymer chemistry of complex polymeric structures, such as ring and brush polymers, block copolymers and dendrimers, is in its infancy. We hypothesized that structures consisting of strapped porphyrins would be useful for controlling the π - π interactions—one of the typical driving forces for supramolecular polymerizations—and for synthesizing advanced supramolecular polymers. For instance, a one-face-strapped porphyrin could ‘terminate’ π - π staking, which could allow for the end-capping and end-functionalization of supramolecular polymers.²⁴

Based on this molecular design concept, we synthesized the porphyrin derivatives P9 and SP9, which have hydrogen-bonding amide groups and long alkyl chains (Figure 6a).²⁵ P9 can form one-dimensional supramolecular polymers in organic solvents through hydrogen bonding and π - π stacking; this has been confirmed by Fourier transform infrared spectroscopy and absorption spectroscopic

methods, and atomic force microscopy images. With an increase in the concentration of P9, the solution became highly viscous and eventually gelatinized (Figures 6b–d). SP9 has a similar structure, with one of the porphyrin surfaces shielded by the strapped structure. Interestingly, the addition of only 0.2 mol% of SP9 significantly decreased the viscosity of the P9 solution (Figure 6e). We hypothesize that SP9 end-caps the supramolecular polymer of P9. If this is indeed the case, end-functionalization of the supramolecular polymers should be possible. We thus synthesized SP9-PS, in which a PS chain hangs on the strap of SP9. This molecular design is expected to lead to an ensemble of conventional and supramolecular polymers with the following structure: PS-*block*-(porphyrin supramolecular polymer)-*block*-PS. When a *p*-xylene solution of P9 was slowly evaporated on a substrate, an assembly of heavily bundled supramolecular polymers was obtained. This was also the case when the sample was prepared in the presence of PS (Figure 7a). Interestingly, in contrast, the addition of SP9-PS to the supramolecular polymer of P9 resulted in a completely different homogenous morphology (Figure 7b). We infer from these observations that the covalent and supramolecular polymer blocks undergo microphase separation, thereby preventing the porphyrin supramolecular polymers from bundling into thick fibers. Given the extensive developments in conventional block copolymer chemistry²⁶ and in supramolecular polymer chemistry,^{21–23} supramolecular polymer-based block copolymers would find widespread applications due to the synergy of the two distinct blocks. We expect that such a molecular design concept based on strapped porphyrins can lead to unprecedented supramolecular/macromolecular hybrids. Along this line, controlling the supramolecular polymerization pathways is equally crucial in designing complex supramolecular polymer structures. We have recently realized living supramolecular polymerization for the first time,²⁵ and we believe that the combination of the sophisticated molecular designs and polymerization protocols will further advance supramolecular polymer chemistry.

CONCLUSION

In this focus review, we updated strapped porphyrin-based polymeric systems that we have recently developed. Strapped porphyrin derivatives have a long history in biomimetic chemistry, and their unique structure–function relationships have been demonstrated through a number of examples.^{3–5} It would appear that the strapped porphyrins

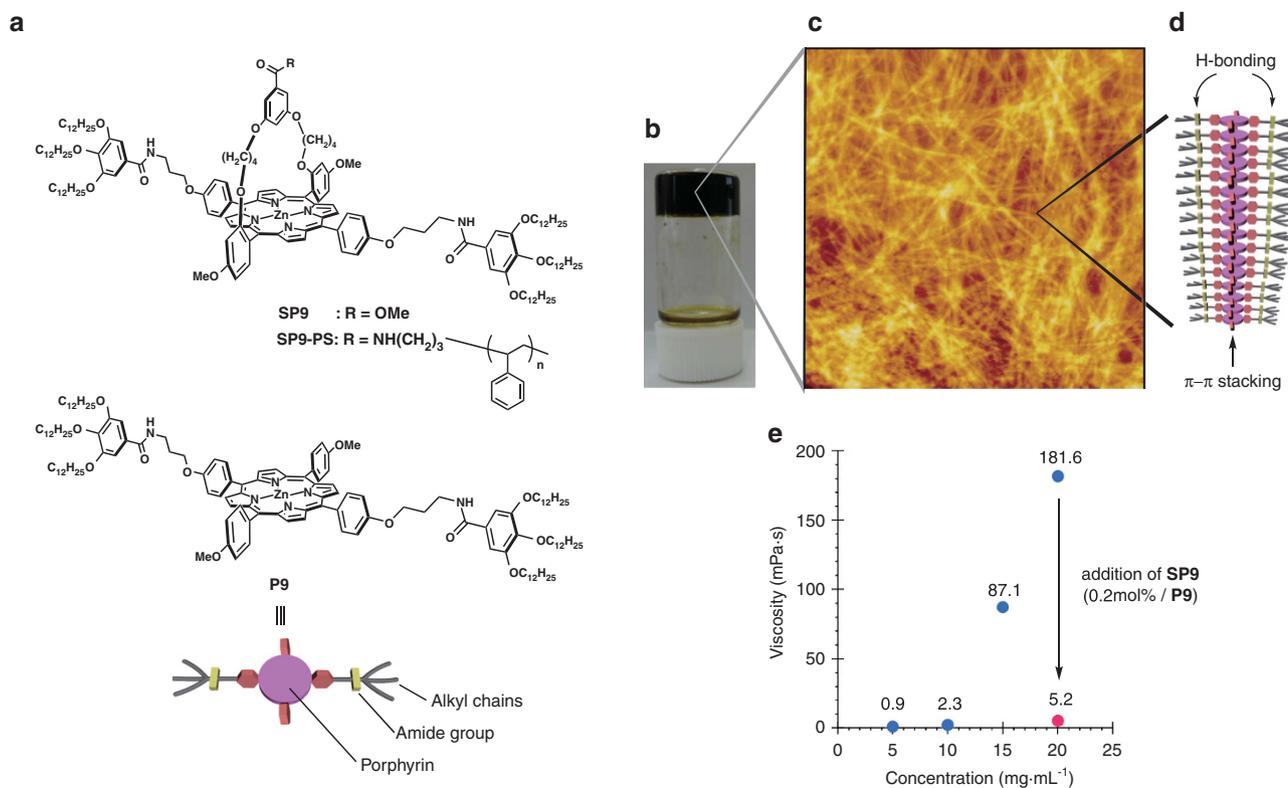


Figure 6 (a) Structures of SP9, SP9-PS and P9. (b) Photograph and (c) atomic force microscopy (AFM) image ($10\ \mu\text{m} \times 10\ \mu\text{m}$) of an organogel of P9. (d) Diagrammatic sketch of a supramolecular polymer of P9. (e) Change in the viscosity of a solution of P9 as a function of concentration; the viscosity markedly decreased with the addition of SP9. The results shown here were obtained using methylcyclohexane.

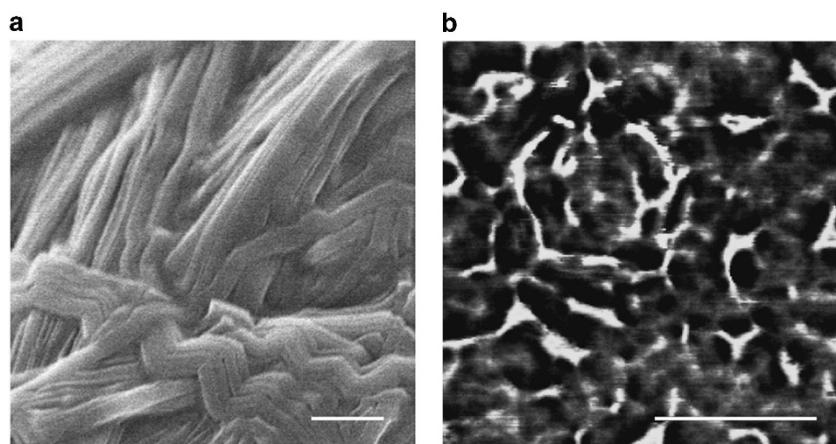


Figure 7 (a) Scanning electron microscope (SEM) image of P9 with PS (scale bar = $1\ \mu\text{m}$) and (b) atomic force microscopy (AFM) image of P9 with SP9-PS (scale bar = $200\ \text{nm}$) assembled from a *p*-xylene solution on silicon substrates under the slow evaporation of the solvent. A full color version of this figure is available at *Polymer Journal* online.

should also find use in polymer chemistry and material science because 3D molecular design on the basis of a built-in two-dimensional porphyrin molecule allows for the synthesis of sophisticated molecular systems. Taking the blueprint shown in Figure 1b as a starting point and keeping the unique structures and properties of polymeric materials in mind, it should be possible to develop a number of similar functional polymeric systems. (A similar molecular design concept can also be applied not only to the porphyrin molecules but also to other materials such as π -conjugated

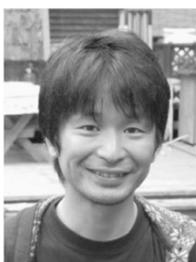
polymers. Relevant examples published from our group are cited in refs 27–33.)

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Dr Kazunori Sugiyasu was born in Kagoshima in 1977. He earned his BS degree in 2000 and PhD degree in 2005 from Kyushu University under the supervision of Professor Seiji Shinkai. He then moved to MIT to work with Professor Timothy M Swager (April 2005 to June 2007). He is currently a senior researcher in Organic Materials Group, National Institute for Materials Science. He is also an Associate Professor of Kyushu University since 2013.



Dr Soichiro Ogi was born in Fukuoka in 1984. He earned his MSc degree in 2008 from Kyushu University under the supervision of Professor Seiji Shinkai. In 2011, he earned his PhD degree from the University of Tsukuba under the supervision of Professor Masayuki Takeuchi. He then worked as a postdoctoral fellow in Organic Materials Group, National Institute for Materials Science (April 2011 to December 2013). In 2014, he moved to the University of Würzburg to work with Professor Frank Würthner.



Dr Masayuki Takeuchi was born in Kyoto in 1966. He earned his BS degree in 1990 and PhD degree in 1994 from Doshisha University under the supervision of Professor Koji Kano. In 1994, he was appointed as an Assistant Professor in the laboratory of Professor Seiji Shinkai, Kyushu University. In 2007, he moved to National Institute for Materials Science as a Group Leader.