Supramolecular Chemistry

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Planar or Perpendicular? Conformational Preferences of π-Conjugated Metalloporphyrin Dimers and Trimers in Supramolecular Tubular Arrays**

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Conformational aspects of π-conjugated molecules are important not only for the basic understanding of their electronic properties but also for their practical application in molecular electronics and photonics.[1–3] The absorption and fluorescence properties of porphyrin pigments are highly sensitive to their π-electronic structures and so π-conjugated multiporphyrin arrays have been studied extensively.[4–10] Another advantage of π-conjugated multiporphyrin arrays is the possibility of controlling their conformation through supramolecular chemistry.[11–13] Studies on the conformational aspects of monoalkynylene-bridged bisporphyrins have suggested that these compounds, despite their rotational freedom around the triple bond, prefer to adopt a planar conformation since planar conformers are enthalpically more favorable than perpendicular conformers as a consequence of the extension of the π conjugation.[8] We have reported that the zinc complex of a monoalkynylene-bridged bisporphyrin with *meso*-pyridyl functionalities **2(≡)$_1$** forms a box-shaped cyclic tetramer, in which the dyad incorporated into the supramolecular box exclusively adopts the planar conformation **2(≡)$_1$//** (Figure 1).[13] Although bisporphyrins with a dialkynylene bridge have a much higher rotational freedom than the monoalkynylene-bridged versions, theory still suggests an energetic bias toward the planar conformation.[9] Anderson and co-workers have succeeded in fixing a dialkynylene-bridged zinc porphyrin oligomer in the planar conformation during the bipyridine-mediated formation of a supramolecular ladder.[11] In the present study we investigated cyclotetramerization[13–17] of zinc complex **2(≡)$_2$**, a dialkynylene-bridged analogue of **2(≡)$_1$**.[18] As with **2(≡)$_1$**, cyclotetramerization of **2(≡)$_2$** can possibly form two isomeric supramolecular boxes **[2(≡)$_2$//]$_4$** and **[2(≡)$_2$ ⊥]$_4$**, where **[2(≡)$_2$//]$_4$** consists

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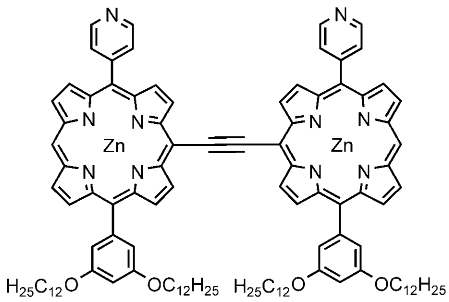
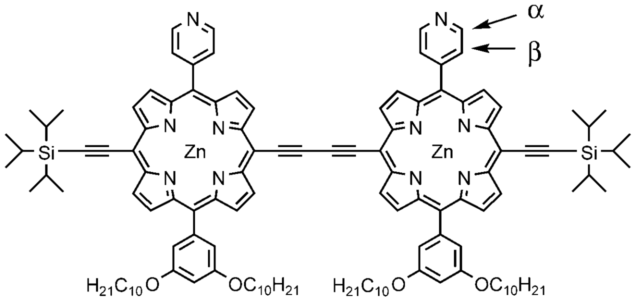
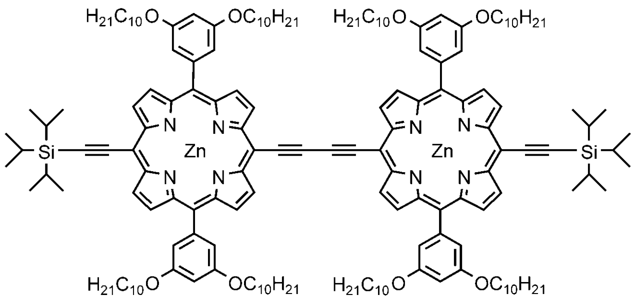


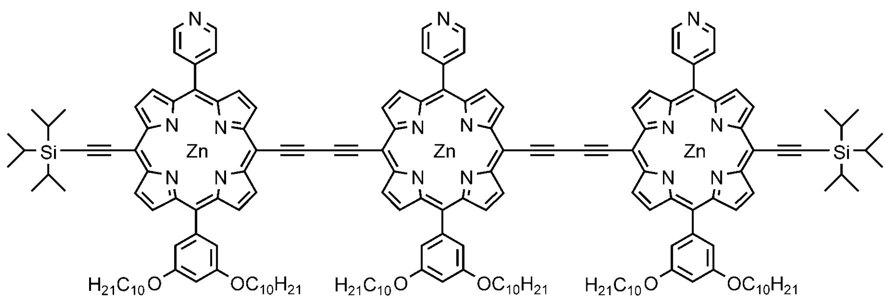
2(≡)₁



2(≡)₂



ref-**2(≡)₂**



3(≡)₂

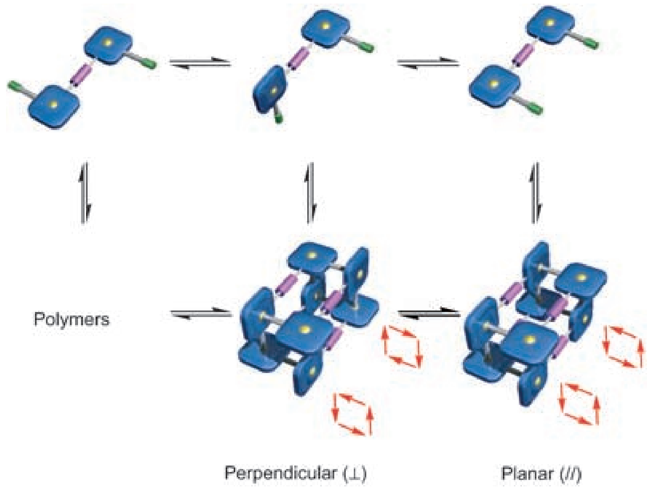


Figure 1. Schematic representation of the cyclotetramerization of alkynylene-bridged zinc pyridylporphyrin dimers. Pink cylinders represent either mono- or dialkynylene units. Red arrows indicate the direction of the Py→Zn coordination.

of the planar conformer of **2(≡)₂** (**2(≡)₂//**), while **[2(≡)₂ ⊥]₄** is composed of the perpendicular conformer (**2(≡)₂** ⊥; Figure 1). To our surprise, detailed spectroscopic studies indicated that **2(≡)₂** ⊥ is favored over **2(≡)₂//** in the resulting supramolecular tubular array.

Compound **2(≡)₂** was prepared by treatment of the zinc complex of [5-(4-pyridyl)-10,20-bis(triisopropylsilylethynyl)-15-(3,5-didecyloxyphenyl)porphyrin (**1**) with 0.5 equivalents of tetrabutylammonium fluoride (TBAF), followed by Glaser–Hay coupling of the resulting mixture of derivatives in which the silyl group had been cleaved.[19] Demetalation under acidic conditions and subsequent preparative size-exclusion chromatography (SEC) allowed isolation of the free-base forms of **2(≡)₂** and **3(≡)₂** in 17 and 2 % yields, respectively. Analytical SEC of zinc complex **2(≡)₂** with $CHCl_3$ as the eluent displayed a sharp elution peak with a shorter retention time (49.6 min) than that of a non-assembling reference compound without pyridyl groups (ref-**2(≡)₂**, 54.8 min).[19] Since the elution time of this chromatographic peak is shorter than that of the cyclic tetramer of the monoalkynylene-bridged analogue (**[2(≡)₁]₄**, 50.8 min) under identical SEC conditions, **2(≡)₂** most likely forms a cyclic oligomer with a larger hydrodynamic volume than **[2(≡)₁]₄** (Figure 1).[13]

^{1}H NMR spectroscopic analysis of **2(≡)₂** in $CDCl_3$ at 20 °C provided two sets of characteristic signals corresponding to the porphyrin and pyridyl protons (Figure 2a). By analogy to the spectral patterns[19] of other box-shaped cyclic tetramers so far reported,[13,14] it is most likely that these two sets are both attributed to cyclotetrameric **[2(≡)₂]₄** (Figure 1). The most characteristic resonances are eight doublets a–d and e–h observed at $\delta = 2.4$–3.0 and 6.2–6.4 ppm, respectively. Addition of [D₅]pyridine (5 %), a competitive ligand for the Zn-N coordination, to the system resulted in these characteristic signals disappearing completely, while new doublet signals appeared in the downfield region of $\delta = 8.05$ and 8.86 ppm. These new signals are

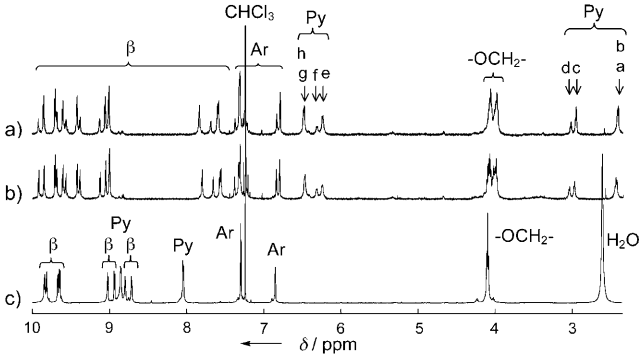


Figure 2. ^{1}H NMR spectra (500 MHz) of $\mathbf{2(\equiv)_2}$ at a) 20 °C, b) 50 °C in $CDCl_3$, and c) 20 °C in $CDCl_3$/[D_5]pyridine (0.95/0.05). β: β-Pyrrole, Ar: aryl, Py: pyridyl.

assigned to the *ortho* and *meta* protons of the pyridyl groups (Py), respectively, of non-associated $\mathbf{2(\equiv)_2}$ on the basis of the ^{1}H NMR spectral profile of the free-base form of $\mathbf{2(\equiv)_2}$ (δ = 8.10 and 9.01 ppm, respectively). Therefore, upfield-shifted signals a–d and e–h can be assigned to the Py groups of $\mathbf{2(\equiv)_2}$ coordinating to the metal centers. We have reported that the reference tetrameric complex $\mathbf{[2(\equiv)_1]_4}$, which bears inner and outer Py protons as a result of its cyclic structure (Figure 1), shows a set of four upfield-shifted Py signals.[13] Together with the 2D {^{1}H-^{1}H} COSY spectrum of $\mathbf{2(\equiv)_2}$,[19] the two sets of such unique multiple Py signals in Figure 2 can reasonably be assigned to cyclotetrameric $\mathbf{[2(\equiv)_2]_4}$, provided that it is a mixture of two stereoisomers, namely, $\mathbf{[2(\equiv)_2\perp]_4}$ and $\mathbf{[2(\equiv)_2/\!/]_4}$ which consist of the perpendicular and planar conformers of $\mathbf{2(\equiv)_2}$, respectively (Figure 1). The ratio of the integrals of signals c and d, for example, indicates that the two stereoisomers exist in a ratio of 3:1 at 20 °C. We also found that the isomer ratio is temperature-dependent: raising the temperature from 20 to 50 °C results in the isomer ratio changing to 3:2 (Figure 2b).

Correlation of the ^{1}H NMR spectral profile of $\mathbf{2(\equiv)_2}$ with its absorption and emission spectral features allows the determination of which tetrameric stereoisomer is predominant in the self-assembly of $\mathbf{2(\equiv)_2}$ (Figure 3). A solution of $\mathbf{[2(\equiv)_2]_4}$ in $CHCl_3$ at 20 °C displayed Soret and Q-bands at 454 (A_I) and 657 nm (A_{III}), respectively. A pair of red-shifted minor bands were also observed at 490 (A_{II}) and 721 nm (A_{IV}). Photoexcitation of $\mathbf{[2(\equiv)_2]_4}$ at 450 nm (A_I) resulted in the appearance of a major fluorescence band at 663 nm (F_I), together with a minor emission at 735 nm (F_{II}; Figure 3b, black solid curve). However, photoexcitation at 500 nm (A_{II}) resulted in a notable enhancement of the minor emission F_{II} (Figure 3b, gray solid curve). A major band was observed at 454 nm (E_I) in the Soret-band region of the excitation spectrum monitored at 660 nm (F_I; Figure 3c, solid curve). Monitoring the fluorescence at 760 nm (F_{II}) provided an excitation spectrum with a split band at 464/494 nm (E_I/E_{II}) in the Soret-band region, along with two low-energy bands at 664 (E_{III}) and 720 nm (E_{IV}) in the Q-band region (Figure 3c, dashed curve). It is clear that the absorption profile of $\mathbf{[2(\equiv)_2]_4}$ (Figure 3a) can be represented by the summation of these two excitation spectra. Band-gap theory for π-conju-

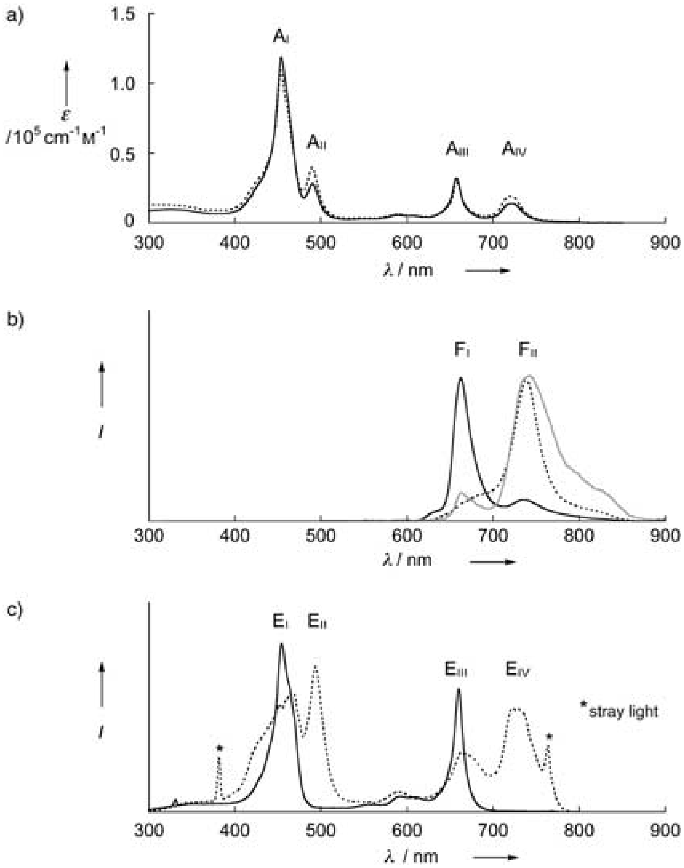


Figure 3. a) Absorption spectra of $\mathbf{2(\equiv)_2}$ at 20 °C (——) and 50 °C (-----) in $CHCl_3$. b) Fluorescence spectra of $\mathbf{2(\equiv)_2}$ upon photoexcitation at 450 (——) and 500 nm (——) in $CHCl_3$, and 450 nm in $CHCl_3$/pyridine (9:1, -----) at 20 °C. c) Fluorescence excitation spectra of $\mathbf{2(\equiv)_2}$ monitored at 660 (——) and 760 nm (-----) in $CHCl_3$ at 20 °C.

gated molecules suggests that the higher-energy set of the Soret and Q-bands (A_I and A_{III}, respectively) most likely originates from $\mathbf{[2(\equiv)_2\perp]_4}$ containing the perpendicular conformer of $\mathbf{2(\equiv)_2}$, while the lower-energy set (A_{II} and A_{IV}) can be assigned to the planar conformer of $\mathbf{2(\equiv)_2}$ in $\mathbf{[2(\equiv)_2/\!/]_4}$.[9] Non-associated $\mathbf{2(\equiv)_2}$, generated upon addition of pyridine to $\mathbf{[2(\equiv)_2]_4}$, showed a luminescence at 738 nm (Figure 3b, dashed curve) upon photoexcitation at 450 nm (A_I). Since alkynylene-bridged multiporphyrin arrays without any external conformational restriction have been reported to emit mainly from their planar conformers,[20] the fluorescence observed from $\mathbf{2(\equiv)_2}$ at 738 nm provides good experimental support for the assignment that the lower-energy F_{II} (735 nm) band in Figure 3b arises from $\mathbf{[2(\equiv)_2/\!/]_4}$. Heating the solution from 20 to 50 °C resulted in the latter set of signals arising from $\mathbf{[2(\equiv)_2/\!/]_4}$ in the absorption spectrum intensifying at the expense of the former set assigned to $\mathbf{[2(\equiv)_2\perp]_4}$ (Figure 3a). The combination of this temperature dependency and the ^{1}H NMR spectral profile (see above) leads to the conclusion that $\mathbf{[2(\equiv)_2\perp]_4}$ is the major isomer, which exists in a ratio of 3:1 with the minor isomer $\mathbf{[2(\equiv)_2/\!/]_4}$ at 20 °C and 3:2 at 50 °C. It should also be noted that the absorption and NMR spectral changes are both thermoreversible but extremely slow. As shown in Figure 4, the change in the absorption spectrum on

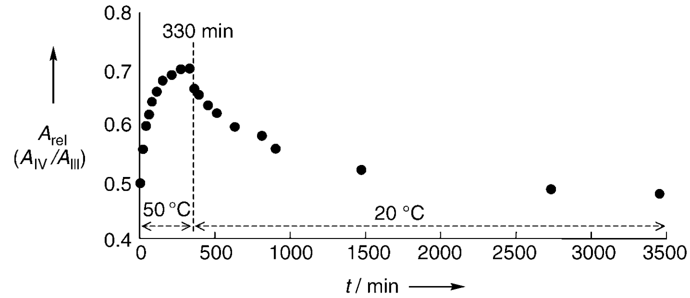


Figure 4. Changes in the relative absorbance (band A_{IV}/A_{III}) of $\mathbf{[2(\equiv)_2]_4}$ in $CHCl_3$ as a function of time upon heating from 20 to 50 °C and cooling from 50 to 20 °C.

heating from 20 to 50 °C subsided in 5 h. Subsequent cooling to 20 °C resulted in a complete recovery of the original spectrum in two days. Such a slow reorganization process indicates a very high thermodynamic stability of tetrameric $\mathbf{[2(\equiv)_2]_4}$, most likely because of the presence of eight Zn–N coordination bonds.

As described earlier, it is considered that the perpendicular conformers of bis(porphyrins) with π-conjugated bridges are, in general, thermodynamically less stable than the planar conformers. However, the conformational preference toward $\mathbf{2(\equiv)_2\perp}$ in the cyclotetramerization is opposite to this general consideration for monomeric $\mathbf{2(\equiv)_2}$. We consider that this conformational preference may reflect the extent of the possible interaction of the dipole moments associated with the directions of the eight pyridyl groups in self-assembled $\mathbf{[2(\equiv)_2]_4}$. Namely, cyclic tetramer $\mathbf{[2(\equiv)_2]_4}$ has two rotational arrays of pyridyl groups, whose directions are identical to one another in $\mathbf{[2(\equiv)_2//]_4}$ but opposite in $\mathbf{[2(\equiv)_2\perp]_4}$ (Figure 1). Since $\mathbf{[2(\equiv)_2\perp]_4}$ allows an efficient cancellation of the dipole moments of the pyridyl groups, $\mathbf{[2(\equiv)_2\perp]_4}$ is favored over $\mathbf{[2(\equiv)_2//]_4}$.

With this assumption in mind, we investigated the self-assembling behavior of $\mathbf{3(\equiv)_2}$, a trimeric version of $\mathbf{2(\equiv)_2}$, which contains three dialkynylene-bridged zinc porphyrin units. Although the ^{1}H NMR spectral profile of $\mathbf{3(\equiv)_2}$ in $CDCl_3$ was less informative of its self-assembled structure, as a result of an enhanced complexity and considerable overlap of the signals, SEC of $\mathbf{3(\equiv)_2}$ with $CHCl_3$ as the eluent displayed a single, unimodal elution peak with a shorter retention time (47.6 min)[19] than $\mathbf{[2(\equiv)_2]_4}$ (49.6 min), thus suggesting that $\mathbf{3(\equiv)_2}$ also forms a cyclic oligomer ($\mathbf{[3(\equiv)_2]_{\mathit{n}}}$), most likely a discrete cyclic tetramer ($n = 4$) analogous to $\mathbf{[2(\equiv)_2]_4}$. The electronic absorption spectrum of $\mathbf{[3(\equiv)_2]_{\mathit{n}}}$ in $CHCl_3$ at 20 °C was very similar to that of $\mathbf{[2(\equiv)_2]_4}$ (Figure 5 a). However, photoexcitation of $\mathbf{[3(\equiv)_2]_{\mathit{n}}}$ at its major absorption band (460 nm; A_I) resulted in a slightly different emission profile from that of $\mathbf{[2(\equiv)_2]_4}$ (Figure 5 b, black solid curve). The fluorescence spectrum obtained consists of two distinct bands at 676 (F_I) and 746 nm (F_{II}), which are nearly identical in wavelength to those of $\mathbf{[2(\equiv)_2]_4}$ (Figure 3 b). In addition to these major bands, a shoulder (F_{III}) appeared around 790 nm. However, the F_{II} and F_{III} bands were intensified relative to that of F_I when $\mathbf{[3(\equiv)_2]_{\mathit{n}}}$ was excited at a lower-energy minor absorption band (510 nm, A_{II}; Figure 5 b, gray solid curve). From the HOMO–LUMO gap theory of π-conjugated molecules, along with the spectral analogy to $\mathbf{[2(\equiv)_2]_4}$, the highest-energy F_I and lowest-energy F_{III} bands are assigned to isomers formed exclusively from the perpendicular and planar conformers $\mathbf{[3(\equiv)_2\perp]_{\mathit{n}}}$ and $\mathbf{[3(\equiv)_2//]_{\mathit{n}}}$, respectively, while the middle band (F_{II}) is attributable to $\mathbf{[3(\equiv)_2\perp//]_{\mathit{n}}}$ consisting of both the planar and perpendicular conformers (Figure 6). Photoexcitation at 460 nm resulted in the non-associated $\mathbf{3(\equiv)_2}$, formed by the addition of pyridine to $\mathbf{[3(\equiv)_2]_{\mathit{n}}}$, displaying a luminescence centered at 789 nm (Figure 5 b, dashed curve), which is close

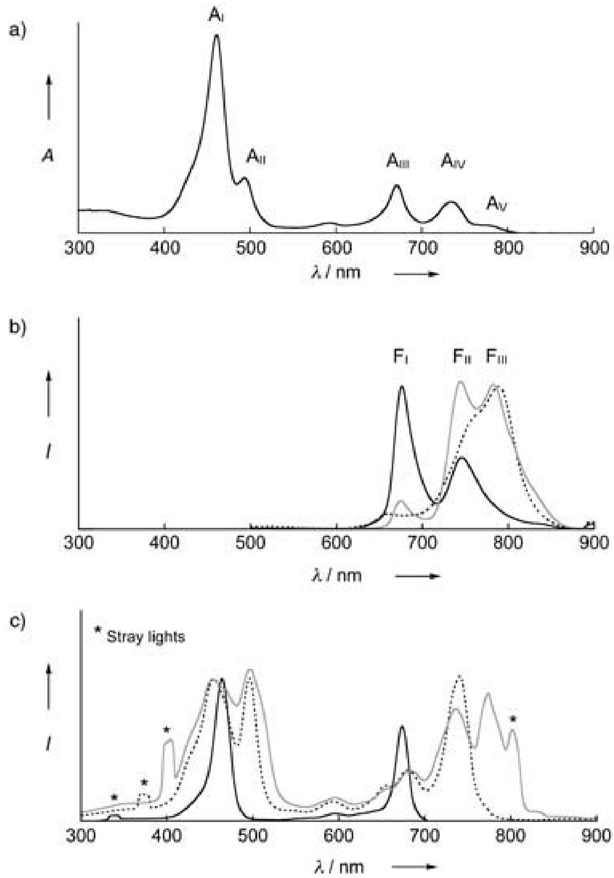


Figure 5. a) Absorption spectrum of $\mathbf{3(\equiv)_2}$ in $CHCl_3$ at 20 °C. b) Fluorescence spectra of $\mathbf{3(\equiv)_2}$ upon photoexcitation at 460 (——) and 510 nm (——) in $CHCl_3$, and 460 nm in $CHCl_3$/pyridine (9:1, -----) at 20 °C. c) Fluorescence excitation spectra of $\mathbf{3(\equiv)_2}$ monitored at 675 (——), 744 (-----), and 800 nm (——) in $CHCl_3$ at 20 °C.

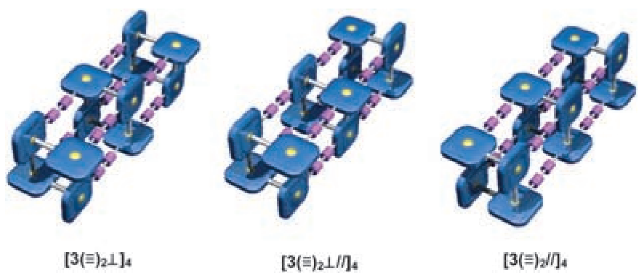


Figure 6. Schematic structures of three conformational isomers in the cyclotetramerization of $\mathbf{3(\equiv)_2}$.

to the F_{III} band assigned to **[3(≡)$_2$//]$_n$** composed exclusively of the planar conformer of **3(≡)$_2$**. Examination of the excitation spectra of **[3(≡)$_2$]$_n$** monitored at 675 (F_I), 744 (F_{II}), and 800 nm (F_{III}; Figure 5c) showed that the Q-bands observed at 671 (A_{III}), 735 (A_{IV}), and 780 nm (A_V) in the absorption spectrum (Figure 5a) originated mainly from **[3(≡)$_2$⊥]$_n$**, **[3(≡)$_2$⊥//]$_n$**, and **[3(≡)$_2$//]$_n$**, respectively. Provided that the molar absorption coefficients of the Q-bands of these three isomers are identical to one another, the relative intensity of A_{III}, A_{IV}, and A_V in Figure 5a may indicate that isomer **[3(≡)$_2$//]$_n$** appears to be the least abundant among the three possible isomers. It should be noted that the dipole moments are cancelled to only a small extent in **[3(≡)$_2$⊥]$_n$**. Thus, similar to the case of **[2(≡)$_2$]$_4$**, a conformer that allows an efficient cancellation of the dipole moments in its supramolecular tubular array is preferred even if its enthalpic gain at the monomer level, associated with the π-electronic conjugation, is smaller than that of its counterpart. The trend observed for **[2(≡)$_2$]$_4$** and **[3(≡)$_2$//]$_n$** is in sharp contrast with that of **[2(≡)$_1$]$_4$**, which has only a single triple bond between the zinc porphyrin units, where the π-electronic conjugation at the monomer level is a dominant factor for determining the conformational aspect of **2(≡)$_1$**.[13]

In conclusion, we have reported the first supramolecular approach to the preferential fixation of the perpendicular conformers of dialkynylene-bridged zinc porphyrin dimer **2(≡)$_2$** and trimer **3(≡)$_2$** by coordinative cyclooligomerization. The contrasting conformational preferences of **2(≡)$_2$** and **3(≡)$_2$** with **2(≡)$_1$**[13] in cyclooligomerization are clearly the result of the lower enthalpic gains of the former two complexes upon planarization compared to the latter. Since cyclic tetramer **[2(≡)$_2$⊥]$_4$** is chiral, and therefore has a variety of potential applications, structural optimization of **2(≡)$_2$** to realize the perfect conformational selectivity toward **[2(≡)$_2$⊥]$_4$** is one of the interesting subjects worthy of further investigations.

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