

# On the influence of porphyrin $\pi$ – $\pi$ stacking on supramolecular chirality created in the porphyrin-based twisted tape structure†

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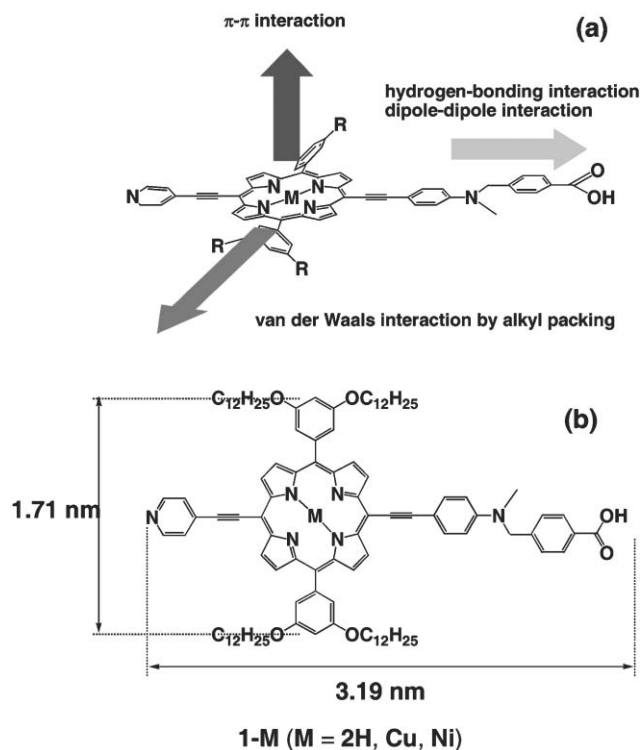
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Achiral porphyrin derivatives **1-M** form twisted supramolecular assemblies and the pitch of the twisted tape structure can be altered by changing the central metal.

Exploring a general principle to control the morphology and the electronic state of  $\pi$ -conjugated molecule-based assemblies has been the most important research target in supramolecular chemistry, which leads to the creation of various functional materials with optimized  $\pi$ -electronic properties.<sup>1</sup> The major driving force operating in these supramolecular assemblies is considered to be a  $\pi$ – $\pi$  stacking interaction inherent to their  $\pi$ -conjugated skeletons. One approach towards exploring this interaction is with various supramolecular architectures constructed in organogels and this has attracted widespread attention from supramolecular chemists.<sup>2</sup> The origin of organogel formation is considered to be a one-dimensional alignment of gelator molecules supported by  $\pi$ – $\pi$  stacking interactions, van der Waals interactions, and/or hydrogen-bonding interactions. In particular, the attractive helical superstructures are frequently observable therein, which are considered to appear as a result of mutual competition of several different forces. However, the details of this ‘mutual competition’ are scarcely interpreted so far and in most cases, the helical superstructures have been obtained by accident. To obtain systematic insights into the creation of these helical superstructures, we designed a porphyrin-based gelator<sup>3</sup> bearing three orthogonal interaction axes<sup>4–6</sup> consisting of peripheral hydrogen-bond donating/accepting groups, four alkoxy groups and porphyrin–porphyrin  $\pi$ – $\pi$  stacking planes (Fig. 1A), in which the morphology can be controlled by a subtle change in the relative forces among the three different interactions. For example, we previously found that a 2D sheet-like superstructure created in cyclohexane is transformed into a 1D fibrous superstructure in *t*-butanol; this change was reasonably explained in terms of the weakened hydrogen-bonding interaction.<sup>3</sup> In the course of this study, it occurred to us that selective perturbation of the porphyrin–porphyrin  $\pi$ – $\pi$  stacking axis can be achieved by metallation, which would induce a new morphological change in the 1D fibrous superstructure in *t*-butanol. Herein, we report our new intriguing finding that achiral porphyrin derivatives **1-M** (Fig. 1) self-assemble into a twisted tape structure<sup>7</sup> and the pitch of the twisted tape structure can be altered by a change in the strength



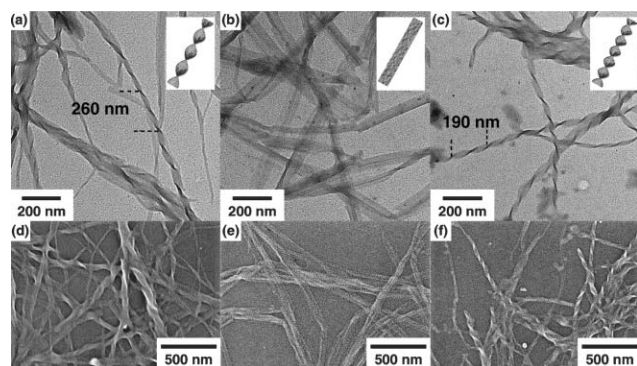
**Fig. 1** (a) Molecular design of **1-M** and (b) molecular size of **1-M** (*M* = 2H, Cu, Ni) estimated from computational energy-minimization (Insight II, Discover-3).

of the porphyrin–porphyrin  $\pi$ – $\pi$  stacking interaction between molecules of **1-M**.

**1-M** (0.01 wt%) was mixed in a capped tube with *t*-butanol, and the mixture was heated until **1-M** was dissolved. When the sample was cooled in air to room temperature, **1-M** formed a suspension in *t*-butanol.<sup>8</sup> The assemblies of **1-M** were first observed with a transmission electron microscope (TEM) and a scanning electron microscope (SEM). In *t*-butanol, the hydrogen-bonding interaction should be weakened, which facilitates the production of a fibrous structure.<sup>3</sup> Fig. 2 shows TEM and SEM images for the precipitates obtained from suspensions of **1-2H**, **1-Cu** and **1-Ni**. It is clearly seen from these TEM and SEM images that well-developed supramolecular tapes several micrometers in length and 20–50 nm in width have been created. Interestingly, achiral molecules, **1-2H** and **1-Ni**, formed a twisted tape structure, whereas **1-Cu** formed a flat tape structure. From the SEM images for **1-2H** and **1-Ni**, the ratio of left-handed to right-handed twists was estimated to be 1 : 1. Using the TEM images of the twisted

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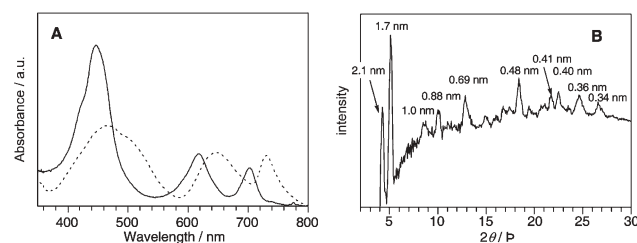
† Electronic supplementary information (ESI) available: experimental section. See DOI: 10.1039/b512128k



**Fig. 2** TEM images without staining of (a) **1-2H** (0.01 wt%), (b) **1-Cu** (0.01 wt%), and (c) **1-Ni** (0.01 wt%), and SEM images of (d) **1-2H** (0.01 wt%), (e) **1-Cu** (0.01 wt%), and (f) **1-Ni** (0.01 wt%) prepared from *t*-butanol.

tape structures we were able to measure the pitch length of the tape. The averaged pitch lengths for **1-2H** and **1-Ni** were evaluated to be 260 nm (from 212 samples) and 190 nm (from 338 samples), respectively.

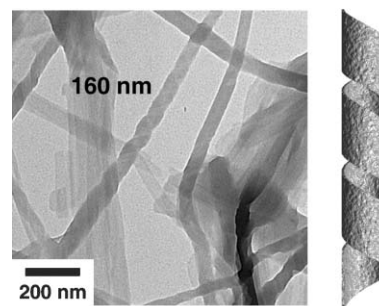
The stacking mode of supramolecular assemblies of **1-M** was further examined by UV-Vis spectroscopy and X-ray diffraction (XRD). As shown in Fig. 3A, the Soret band (463.0 and 508.5 (sh) nm) and the Q bands (649.0 and 731.0 nm) of the supramolecular assembly of **1-2H** were significantly broadened and shifted to longer wavelengths in comparison with those in the dilute THF solution (422.5 (sh) and 448.0 nm for the Soret band and 619.0 and 702.5 nm for the Q bands), indicating J-aggregate formation in the supramolecular assembly.<sup>6b,9</sup> Absorption spectra of **1-Cu** and **1-Ni** in the aggregate state showed similar bathochromic shifts of 30–50 nm in the Soret band and the Q bands (Fig. S1). As we proposed in our recent paper,<sup>3</sup> the long axis of the porphyrin tends to stack with a significant porphyrin skeleton slip, because the long axis is constructed from electron push–pull-type substituents with hydrogen-bonding ability. The suspended solids prepared from *t*-butanol of **1-2H**, **1-Cu** and **1-Ni** gave XRD peaks at  $2\theta$  ( $d = 4.7^\circ$  (2.1 nm),  $5.5^\circ$  (1.8 nm), and  $5.3^\circ$  (1.9 nm), respectively (Figs. 3B and S2) along with their 1/2 and 1/3 peaks. Judging from the results of molecular modeling in Fig. 1 and our recent results,<sup>3</sup> the diffraction peaks at  $d = 1.8$ –2.1 nm of **1-M** would be ascribed to the periodical distance of alkyl groups packed



**Fig. 3** (A) UV-Vis spectra of **1-2H** ( $1.0 \times 10^{-6}$  M) in THF (solid line) and assembly of **1-2H** (1.00 wt%) prepared from *t*-butanol (dotted line) at 25 °C. The concentration of **1-2H** in the aggregate state was so high that the spectra could not be obtained using a conventional optical cell. Thus, the spectra were measured with a wet precipitate sandwiched by two quartz glass plates. (B) XRD pattern of the freeze-dried suspended solid of **1-2H** (1.00 wt%) prepared from *t*-butanol.

along the 3,5-didodecyloxyphenyl axis. These findings clearly support the view that **1-Ms** are self-organized into the supramolecular tape structure and contain a similar stacking mode to that observed previously. Thus, the difference in the pitch length in the twisted tape (**1-Cu** > **1-2H** > **1-Ni**) should stem from a change along the  $\pi$ - $\pi$  stacking interaction axis but neither by the hydrogen-bond axis nor the alkyl packing axis; that is, the apparent difference in the pitch length could be rationalized by the difference in the planarity of the porphyrin ring in **1-M**. In the case of free base porphyrins like **1-2H**, a porphyrin ring is usually planar but flexible because of the lack of the central metal ion, so that it can adopt several different conformations. On the other hand, Cu(II) porphyrin complexes are rigid and have the highest planarity and can make the supramolecular tape flat.<sup>10</sup> Ni(II) porphyrin complexes are also rigid but have the lowest planarity and usually adopt a ruffled conformation,<sup>11</sup> a curved tape structure can result in the self-assembly state. From the results of molecular modeling (Fig. S3), it is noteworthy to mention that the two aromatic rings connected by an *N*-methylaminomethyl group in the *N*-(4-carboxyphenylmethyl)-*N'*-methylaniline moiety cannot become coplanar owing to the *N*-methyl substituent. We infer, therefore, that this non-planarity acts as a chiral center to twist the tape structure either into the right handedness or into the left handedness, as seen in the chiral mesophase created from achiral phenyl benzoate derivatives.<sup>12</sup> As a result, **1-2H** and **1-Ni** can form a twisted tape structure and the less planar **1-Ni** has a pitch length shorter than **1-2H**, whereas the stronger  $\pi$ - $\pi$  stacking interaction between **1-Cu** offsets the twisting motif generated by the *N*-methylaminomethyl group.<sup>10</sup>

The fact that **1-Ms** are assembled according to a similar packing mode suggests that different **1-M** molecules would be compatible with each other to form amalgamated supramolecular assemblies. **1-Cu** that tends to adopt a flat tape structure, and **1-Ni** that tends to adopt a helical tape structure with short pitch length, were mixed in different ratios in a capped tube with *t*-butanol, and the mixtures were heated until dissolved. After cooling to room temperature, the resultant supramolecular structures obtained as precipitates were monitored by TEM. **1-Cu** and **1-Ni** do not undergo a lateral phase separation into the different tapes when mixed in a 1 : 1 proportion. Instead, they mix homogeneously to form a helical ribbon structure rather than a twisted tape structure (Fig. 4).<sup>13,14</sup> Interestingly, the pitch length becomes longer with the increase in the ratio of **1-Cu**/**1-Ni**: 130 nm for 3/7, 160 nm for 5/5 and 220 nm for 7/3. In general, it is very difficult to ‘control’ the helical pitch length in supramolecular assemblies. One of the rare



**Fig. 4** TEM image (without staining) of a mixture of **1-Cu** (0.01 wt%) and **1-Ni** (0.01 wt%) prepared from *t*-butanol.

successful examples is a cationic 'gemini' surfactant bearing tartrates as counteranions reported by a French group: therein, the helical pitch length can be controlled by the optical purity of D/L-tartrates.<sup>14</sup> The present results indicate that in the porphyrin-based assemblies, it can be also controlled by the strength of the porphyrin–porphyrin  $\pi$ – $\pi$  stacking interaction.

In summary, we have demonstrated that achiral porphyrin derivatives **1-Ms** form twisted supramolecular assemblies and the helical pitch is controllable by changing the strength of porphyrin–porphyrin  $\pi$ – $\pi$  stacking by the central metal. So far, it has been difficult to control the helical pitch in the chirally-twisted tape structure of supramolecular assemblies from an achiral molecule because they formed accidentally and therefore it is not clear what kind of factor influences the pitch of the twisted tape structure. In this system, one can readily modulate the pitch and the morphologies by the metallation that selectively influences the conformational freedom of the porphyrin rings. We believe, therefore, that the creation of novel  $\pi$ -conjugated molecule-based aggregates is possible by 'mutual competition' of different forces such as  $\pi$ – $\pi$  stacking interactions, hydrogen-bonding interactions, van der Waals interactions and so forth, when they are introduced into the orthogonal axial directions.

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