Energy Transfer and Concentration-Dependent Conformational Modulation: A Porphyrin-Containing [3]Rotaxane

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Energy Transfer and Concentration-Dependent Conformational Modulation: A Porphyrin-Containing [3]Rotaxane

Xiao-Ye Wang, Ji-Min Han, and Jian Pei*[a]

Abstract: A zinc porphyrin-containing [3]rotaxane **A** was synthesized through a copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction. Energy donors and acceptor porphyrin were introduced to dibenzo[24]crown-8 (DB24C8) and dibenzyl ammonium (DBA) units of [3]rotaxane **A** to understand the intramolecular energy transfer process. Investigations of the photophysical properties of [3]rotaxane **A** demonstrated that the intramolecular efficient energy transfer readily occurred from the donors on the wheels to the porphyrin center on the axis. The fluorescence of energy donors in the region of 400 to 450 nm was efficiently absorbed by the porphyrin acceptor under irradiation at 345 nm, and finally a red light emission at about 600 nm was achieved. Further investigation indicated that the conformation of [3]rotaxane **A** was self-modulated by changing its concentration in CH_2Cl_2. The triazole groups on the wheel coordinated or uncoordinated to Zn^{2+} through intramolecular self-coordination with the change in the concentration of [3]rotaxane **A** in CH_2Cl_2. Therefore, this conformational change was reversible in a non-coordinating solvent such as CH_2Cl_2 but inhibited in a coordinating solvent such as THF. Such interesting behaviors were rarely observed in porphyrin derivatives. This self-modulation feature opens up the possibility of controlling molecular conformation by varying concentration.

Keywords: conformational change · cycloaddition · energy transfer · porphyrinoids · rotaxanes

Introduction

Mechanically interlocked molecules (MIMs), such as catenanes and rotaxanes, have attracted substantial research interest for their functional properties and potential applications in molecular machines.[1] The interlocked components in MIMs have a large mobility in nature, hence various stimuli-responsive molecular movements are realized. A myriad of molecular machines were constructed and successfully operated by several external stimuli, such as light,[2] redox reactions,[3] pH changes,[4] and ions.[5]

Porphyrin and its derivatives have exhibited their unique applications in organic materials and supramolecular chemistry.[6,7] Particularly, they were extensively studied in synthetic models of photosynthesis to mimic the functions of the light-harvesting antenna complexes and the photosynthetic reaction center in natural systems.[8] The incorporation of porphyrins into MIMs creates a new family of compounds which combines the excellent optoelectronic properties of porphyrins with the flexibility of the mechanically interlocked structures, thus providing potential applications in both artificial photosynthetic models and stimuli-responsive molecular machines.[9] Most porphyrin-containing MIMs were developed in relation to energy transfer (ET) and electron transfer as mimics of photosynthetic systems.[10] Few examples were reported in host–guest chemistry with porphyrin units as receptors.[11] This situation prompts us to explore new structures of this class of molecules and to investigate their novel properties and functions.

Herein, we develop a highly functionalized zinc porphyrin-containing [3]rotaxane **A** (Scheme 1), in which the porphyrin segment functions not only as the energy acceptor in an ET process, but also as the coordination center for conformational change. The molecule is comprised of two truxene units on the wheels and a porphyrin core on the axis. Efficient intramolecular ET readily occurs from the wheels to the porphyrin center due to the mechanical linkage of energy donors and acceptors. Furthermore, a conformational change is observed due to the coordination of triazole ligands to the zinc(II) porphyrin in dilute solutions, and such a molecular movement is well controlled by varying concentrations. To the best of our knowledge, this is the first report on concentration-dependent conformational change in porphyrin-containing rotaxanes.

Results and Discussion

Design and Synthesis

The chemical structures of [3]rotaxane **A** along with models **B**, **C**, and **D** are shown in Scheme 1. The truxene skeleton

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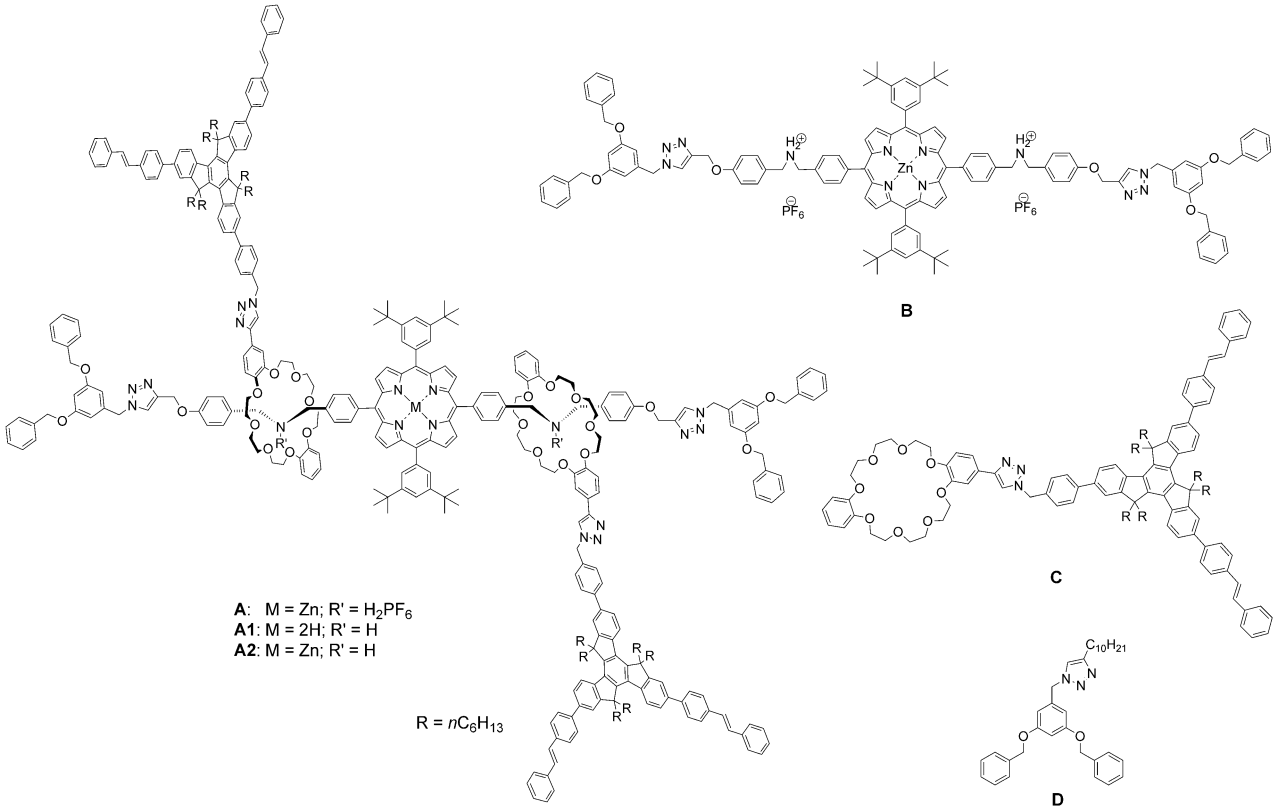

Scheme 1. The chemical structures of [3]rotaxane **A**, its corresponding derivatives **A1** and **A2**, axis **B**, wheel **C**, and model **D**.

functions as the energy donors due to its high fluorescence quantum efficiency.[12] [3]Rotaxane **A** was synthesized utilizing a "threading-followed-by-stoppering" strategy among various template-directed protocols.[13] The well-known interaction between dibenzo[24]crown-8 (DB24C8) and dibenzyl ammonium (DBA) was chosen for the mechanical assembly,[14] and the Cu^I-catalyzed azide–alkyne cycloaddition (CuAAC) was applied for the stoppering due to its good functional-group tolerance and high efficiency.[14a,15]

The synthetic route to wheel **C** is illustrated in Scheme 2. Compound **1** was synthesized following our previous report.[16] A Horner–Wadsworth–Emmons (HWE) reaction between **1** and diethyl benzylphosphonate **2** afforded **3** in 91% yield, which was converted to compound **4** by a Suzuki cross-coupling reaction with 4-formylphenyl boronic acid. Reduction of **4** followed by bromonation afforded **6** in 83% yield for two steps. Subsequently, a nucleophilic substitution with NaN_3 afforded azide-functionalized derivative **7**, which was applied for the CuAAC reaction with ethynyl-substituted DB24C8 **8** to give wheel **C** as a white solid.

The synthetic approach to [3]rotaxane **A** is depicted in Scheme 3. Compound **10** was prepared and converted to porphyrin **12** according to the literature.[17] The ester group was reduced by $LiAlH_4$ to produce diol **13**, which was further oxidized to afford dialdehyde **14**. A condensation of compound **14** and benzylamine **15** in refluxing chloroform gave imine in quantitative yield, which was used for the subsequent reduction without further purification. Compound **16** was obtained in 91% yield for two steps as a red solid. Unfortunately, when we tried to acidify benzyl amine with 6 M HCl, trifluoroacetic acid (TFA), or trifluoromethanesulfonic acid (TfOH), the nitrogen atoms in the porphyrin moiety were also protonated.[18] Finally, we succeeded in solely protonating the amine part with dilute aqueous acetic acid (HOAc). However, the free-base porphyrin could not survive from the CuAAC reaction because Cu^I inserted into its central cavity.[19] Therefore, we turned the free-base porphyrin derivative **16** to its corresponding zinc porphyrin, which was more stable in acidic conditions and tolerant to the CuAAC reaction. Subsequent acidification with dilute aqueous HCl (pH 1) followed by anion exchange with NH_4PF_6 afforded DBA **17** in 83% yield. We chose the "threading-followed-by-stoppering" strategy for the synthe-

Abstract in Chinese:

通过铜催化的叠氮-炔环加成反应合成了含有锌卟啉的[3]轮烷 **A**。两个以三聚茚衍生物为基础的能量给体连接于二苯并 24-冠-8 上；卟啉衍生物作为能量受体连接于二苄铵盐单元上。光物理研究结果表明含有三聚茚片段的能量给体到卟啉片段的能量受体之间发生了高效的能量转移。进一步研究表明分子 **A** 的构象可以通过溶液浓度来调控。随着浓度降低，连接于冠醚上的三唑可与锌离子形成分子内配位的构象。这一浓度依赖的构象变化过程在非配位溶剂如二氯甲烷中是完全可逆的，而在配位溶剂如四氢呋喃中则被阻碍。

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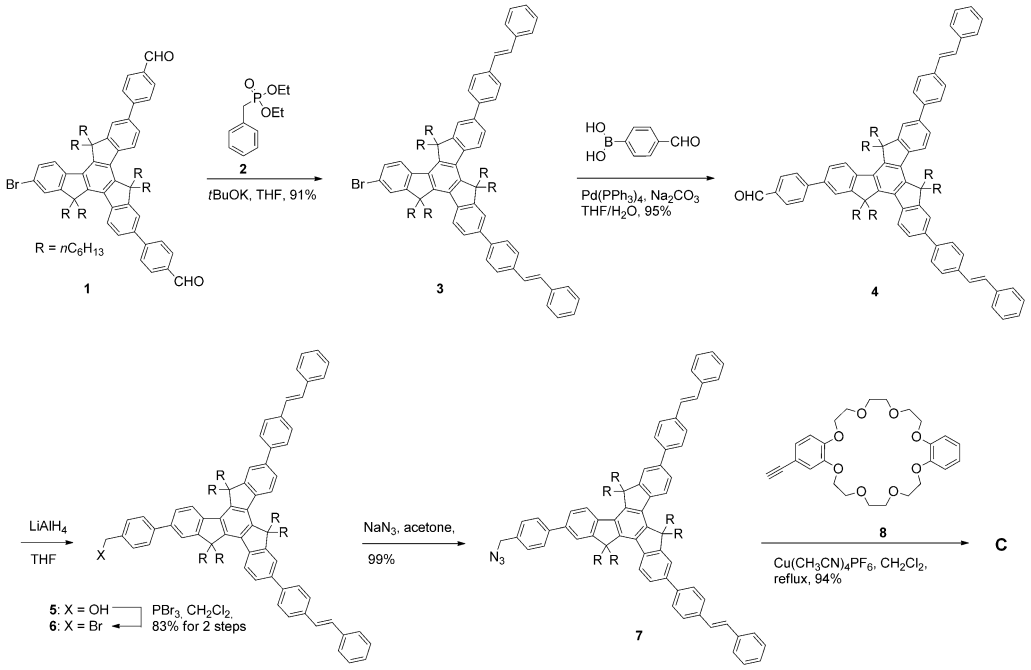
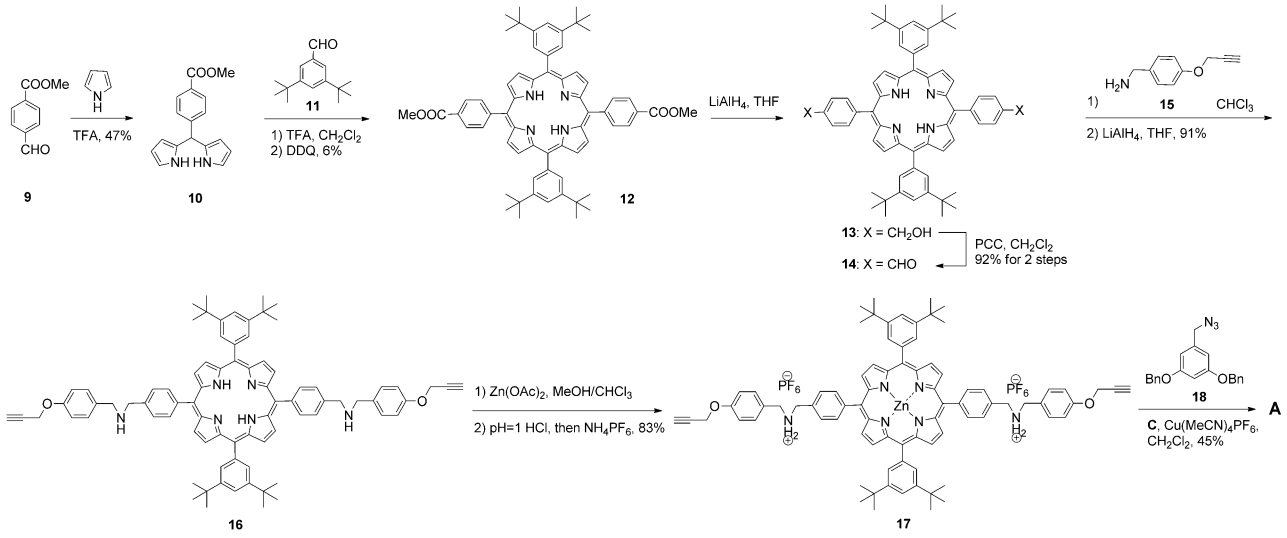


Scheme 2. The synthetic route to wheel **C**.



Scheme 3. The synthetic route to [3]rotaxane **A**. TFA = trifluoroacetic acid, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, PCC = pyridinium chlorochromate.

sis of [3]rotaxane **A**. Although the binding constant of DB24C8 and DBA in CH_2Cl_2 is quite large, excess of **C** was present to ensure complete threading. Such a well-established process was very fast, and the threaded assembly was then subjected to the stoppering reaction. [3]Rotaxane **A** was purified by flash chromatography and recycling preparative GPC and isolated in 45% yield. Model **B** was also prepared for comparison.

The chemical structure of [3]rotaxane **A** was verified by ^1H and ^{13}C NMR spectroscopy and ESI-HRMS characterization (Figure 1). The peak at $m/z = 2778.0$ corresponded to $[\mathbf{A}-2PF_6]^{2+}$, while no signals of by-product **B** or monothreaded [2]rotaxane was observed, indicating high purity of [3]rotaxane **A**. The ESI-HRMS characterization perfectly matched with the calculated results for $[C_{372}H_{416}N_{18}O_{22}Zn]^{2+}$, which strongly confirmed the identity of **A**.

Photophysical Properties

The absorption spectra of [3]rotaxane **A** and models **B** and **C** are illustrated in Figure 2a. Compound **C** showed a broad

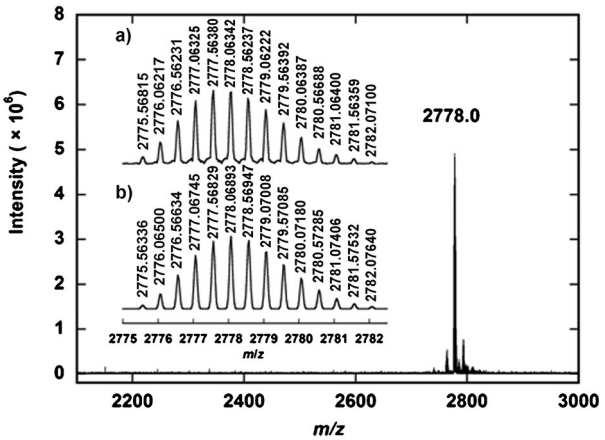


Figure 1. ESI-MS spectra of [3]rotaxane **A**. The peak at $m/z = 2778.0$ corresponds to $[\mathbf{A}-2PF_6]^{2+}$. Shown in the inset are the ESI-HRMS spectra of a) experimental results; b) calculated results.

absorption band with $\lambda_{max} = 345$ nm, which was assignable to the π-extended truxene derivatives. Compound **B** showed typical absorption features of zinc porphyrin (ZnP) with a sharp Soret band at 425 nm and Q bands in the region of 500 to 650 nm. The absorption of compound **A** was constructed by weighted addition of that of axis **B** and two-fold intensity of wheel **C**, suggesting a 1:2 molar ratio of **B** and **C** in [3]rotaxane **A** without ground-state interaction in THF solution.

As shown in Figure 2b, for compound **B**, an emission maximum at 604 nm with a shoulder peak at 652 nm was observed, featuring fluorescence from the ZnP moiety. Compound **C** showed an intense emission from 380 to 500 nm, which had a large overlap with the absorption of **B**. This spectral overlap together with the close proximity caused by the mechanical linkage was crucial for fluorescence resonance energy transfer (FRET).[20] To investigate the FRET process, we examined the photoluminescence (PL) spectra of [3]rotaxane **A** excited at different wavelengths. As shown in Figure 2c, under excitation at the absorption maximum of axis **B** (425 nm), compound **A** exhibited a typical fluorescence from the ZnP moiety as discussed above. When excited at the absorption λ_{max} of wheel **C** at 345 nm, compound **A** also showed similar emission characteristics, which was not observed in axis **B** when it was exited at the same wavelength, thus indicating efficient intramolecular energy transfer occurred from wheel **C** to the ZnP unit. To further understand this ET process, we compared the emission spectra of **A** and **C**. As shown in Figure 2d, the fluorescence feature of [3]rotaxane **A** from 380 to 500 nm was split into two main peaks. Compared to that of free molecule **C**, the intensity was greatly weakened in the region of 400 to 450 nm, which corresponded to the absorption of the porphyrin moiety. Therefore, it was concluded that excitons generated in the energy donors partially went to the energy-acceptor chromophore, ZnP unit in this case. The fluorescence quantum yield (Φ_F) of **A** was measured to be 1.8% under excitation at 345 nm, using tetraphenylporphyrin (TPP) as a standard.[21]

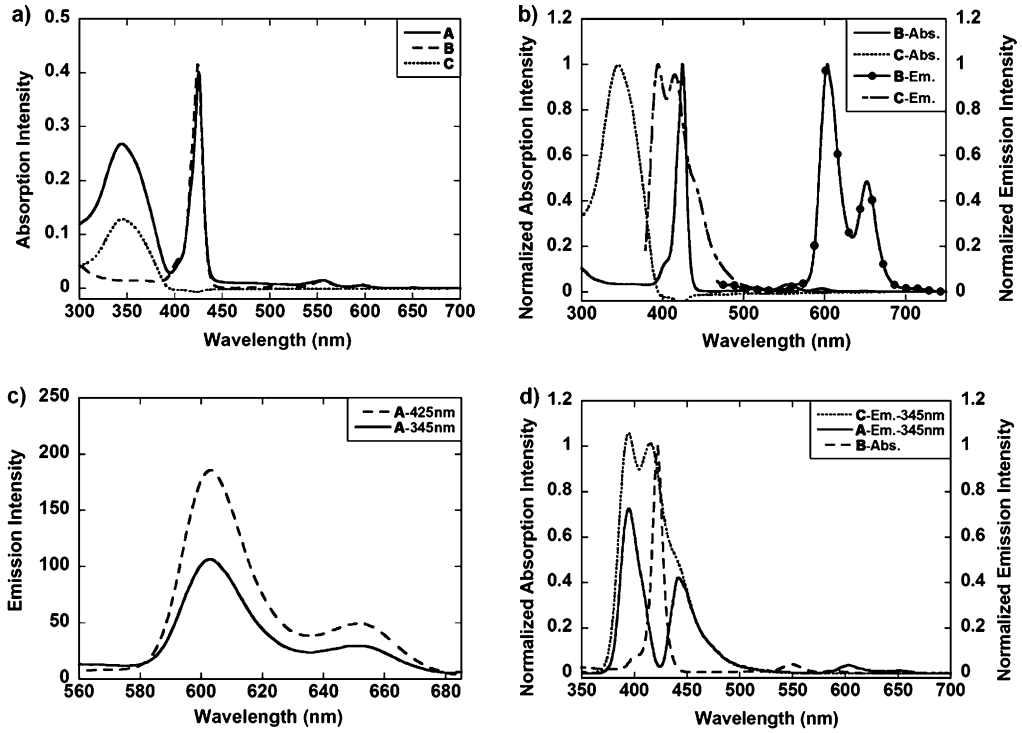


Figure 2. a) The absorption spectra of **A**, **B**, and **C**. b) The absorption and emission spectra of **B** and **C**. c) The emission spectra of **A** excited at different wavelengths. d) The absorption spectrum of **B** and emission spectra of **A** and **C** excited at 345 nm. All the spectra were recorded in THF (1×10^{-6} M).

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Conformational Change in Dilute Solution

We further investigated the absorption features of [3]rotaxane **A** in dilute CH_2Cl_2. A new peak at 435 nm in the Soret band appeared after 24 h, and the intensity of the peak at 420 nm decreased (Figure 3b,c). This phenomenon was more significant in dilute solutions and turned out to be concentration-dependent. Such a change was not observed in our previous study in THF solution. Considering the different solvent effects on coordination between THF and CH_2Cl_2, we attributed this emerging peak at longer wavelength to the coordination of triazole groups to Zn^{II} ion in the porphyrin nucleus.[22] CH_2Cl_2 is a non-coordinating solvent, so that triazole groups coordinate to the ZnP moiety through intramolecular interaction in dilute solutions, whereas such a complex was disrupted in a coordinating solvent such as THF. This explanation is also consistent with the fact that the Soret band at 425 nm in THF showed a slight bathochromic shift compared to 420 nm in CH_2Cl_2.

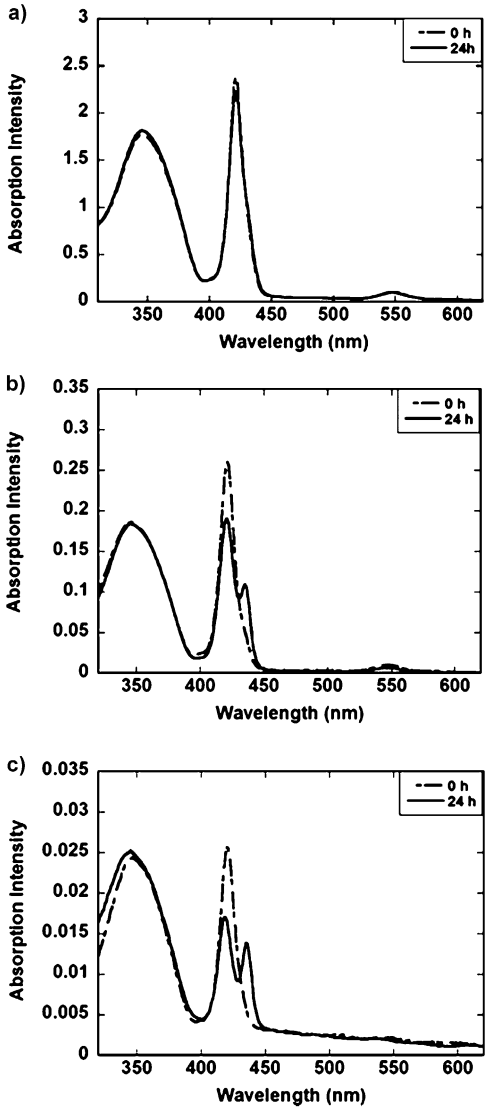


Figure 3. The absorption spectra of [3]rotaxane **A** monitored at different times (0 h and 24 h) in CH_2Cl_2: a) 1×10^{-5} M; b) 1×10^{-6} M; c) 1×10^{-7} M.

To further demonstrate this assumption, we carried out the demetalation of **A** to afford the free-base porphyrin. Although the obtained [3]rotaxane **A1** exhibited identical peaks at 345 and 420 nm, the Q bands of **A1** showed the four characteristic peaks (517, 547, 590, and 645 nm) of a free-base porphyrin (Figure S1 in the Supporting Information). More importantly, the absorption features of [3]rotaxane **A1** did not change with concentration and time, suggesting that Zn^{2+} in the porphyrin core was necessary for such a process. That means the emerging peak at 435 nm implied the occurrence of coordination to the Zn^{II} ion in the porphyrin.

Since there are two kinds of triazole groups separately attached on the wheels and the thread, we speculate that the ones on the wheels have more opportunities to coordinate to ZnP due to their flexible conformation. When we examined the absorption spectra of model **B** in CH_2Cl_2 at different concentrations (Figure S2 in the Supporting Information), only one sharp peak in the Soret band at 420 nm was observed, and no peak at 435 nm appeared even after 24 h. These results strongly supported our speculation that only the triazole groups on the wheel played a key role in coordinating to ZnP moiety on the thread. However, the conformation of the wheel in [3]rotaxane **A** is partially fixed by the hydrogen bonding between DB24C8 and DBA units, which explains why it takes a long time for their geometry to adjust to a thermodynamically favored self-coordinated conformation.[23] In order to confirm our hypothesis on the above kinetic issues, we managed to break the hydrogen bonding by treating [3]rotaxane **A** with Na_2CO_3 to deprotonate the ammonium groups, thus reducing the energy barriers for adjusting conformation of the wheels. The absorption spectra of the obtained [3]rotaxane **A2** in dilute CH_2Cl_2 solutions were recorded (Figure 4a). The new peak at 435 nm showed up immediately after dilution, and the peak intensity at 420 nm decreased gradually. By concentrating the solution, we confirmed that this process was exactly reversible, as a reversed tendency could be observed. These results not only confirm the above-mentioned coordination hypothesis, but also indicate that such a concentration-dependent conformational change shows fast response without the hydrogen-bonding fixture between wheels and axis.

To give more insight into this process, we synthesized another model **D** containing a triazole group. By adding compound **D** to a solution of **B** in CH_2Cl_2 (5×10^{-6} M), a significant bathochromic shift of the Soret band was observed (Figure 4b). The intensity of the peak at 420 nm decreased gradually, and a new peak at 432 nm emerged. A clear isosbestic point was observed during the titration, thus indicating that the transformation happened between two identical states. The association constant (K_a) was estimated to be 2×10^2 M^{-1}, suggesting a quite weak interaction between the triazole groups and ZnP motif in this system. Scheme 4 illustrates the concentration-dependent conformational change in [3]rotaxane **A**, which is achieved by such a weak interac-

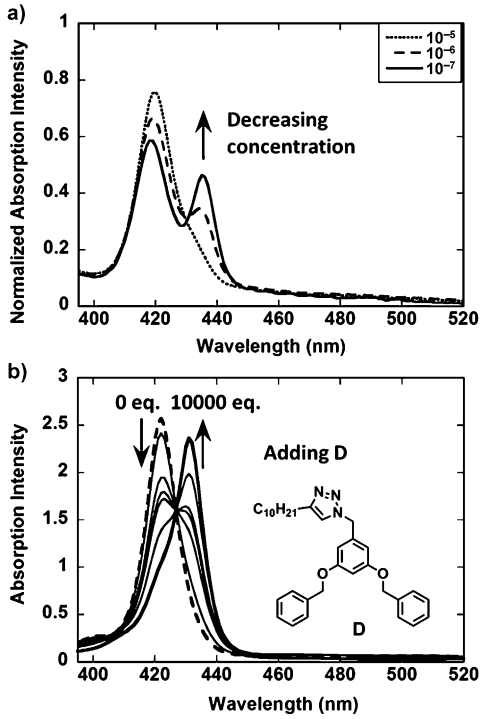
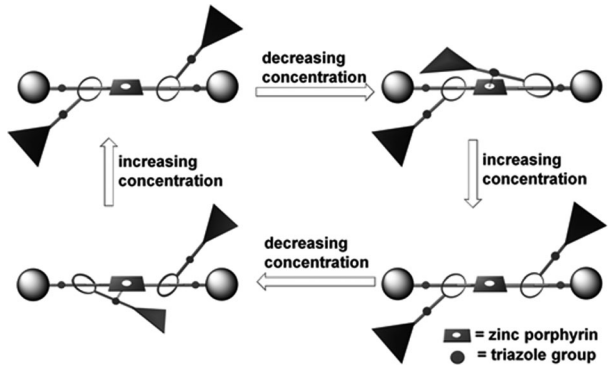


Figure 4. The absorption spectra of a) the neutral [3]rotaxane **A2** in different concentrations; b) the model compound **B** in CH_2Cl_2 (5×10^{-6} M) after adding different amounts of compound **D** at room temperature.



Scheme 4. Graphical representation of the concentration-dependent conformational change in dilute CH_2Cl_2 solution. This process is inhibited in a coordinating solvent such as THF.

tion. In extremely dilute solutions, the complex favored a self-coordinated conformation between the triazole groups on the wheel and the ZnP unit on the thread; whereas by increasing the concentration, such a weak interaction was easily disrupted by intermolecular van der Waals interactions and the [3]rotaxane adopted an extended conformation. Such a low K_a value ensures the sensitivity of the [3]rotaxane to concentration and makes the concentration-dependent conformational change possible.

Conclusions

We have synthesized a highly functionalized zinc(II) porphyrin-containing [3]rotaxane **A** through the CuAAC reaction. The detailed investigation of the photophysical properties of [3]rotaxane **A** indicates that the efficient intramolecular ET process readily occurs from the wheels to the porphyrin moiety on the axis. Further investigation demonstrates that a concentration-dependent conformational change is exactly reversible in the dilute solution of [3]rotaxane **A** in CH_2Cl_2. This is the first example of modulating conformation by changing concentration of porphyrinic rotaxanes. The investigation results demonstrate that concentration variations can be used as a stimulus to trigger the conformational change in a mechanically interlocked molecule. Such a conformational change is reversible in CH_2Cl_2 and inhibited in a coordinating solvent such as THF. This work greatly enriches the structures and properties of the family of porphyrin-containing MIMs, and such a unique concentration-dependent conformational change shows potential in its application to magnetic spin switching of molecules in solution.[24]

Experimental Section

General Methods

All commercially available chemicals were used without further purification unless otherwise noted. Dichloromethane was distilled from CaH_2 under a nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from sodium under a nitrogen atmosphere prior to use. Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel coated glass sheets with F254 indicator. All yields given refer to yields of isolated products. Nuclear magnetic resonance (NMR) spectra were recorded on 300 or 400 MHz Varian spectrometers. Chemical shifts were reported in ppm. Coupling constants (J values) were reported in Hertz. ^{1}H NMR chemical shifts were referenced to TMS (0 ppm) or $CHCl_3$ (7.26 ppm) or CHD_2CN (1.94 ppm) and ^{13}C NMR chemical shifts were referenced to $CDCl_3$ (77.00 ppm) or CD_3CN (118.69 ppm). HRMS (ESI) spectra were recorded on a Bruker Apex IV FTMS. The recycling preparative GPC separation was performed by using JAI LC-9201 recycling preparative HPLC with 1H and 2H GPC column. Absorption spectra were recorded on PerkinElmer Lambda 750 UV/Vis Spectrometer. Photoluminescence (PL) spectra were recorded on a PerkinElmer LS 55 Luminescence Spectrometer.

*Compound **3***

A mixture of compound **1** (4.02 g, 3.54 mmol) and diethyl benzylphosphonate **2** (2.02 g, 8.86 mmol) was dissolved in anhydrous THF (50 mL) under a nitrogen atmosphere. After the mixture was cooled to −78 °C, a solution of *t*BuOK (1.00 g, 8.91 mmol) in THF (15 mL) was added dropwise. The mixture was stirred for 3 h and then warmed to room temperature for another 12 h. Aqueous HCl (10 mL, 3 M) was added and the aqueous layer was extracted with CH_2Cl_2. The organic extraction was washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (petroleum ether/CH_2Cl_2 = 15:1) to afford 4.05 g (91 %) of **3** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.46–8.37 (m, 2H), 8.25 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.2 Hz, 4H), 7.73–7.65 (m, 8H), 7.60–7.52 (m, 6H), 7.38 (t, J = 7.4 Hz, 4H), 7.28 (t, J = 7.4 Hz, 2H), 7.21 (s, 4H), 3.04–2.88 (m, 6H), 2.19–2.04 (m, 6H), 0.95–0.82 (m, 36H), 0.64–0.54 ppm (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 156.0, 154.3, 154.2, 145.6, 145.2, 144.5, 140.3, 139.5, 139.4,

139.3, 138.6, 138.2, 138.0, 137.4, 137.3, 136.3, 129.2, 128.7, 128.6, 128.2, 127.7, 127.3, 127.0, 126.5, 125.9, 125.4, 125.0, 124.9, 124.8, 120.7, 120.3, 56.0, 55.8, 55.7, 37.1, 36.9, 31.5, 29.5, 29.4, 23.9, 22.3, 13.9 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{91}H_{109}Br$: 1280.7707; found: 1280.7709 $[M]^+$.

Compound ***4***

To a solution of 4-formylbenzeneboronic acid (226 mg, 1.56 mmol), compound **3** (1.0 g, 0.78 mmol), and $[Pd(PPh_3)_4]$ (45 mg, 0.04 mmol) in THF (100 mL) was added aqueous Na_2CO_3 (331 mg, 3.12 mmol) under nitrogen. The mixture was heated at reflux for 12 h under a nitrogen atmosphere. The organic layer was separated and washed with saturated aqueous NH_4Cl and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography over silica gel (petroleum ether/CH_2Cl_2 = 8:1 to 1:1) to afford 0.97 g (95%) of **4** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 10.10 (s, 1H), 8.52–8.43 (m, 3H), 8.03 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.3 Hz, 4H), 7.78–7.70 (m, 6H), 7.68 (d, J = 8.4 Hz, 4H), 7.58 (d, J = 7.3 Hz, 4H), 7.39 (t, J = 7.6 Hz, 4H), 7.28 (m, 2H), 7.21 (s, 4H), 3.04–2.88 (m, 6H), 2.19–2.04 (m, 6H), 0.95–0.82 (m, 36H), 0.64–0.54 ppm (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 191.9, 154.5, 154.3, 154.2, 147.3, 145.6, 145.5, 145.2, 140.9, 140.3, 139.6, 139.5, 138.6, 138.2, 138.1, 137.7, 137.4, 137.3, 136.3, 135.0, 130.3, 128.7, 128.6, 128.2, 127.6, 127.5, 127.3, 127.0, 126.5, 125.5, 125.0 124.9, 120.8, 120.3, 55.9, 55.8, 37.1, 31.5, 29.5, 23.9, 22.3, 13.9 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{98}H_{114}O$: 1306.8864; found: 1306.8858 $[M]^+$.

Compound ***5***

$LiAlH_4$ (52 mg, 1.38 mmol) was added slowly to a solution of compound **4** (900 mg, 0.69 mmol) in anhydrous THF (30 mL) at 0°C. The mixture was warmed to room temperature and stirred overnight. Then the mixture was quenched with aqueous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to afford **5** in quantitative yield as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.45 (d, J = 8.2 Hz, 3H), 7.77–7.80 (m, 6H), 7.67–7.74 (m, 10H), 7.58 (d, J = 7.3 Hz, 4H), 7.52 (d, J = 7.9 Hz, 2H), 7.39 (t, J = 7.6 Hz, 4H), 7.31–7.28 (m, 2H), 7.21 (s, 4H), 4.79 (d, J = 5.0 Hz, 2H), 3.04–2.88 (m, 6H), 2.19–2.04 (m, 6H), 0.95–0.82 (m, 36H), 0.64–0.54 ppm (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.3, 145.2, 140.8, 140.4, 139.8, 139.7, 139.6, 138.6, 138.4, 138.0, 137.3, 136.2, 128.7, 128.6, 128.2, 127.6, 127.5, 127.2, 127.0, 126.5, 125.1, 124.9, 120.5, 120.3, 65.2, 55.8, 37.1, 31.5, 29.5, 23.9, 22.3, 13.9 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{98}H_{116}O$: 1308.9021; found: 1308.8989 $[M]^+$.

Compound ***6***

PBr_3 (373 mg, 1.38 mmol) was added slowly to a solution of compound **5** (900 mg, 0.69 mmol) in anhydrous CH_2Cl_2 at 0°C. The mixture was warmed to room temperature and stirred overnight and then quenched with MeOH in an ice bath. After evaporation of the solvents, the residue was purified by column chromatography over silica gel (petroleum ether/CH_2Cl_2 = 10:1) to afford 780 mg (83%) of **6** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.45 (d, J = 8.4 Hz, 3H), 7.79 (d, J = 8.3 Hz, 4H), 7.77–7.62 (m, 12H), 7.57 (d, J = 7.3 Hz, 4H), 7.54 (d, J = 8.3 Hz, 2H), 7.39 (t, J = 7.6 Hz, 4H), 7.34–7.24 (m, 2H), 7.21 (s, 4H), 4.60 (s, 2H), 3.04–2.88 (m, 6H), 2.19–2.04 (m, 6H), 0.95–0.82 (m, 36H), 0.64–0.54 ppm (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.3, 145.3, 145.2, 141.5, 140.4, 139.9, 139.7, 138.5, 138.2, 138.1, 137.9, 137.3, 136.6, 136.3, 129.6, 128.7, 128.6, 128.3, 127.6, 127.5, 127.3, 127.0, 126.5, 125.1, 124.9, 120.6, 120.3, 55.8, 37.1, 33.5, 31.5, 29.5, 23.9, 22.3, 13.9 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{98}H_{116}Br$: 1371.8255; found: 1371.8272 $[M+H]^+$.

Compound ***7***

NaN_3 (74 mg, 1.14 mmol) was added to a solution of compound **6** (780 mg, 0.57 mmol) in acetone and the mixture was heated at reflux for 6 h. After filtration, the mixture was concentrated under reduced pressure to afford 750 mg (99%) of **7** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.46 (d, J = 8.0 Hz, 3H), 7.80 (d, J = 8.0 Hz, 6H), 7.77–7.63 (m, 10H), 7.58 (d, J = 7.4 Hz, 4H), 7.47 (d, J = 8.1 Hz, 2H), 7.39 (t, J = 7.6 Hz, 4H), 7.33–7.24 (m, 2H), 7.21 (s, 4H), 4.42 (s, 2H), 3.04–2.88 (m, 6H), 2.19–2.04 (m, 6H), 0.95–0.82 (m, 36H), 0.64–0.54 ppm (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.3, 145.3, 145.2, 141.4, 140.4, 139.9, 139.7, 138.5, 138.3, 138.0, 137.9, 137.3, 136.2, 134.1, 128.8, 128.7, 128.6, 128.2, 127.6, 127.5, 127.2, 127.0, 126.5, 125.1, 124.9, 120.5, 120.3, 55.8, 54.5, 37.1, 31.5, 29.5, 23.9, 22.3, 13.9 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{98}H_{115}N_3$: 1333.9086; found: 1333.9068 $[M]^+$.

Compound ***C***

A mixture of **7** (700 mg, 0.524 mmol), **8** (495 mg, 1.05 mmol), and $[Cu(MeCN)_4]PF_6$ (174 mg, 0.524 mmol) was heated at reflux in dry CH_2Cl_2 overnight. The mixture was washed with dilute aqueous HCl and water. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvents under reduced pressure, the residue was purified by column chromatography (eluent: CH_2Cl_2 to EtOAc) to afford the crude product. Preparative GPC (eluent: $CHCl_3$) was used to obtain 892 mg (94%) of product **C** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, ppm): δ = 8.56–8.32 (m, 3H), 7.86–7.77 (m, 6H), 7.76–7.62 (m, 10H), 7.58 (d, J = 7.6 Hz, 4H), 7.47 (d, J = 7.4 Hz, 3H), 7.39 (t, J = 7.6 Hz, 4H), 7.34–7.23 (m, 5H), 7.21 (s, 4H), 6.89 (s, 4H), 5.65 (s, 2H), 4.31–4.12 (m, 8H), 4.01–3.87 (m, 8H), 3.83 (s, 8H), 3.04–2.88 (m, 6H), 2.19–2.04 (m, 6H), 0.95–0.82 (m, 36H), 0.64–0.54 ppm (m, 30H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.4, 154.3, 148.8, 145.3, 145.1, 141.9, 140.4, 140.0, 139.6, 138.5, 138.1, 138.0, 137.9, 137.3, 136.3, 133.5, 129.0, 128.9, 128.7, 128.6, 128.3, 128.2, 127.7, 127.6, 127.2, 127.0, 126.5, 125.3, 125.1, 124.9, 121.4, 120.5, 120.3, 114.0, 71.2, 69.8, 69.4, 69.3, 55.8, 54.0, 37.1, 31.5, 29.5, 23.9, 22.2, 13.9 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{124}H_{148}N_3O_8$: 1807.1261; found: 1807.1239 $[M+H]^+$; calcd for $C_{124}H_{151}N_4O_8$: 1824.1526; found: 1824.1556 $[M+NH_4]^+$.

Compound ***13***

$LiAlH_4$ (77 mg, 2.04 mmol) was added slowly to a solution of compound **12** (195 mg, 0.204 mmol) in anhydrous THF (30 mL) at 0°C. The mixture was warmed to room temperature and stirred overnight, and then quenched with aqueous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure to afford **13** in nearly quantitative yield as a purple-red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.90 (d, J = 4.9 Hz, 4H), 8.84 (d, J = 4.9 Hz, 4H), 8.22 (d, J = 8.0 Hz, 4H), 8.09 (d, J = 1.8 Hz, 4H), 7.80 (t, J = 1.8 Hz, 2H), 7.74 (d, J = 8.0 Hz, 4H), 5.05 (s, 4H), 1.53 (s, 36H), −2.73 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 148.7, 141.8, 141.1, 140.1, 134.6, 130.0, 125.2, 121.5, 121.0, 119.5, 65.4, 35.0, 31.7, 29.7 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{62}H_{67}N_4O_2$: 899.5258; found: 899.5246 $[M+H]^+$.

Compound ***14***

A mixture of PCC (88 mg, 0.407 mmol) and compound **13** (183 mg, 0.203 mmol) in anhydrous CH_2Cl_2 was stirred overnight. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography over silica gel (petroleum ether/EtOAc = 10:1). The crude product was washed with MeOH to afford 169 mg (92%) of **14** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 10.39 (s, 2H), 8.94 (d, J = 4.9 Hz, 4H), 8.79 (d, J = 4.9 Hz, 4H), 8.42 (d, J = 8.0 Hz, 4H), 8.29 (d, J = 8.0 Hz, 4H), 8.08 (d, J = 1.8 Hz, 4H), 7.81 (t, J = 1.8 Hz, 2H), 1.53 (s, 36H), −2.74 ppm (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 192.1, 149.1, 148.9, 141.0, 135.9, 135.1, 131.9, 130.5, 129.9, 127.9, 122.3, 121.3, 118.4, 35.1, 31.8 ppm; HRMS (ESI, *m*/*z*): Calcd for $C_{62}H_{63}N_4O_2$: 895.4945; found: 899.4926 $[M+H]^+$.

Compound ***16***

A solution of **14** (125 mg, 0.140 mmol) and **15** (67 mg, 0.560 mmol) in $CHCl_3$ was heated at reflux for 5 h. After removal of the solvents under reduced pressure, the red solid was dissolved in anhydrous THF. $LiAlH_4$ (56 mg, 1.40 mmol) was added slowly to the solution at 0°C. The mixture was stirred for 5 h and then quenched with aqueous Na_2SO_4. After filtration, the solution was concentrated under reduced pressure. The crude product was washed with MeOH to afford 150 mg (91% for two steps) of **16** as a purple solid. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ = 8.90 (d, J = 4.9 Hz, 4H), 8.85 (d, J = 4.9 Hz, 4H), 8.18 (d, J = 8.0 Hz, 4H), 8.09 (d, J = 1.7 Hz, 4H), 7.79 (t, J = 1.7 Hz, 2H), 7.70 (d, J = 8.0 Hz, 4H), 7.44 (d,

J=8.5 Hz, 4H), 7.03 (d, J=8.5 Hz, 4H), 4.73 (d, J=2.4 Hz, 4H), 4.14 (s, 4H), 4.00 (s, 4H), 2.54 (t, J=2.4 Hz, 2H), 1.53 (s, 36H), −2.73 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ=206.9, 156.6, 148.7, 141.2, 141.0, 139.7, 134.5, 133.5, 131.1, 129.9, 129.4, 126.4, 121.4, 120.9, 119.7, 114.9, 78.7, 75.5, 55.8, 53.1, 52.9, 35.0, 31.7, 30.9 ppm; HRMS (ESI, m/z): Calcd for $C_{82}H_{85}N_6O_2$: 1185.6729; found: 1185.6706 $[M+H]^+$.

Compound ***17***

To a solution of **16** (50 mg, 0.0422 mmol) in a mixture of $CHCl_3$ and MeOH (10 mL/10 mL) was added $Zn(OAc)_2{\cdot}2H_2O$ (19 mg, 0.0844 mmol). The mixture was stirred at room temperature for 3 h, and the solvent was removed under reduced pressure. The residue was dissolved in acetone (1 mL), then dilute aqueous HCl (50 mL, pH 1) was added. After 5 min, NH_4PF_6 (28 mg, 0.169 mmol) was added to the aqueous mixture, and purple precipitate appeared immediately. The solid was filtrated and washed with water sufficiently to afford 48 mg (83%) of **17**. The ^{13}C NMR spectrum was not obtained due to the poor solubility of **17** in common organic solvents. ^{1}H NMR (300 MHz, CD_3CN, 298 K, ppm): δ=8.89 (d, J=4.9 Hz, 4H), 8.79 (d, J=4.9 Hz, 4H), 8.26 (d, J=8.1 Hz, 4H), 8.09 (d, J=1.7 Hz, 4H), 7.90 (t, J=1.7 Hz, 2H), 7.79 (d, J=8.1 Hz, 4H), 7.52 (d, J=8.4 Hz, 4H), 7.11 (d, J=8.4 Hz, 4H), 4.81 (d, J=2.4 Hz, 4H), 4.50 (s, 4H), 4.33 (s, 4H), 2.85 (t, J=2.4 Hz, 2H), 1.53 ppm (s, 36H); HRMS (ESI, m/z): Calcd for $C_{82}H_{84}N_6O_2Zn$: 624.2968; found: 624.2981 $[M-2PF_6]^{2+}$.

Compound ***B***

To a solution of **16** (50 mg, 0.0422 mmol) in a mixture of $CHCl_3$ and MeOH (10 mL/10 mL) was added $Zn(OAc)_2{\cdot}2H_2O$ (19 mg, 0.0844 mmol). The mixture was stirred at room temperature for 3 h and then washed with aqueous $NaHCO_3$ and water three times. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvents under reduced pressure, the residue was dissolved in 20 mL of CH_2Cl_2, and then **18** (38 mg, 0.106 mmol) and $[Cu(MeCN)_4]PF_6$ (2 mg, 0.005 mmol) were added. After the mixture was heated at reflux for 24 h, aqueous NH_4Cl (20 mL) was added. The organic layer was washed with water and dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The red solid was purified by column chromatography over silica gel (CH_2Cl_2/Et_3N=30:1) and then by preparative GPC (eluent: $CHCl_3$) to afford the diamide, which was dissolved in DMF (1 mL). Dilute aqueous HCl (50 mL, pH 1) was added. After 5 min, water was evaporated off. The residue was dissolved in MeOH (10 mL), and saturated aqueous NH_4PF_6 (10 mL) was added to provide purple precipitate immediately. The solid was filtrated and washed with water sufficiently to afford 60 mg (64%) of **B**. The ^{13}C NMR spectrum was not obtained due to the poor solubility of **B** in common organic solvents. ^{1}H NMR (300 MHz, CD_3CN, 298 K): δ=8.91 (d, J=4.2 Hz, 4H), 8.81 (d, J=4.2 Hz, 4H), 8.28 (d, J=7.5 Hz, 4H), 8.12 (s, 4H), 7.93 (s, 2H), 7.87–7.81 (m, 6H), 7.54 (d, J=8.4 Hz, 4H), 7.37–7.31 (m, 20H), 7.17 (d, J=8.4 Hz, 4H), 6.55 (s, 2H), 6.47 (s, 4H), 5.39 (s, 4H), 5.21 (s, 4H), 5.00 (s, 8H), 4.55 (s, 4H), 4.37 (s, 4H), 1.52 ppm (s, 36H); HRMS (ESI, m/z): Calcd for $C_{124}H_{124}N_{12}O_6Zn$: 970.4524; found: 970.4489 $[M-2PF_6+2H]^{2+}$.

Compound ***D***

To a solution of **18** (2.00 g, 5.79 mmol) and dodec-1-yne (1.44 g, 8.69 mmol) in 50 mL of CH_2Cl_2 was added $[Cu(MeCN)_4]PF_6$ (216 mg, 0.058 mmol). The mixture was heated at reflux for 20 h, and then aqueous NH_4Cl (50 mL) was added. The organic layer was washed with $NH_3{\cdot}H_2O$ and water and dried over anhydrous Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography over silica gel (CH_2Cl_2/EtOAc=4:1) to afford 2.54 g (86%) of **D** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ=7.28–7.20 (m, 10H), 7.05 (s, 1H), 6.48 (s, 1H), 6.37 (s, 2H), 5.27 (s, 2H), 4.87 (s, 4H), 2.58 (t, J=7.5 Hz, 2H), 1.57–1.51 (m, 2H), 1.30–1.00 (m, 14H), 0.78 ppm (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ=160.2, 148.8, 137.1, 136.3, 128.5, 128.0, 127.4, 120.4, 106.9, 101.9, 70.0, 53.8, 31.8, 29.5, 29.4, 29.3, 29.1, 25.6, 22.6, 14.0 ppm; HRMS (ESI, m/z): Calcd for $C_{33}H_{42}N_3O_2$: 512.3271; found: 512.3266 $[M+H]^+$.

Compound ***A***

A mixture of **17** (100 mg, 0.065 mmol), **18** (90 mg, 0.26 mmol), **C** (1.17 g, 0.65 mmol), and $[Cu(MeCN)_4]PF_6$ (96 mg, 0.26 mmol) was dissolved in dry CH_2Cl_2 (4 mL) and heated at reflux for 48 h. Aqueous NH_4Cl (10 mL) was added. The organic layer was washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was first purified by column chromatography over silica gel (CH_2Cl_2/MeOH=20:1) and then by preparative GPC (eluent: $CHCl_3$) to afford 171 mg (45%) of **A** as a red solid. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ=8.98 (s, 4H), 8.77(s, 4H), 8.42 (s, 10H), 8.20 (s, 4H), 8.05 (s, 4H), 8.00–7.00 (m, 104H), 6.90–6.50 (m, 14H), 5.70–5.30 (m, 12H), 4.99 (s, 8H), 4.60–3.50 (m, 56H), 3.00 (s, 12H), 2.16 (s, 12H), 1.51 (s, 36H), 0.95–0.82 (m, 72H), 0.64–0.54 ppm (m, 60H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ=160.3, 158.6, 154.3, 150.5, 149.7, 148.6, 147.6, 147.5, 145.3, 141.7, 140.4, 139.9, 139.7, 138.5, 138.2, 138.0, 137.3, 136.5, 136.3, 130.9, 129.0, 128.7, 128.6, 128.5, 128.3, 127.9, 127.7, 127.5, 127.3, 127.0, 126.5, 125.1, 124.9, 120.5, 120.3, 114.8, 112.7, 107.5, 102.6, 70.1, 68.0, 55.8, 37.1, 35.0, 31.9, 31.7, 31.5, 29.7, 29.5, 29.4, 29.3, 27.2, 23.9, 22.7, 22.3, 22.2, 14.1, 13.9 ppm; HRMS (ESI, m/z): Calcd for $C_{372}H_{416}N_{18}O_{22}Zn$: 2775.5634; found: 2775.5682 $[M-2PF_6]^{2+}$.

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