

# Synthesis of Highly Twisted and Fully $\pi$ -Conjugated Porphyrinic Oligomers

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## Supporting Information

**ABSTRACT:** Highly twisted  $\pi$ -conjugated molecules have been attractive but challenging targets. We report here an efficient synthesis of highly twisted diporphyrins with 126° and 136° twist angles that involves an oxidative fusion reaction of planar aminoporphyrin precursors at room temperature. Repeated amination–oxidative fusion sequences provide a unidirectionally twisted tetramer. The twisting angle of the tetramer is 298°.

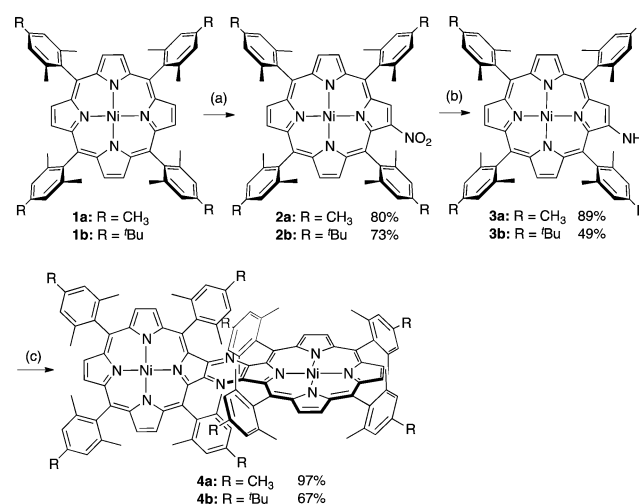
Three-dimensional (3D)  $\pi$ -conjugated molecules have received extensive attention in many chemical research areas due to their interesting structure and unique characteristics.<sup>1–3</sup> Since the discovery of buckminsterfullerenes, synthetic chemists have devoted considerable effort to develop bottom-up approaches to 3D  $\pi$ -conjugated molecules. Construction of 3D structures generally requires harsh conditions, such as laser irradiation, flash vacuum pyrolysis, and photochemical processes, to overcome their high strain energy.<sup>4</sup> However, these protocols could not apply to  $\pi$ -conjugated functional molecules such as porphyrins, which undergo decomposition on heating and light irradiation.

Aniline oxidation is a classic methodology for linking aromatic amines. However, the synthetic usefulness of this method has been overshadowed because of uncontrollable reactions to form a mixture of fused oligomers.<sup>5</sup> In contrast, we have found that the oxidation of 2-amino-5,10,15-triarylporphyrins proceeded selectively to provide planar pyrazine-fused diporphyrins in high yields in one step.<sup>6</sup> Herein, we report the synthesis of highly twisted diporphyrins and tetraporphyrin with very large twisting angles (136° and 298°) from planar 2-aminoporphyrin precursors with more bulky substituents.

Highly twisted molecules, particularly  $\pi$ -systems with 3D character, remain attractive but challenging targets.<sup>7</sup> Twisting  $\pi$ -systems lead to the emergence of intriguing characteristics such as chiroptical properties and anisotropic crystal packing. The twisting approach to 3D  $\pi$ -systems has been investigated in the synthesis of oligoacenes, referred to as “twistacenes”. The maximum edge-to-edge twisting angle of the longest twistacene is 144°. However, additional systems with greater twist angles are needed if the specific features that are induced by molecular twisting are to be explored in detail.

We attempted oxidative fusion of aminoporphyrin **3a** with four mesityl groups, which was prepared through nitration and reduction of **1a**. Oxidation of **3a** with DDQ (2.0 equiv) in CHCl<sub>3</sub> at room temperature afforded fused dimer **4a** in 4% yield. After extensive optimization, we found that the oxidation of **3a** in  $\alpha,\alpha,\alpha$ -trifluorotoluene/trifluoroacetic acid (TFA, 20 equiv) afforded **4a** in 97% yield (Scheme 1). None of the desired product was obtained without TFA. This protocol was also applied to **3b** with sterically more demanding substituents to furnish **4b** in 67% yield. Notably, this procedure enables the synthesis of highly congested diporphyrins **4a** within 10 min even at room temperature.

## Scheme 1. Oxidative Dimerization of Nickel(II) 3-Aminoporphyrins **3** to Diporphyrins **4**<sup>a</sup>

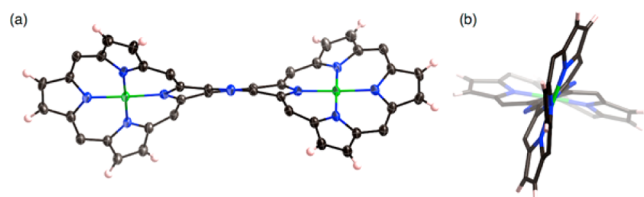


<sup>a</sup>(a) LiNO<sub>3</sub> (2 equiv), CHCl<sub>3</sub>/AcOH/Ac<sub>2</sub>O, 75 °C, 15 h for **1a**; LiNO<sub>3</sub> (4 equiv), CHCl<sub>3</sub>/AcOH/Ac<sub>2</sub>O, 55 °C, 4 h for **1b**. (b) Sn (excess), conc. HCl, CHCl<sub>3</sub>, 60 °C, 1 h for **2a**; Sn (excess), conc. HCl, CHCl<sub>3</sub>, 60 °C, 3 h for **2b**. (c) DDQ (2 equiv), TFA (20 equiv), PhCF<sub>3</sub>, RT, 10 min for **3a**; DDQ (2 equiv), TFA (20 equiv), PhCF<sub>3</sub>, RT, 2 h for **3b**.

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X-ray diffraction analysis of the products revealed that the present oxidative fusion reaction transformed 2D planar precursors into 3D twisted  $\pi$ -systems. The structures of the fused diporphyrins **4a** and **4b** are shown in Figure 1 and Figure



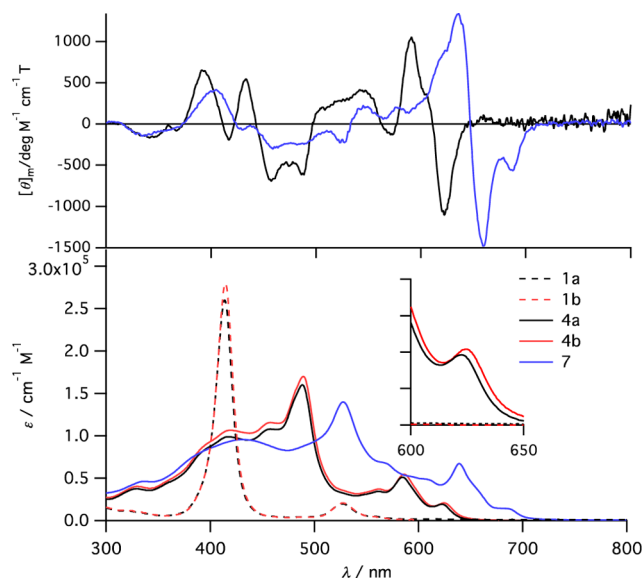
**Figure 1.** X-ray crystal structure of dimer **4a** (a) side and (b) front views. Mesityl groups are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

S11, respectively. Interestingly, both **4a** and **4b** exhibit highly twisted conformations in which the central pyrazine ring is also twisted. The twist angles of the pyrazine rings in **4a** ( $13.01(9)^\circ$ ) and **4b** ( $13.18(8)^\circ$ ) are nearly the same. While **1a** is completely planar (Figure S10), the porphyrin units in **4a** and **4b** adopt ruffled conformations. The two porphyrin units are twisted in the same direction, and the edge-to-edge twisting angles in **4a** and **4b** are  $125.6(8)^\circ$  and  $136.3(7)^\circ$ , respectively. Meanwhile, **4a** and **4b** demonstrate unusually high solubility even in hexane.<sup>8</sup> This fact demonstrates that deformation of  $\pi$ -surfaces leads to significant enhancement of solubility. This is remarkable since porphyrin oligomers typically suffer from low solubility.

Different dynamic behaviors between **4a** and **4b** were observed in  $^1\text{H}$  NMR analysis. At room temperature, **4a** exhibited two broad signals due to protons at the 3- and 5-positions of the mesityl groups. On the other hand, four aryl proton peaks were observed in **4b**. This difference is likely due to the rapid twist inversion of **4a** compared with the relatively stable twisting of **4b** at room temperature. In principle, the aryl proton signals should appear as four peaks in the twisted conformation. However, these peaks are interconvertible and merged into two peaks by twist inversion. This hypothesis was confirmed by variable temperature NMR analysis; four aryl proton signals in **4b** became broader at higher temperatures and coalesced at  $100^\circ\text{C}$  (Figure S5). Because of the high rotation barrier of mesityl groups, the signal broadening can be attributed to the helicity inversion.<sup>9</sup>

In  $^1\text{H}$  NMR spectra, pyrrole proton signals of **4b** were upfield shifted as compared to **4a**, while chemical shifts of monomers **1a** and **1b** were almost the same. This indicates that the  $\pi$ -twisting significantly influences the ring current of the porphyrin unit. The lower NICS(0) values of **4a** than **4b** also support substantially weakened aromaticity of the porphyrin ring (Figure S15).

We expected that the subtle effect of molecular twisting could be detectable on the basis of change in interporphyrinic interactions in the twisted diporphyrins.<sup>10</sup> Figure 2 shows the UV-vis absorption spectra of **1a**, **1b**, **4a**, and **4b** in  $\text{CH}_2\text{Cl}_2$ . Both dimers **4a** and **4b** exhibit bathochromic shift and broadening of the spectra compared with the corresponding monomers **1a** and **1b**, which indicates effective expansion of  $\pi$ -conjugation despite their largely twisted structures.<sup>11</sup> Compared with **4a**, **4b** shows slight bathochromic shift ( $51\text{ cm}^{-1}$ ) of the lowest energy band.<sup>12</sup> The spectrum of **4a** was further assigned by magnetic circular dichroism (MCD) spectral analysis. MCD signals for two bands at 622 and 585 nm



**Figure 2.** Magnetic circular dichroism (MCD) (top) and UV-vis absorption (bottom) spectra of **1a** (black dash line), **1b** (red dash line), **4a** (black solid line), **4b** (red solid line), and **7** (blue solid line) in  $\text{CH}_2\text{Cl}_2$ . The inset displays the enlarged absorption spectra.

showed oppositely signed Faraday  $B$  terms, which indicate the presence of two differently polarized transitions. Considering their optically forbidden character, these bands can be assigned as split Q-bands directed to two different axes (long and short axes, respectively). This type of separation of two Q-bands is often observed for fused multiporphyrins with effective  $\pi$ -conjugation.<sup>13</sup>

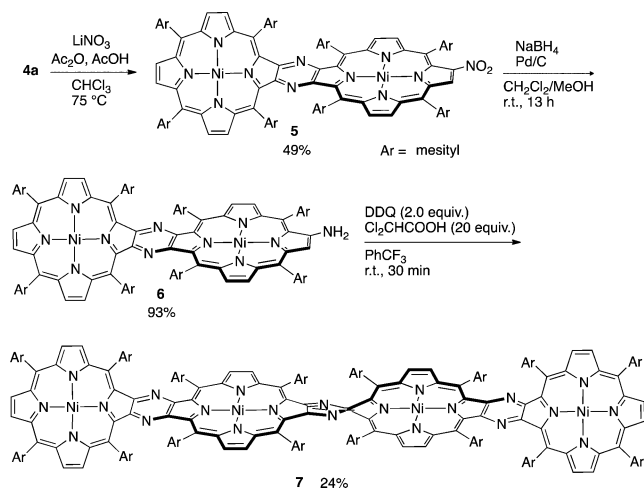
To gain further insight into their electronic transitions, electrochemical analysis was performed. The results of cyclic voltammetry for **4a** and **4b** are summarized in Table S1. Both compounds showed three reversible oxidation and two reversible reduction peaks. Both oxidation and reduction potentials in **4a** and **4b** were split, which indicates the presence of effective electronic communication between two porphyrin units. Only the first oxidation potential of **4b** ( $0.419\text{ V}$ ) was lowered when compared with that of **4a** ( $0.438\text{ V}$ ). This result suggests that twisting affects only the HOMO level to decrease the HOMO-LUMO gap. The HOMO levels of monomers **1a** and **1b** are the same ( $0.50\text{ V}$ ); therefore, the increase in the HOMO energy in **4b** is primarily caused by  $\pi$ -twisting rather than electronic factors of the substituents. These results demonstrate the ability to control HOMO-LUMO gaps by molecular twisting.

Two-photon absorption (TPA) is a third-order nonlinear optical phenomenon, and its probability of occurrence is closely related to  $\pi$ -electron behavior. TPA cross-section values were measured by the Z-scan technique at  $1200\text{ nm}$ .<sup>14</sup> The TPA cross-section value of **4a** ( $640\text{ GM}$ ) was somewhat lower than that of planar dimer **4c** ( $850\text{ GM}$ ) (Figure S9).<sup>15</sup>

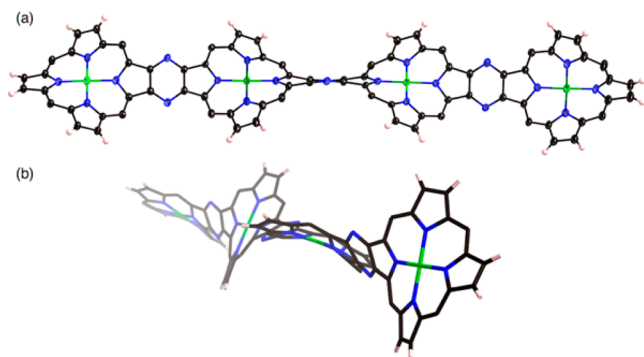
We attempted to synthesize  $\pi$ -extended porphyrin tetramer **7**. The nitration of **4a** with  $\text{LiNO}_3$  afforded nitrodiporphyrin **5** in 49% yield, which was converted to aminodiporphyrin **6** in 93% yield by reduction with  $\text{NaBH}_4$  in the presence of  $\text{Pd/C}$ .<sup>16</sup> Oxidation of **6** under the standard conditions furnished tetraporphyrin **7** in 9% yield. The use of dichloroacetic acid in place of TFA improved the yield of **7** to 24% (Scheme 2).<sup>17</sup>

In contrast to dimer **4a**, six peaks of mesityl groups were observed as relatively sharp signals, which indicate that twist

## Scheme 2. Synthesis of Pyrazine-Fused Tetraporphyrin 7



inversion did not occur at room temperature. The helicity inversion barrier in helical polymers is known to increase in higher polymers.<sup>18</sup> This is the first observation of a similar phenomenon in twisted  $\pi$ -conjugated molecules. The unidirectionality twisted structure of **7** was elucidated by X-ray diffraction analysis (Figure 3). Three slightly different



**Figure 3.** X-ray crystal structure of **7**. (a) Front view and (b) perspective view. The thermal ellipsoids are scaled at 50% probability level. Mesityl groups are omitted for clarity.

conformations were observed in the crystal, with edge-to-edge twisting angles of 298°, 281°, and 295° (Figure S13). Calculated proton chemical shifts of **7** in the twisted structure were obtained by the GIAO method at the B3LYP/6-31G(d) level. A linear correlation between the calculated and observed chemical shifts indicates that tetramer **7** also adopts a twisted conformation in solution (Figure S14). The twisting angles of each two porphyrin fragment were 141°, 161°, and 145°, all of which are larger than that of **4a**. The larger twisting is a reason for higher inversion energy of **7**. Tetramer **7** has remarkable solubility in common organic solvents including hexane.

The UV–vis absorption spectrum of **7** in CH<sub>2</sub>Cl<sub>2</sub> is shown in Figure 2. The substantial bathochromic shift of the lowest energy band suggests the existence of effective  $\pi$ -conjugation over the entire molecule despite large twisting. The presence of electronic communication was also confirmed by electrochemical analysis, which exhibited multiple splitting of oxidation potentials (Figure S2). Interestingly, the average splitting in **7** (0.14 V) was smaller than that in **4a** (0.23 V).

This result demonstrates that  $\pi$ -twisting influences interchromic electronic interactions.

In conclusion, we have successfully synthesized a set of highly twisted, but effectively  $\pi$ -conjugated, fused porphyrin oligomers through oxidative coupling of aminoporphyrins under very mild conditions. We have also demonstrated that the twist angle and the extent of dynamic motion could be controlled via the choice of substituents. Twisting of the  $\pi$ -surface results in reduction of the HOMO–LUMO gap and an enhancement of solubility. The present findings represent an important advance toward the long-term goal of preparing  $\pi$ -conjugated molecular wires, whose properties can be fine-tuned through molecular twisting.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and spectral data for all new compounds. Crystallographic data (CIF files) for **1a**, **4a**, **4b**, and **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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