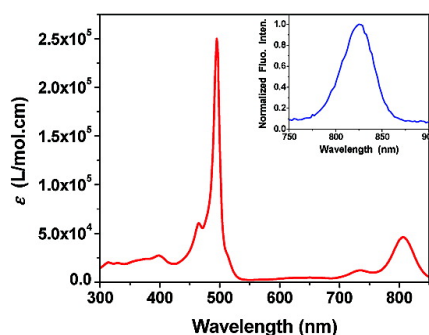
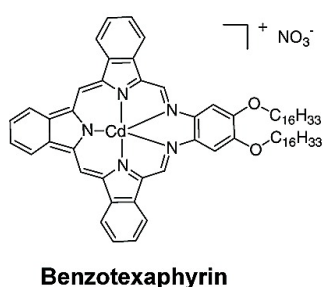


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## Synthesis and Photophysics of Benzotexaphyrin: A Near-Infrared Emitter and Photosensitizer

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Texaphyrins<sup>1</sup> are interesting aromatic macrocycles that show promising applications as nonlinear optical (NLO) materials,<sup>2</sup> photosensitizers,<sup>3</sup> magnetic resonance imaging (MRI) contrasting reagents,<sup>4</sup> and radiation sensitizers.<sup>5</sup> These applications essentially emanate from their unique structural features and photophysical properties, such as their highly conjugated  $\pi$ -electron system, strong Q-band absorption in the near-IR region, long-lived triplet excited state, high quantum yield of the triplet excited-state formation, and high efficiency in generating singlet oxygen.<sup>1,3b,6</sup>

It has been reported that the photophysical properties of texaphyrins could be tuned by structural modifications of the pentaazadentate ligand and the central metal ions.<sup>1,3b,4,6a,b,d</sup> The influence of different numbers of  $\pi$ -electrons, different substituents on the phenyl ring, and different central metals on third-order nonlinearities of texaphyrin derivatives has been systematically investigated by Sun et al.<sup>2</sup> Research has revealed that the texaphyrin derivative with 26  $\pi$ -electrons exhibits a much red-shifted Q-like band at ca. 860 nm, and its molecular second-order hyperpolarizability ( $\gamma$ ) increases drastically in comparison to those of the 18  $\pi$ -electron and the 22  $\pi$ -electron texaphyrins.<sup>2b</sup> However, to date, no efforts have been made to fuse aromatic rings to the pyrrole rings of texaphyrins to further increase the  $\pi$ -conjugation.

To remedy this deficiency, our group designed and synthesized a novel benzotexaphyrin (**8**) that possesses an extensively delocalized  $\pi$ -electron system for the first time. To improve the solubility of **8** in organic solvents, two long alkoxy substituents were introduced. It is expected that, with the extended  $\pi$ -electron system, the energy gap between the HOMO and the LUMO in **8** would be reduced. Therefore, the Q-like band in **8** would be red-shifted compared to that of texaphyrin.

To demonstrate this, the synthesis and photophysical properties of a cadmium benzotexaphyrin (**8**) are reported in this letter. The synthesis follows the general procedure reported by Sessler et al. for texaphyrins.<sup>1</sup> However, due to the instability of isoindole, the strategy used for the synthesis of benzoporphyrin<sup>7,8</sup> was adopted to synthesize the protected tripyrrane dialdehyde and the protected texaphyrin **7**. Finally, the protecting groups were converted to benzene rings through a retro Diels–Alder reaction at 200 °C under vacuum within 10 min.

The bicyclo[2.2.2]octadiene-fused pyrroles **1** and **2** were synthesized according to procedures described in the literature.<sup>8</sup> Condensation of **1** and **2** in dichloromethane in the dark with montmorillonite K-10 clay as catalyst afforded the tripyrrane diester **3**.<sup>9</sup> Trifluoroacetic acid was then used to remove the *tert*-butyl ester groups. Afterwards, Clezy-type formylation<sup>10</sup> yielded the diformyltripyrane **4** as red solids. 1,2-Diamino-4,5-bis(hexadecyloxy)benzene (**5**) was prepared from catechol through alkylation, nitration, and reduction, according to the procedure for 1,2-diamino-4,5-bis((3'-hydroxypropyl)oxy)benzene.<sup>11</sup>

The nonaromatic macrocycle **6** was prepared by an acid catalyzed Schiff base condensation reaction from **4** and **5** in quantitative

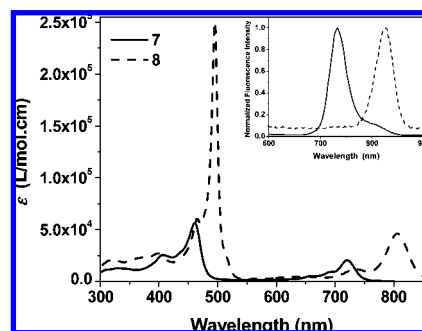


Figure 1. UV-vis absorption spectra and fluorescence spectra (inset) of **7** and **8** in methanol.

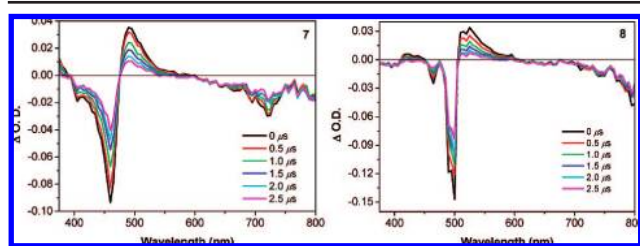
Table 1. Photophysical Parameters of **7** and **8** in Methanol

	$\lambda_{\text{abs}}/\text{nm}$ (log $\epsilon$ )	$\lambda_{\text{f}}/\text{nm}$ ( $\tau_{\text{f}}/\text{ps}$ ; $\Phi_{\text{f}}$ )	$\lambda_{\text{T1-Tn}}/\text{nm}$ ( $\epsilon_{\text{T1-Tn}}/\text{M}^{-1}$ $\text{cm}^{-1}$ ; $\tau_{\text{T}}/\mu\text{s}$ )	$\Phi_{\text{T}}$	$\Phi_{\Delta}$
<b>7</b>	405 (4.41), 461 (4.75); 692 (3.96), 720 (4.31)	734 (594; 0.02)	500 ( $5.4 \times 10^4$ ; 1.93)	0.56	0.11
<b>8</b>	465 (4.78), 495 (5.40), 730 (4.07), 806 (4.66)	825 (895; 0.03)	525 ( $2.9 \times 10^4$ ; 2.21)	0.78	0.65

yield.<sup>12</sup> **7** was synthesized from **6** following the procedure reported for texaphyrins.<sup>12</sup> The crude product was purified by silica gel column chromatography with 10% ethyl acetate in dichloromethane as eluent. The structure and purity of **7** were verified by <sup>1</sup>H NMR and HRMS (see Supporting Information). Benzotexaphyrin **8** was obtained by a retro Diels–Alder reaction of **7** in quantitative yield.<sup>7,8</sup> At ~180 °C under vacuum, the color of the complex changed rapidly from yellowish green to reddish brown in ~10 min, indicating the completion of the reaction. **8** was purified by recrystallization in chloroform and acetone. The formation of benzotexaphyrin was confirmed by its <sup>1</sup>H NMR spectrum, which showed a new peak at 8.3 ppm, while the vinylic proton peaks at 4.6 and 5.3 ppm for **7** disappeared.

The UV-vis spectra of **7** and **8** in methanol are displayed in Figure 1. Similar to the other texaphyrin derivatives,<sup>3b,4,6a,b,d</sup> **7** and **8** exhibit two characteristic absorption bands: the Soret-like bands (B-band) appear in the 400–500 nm region, while the Q-like bands are in the near-IR region. The band maxima and the molar extinction coefficients of **7** and **8** are listed in Table 1. The B(0,0) and Q(0,0) bands of **8** exhibit a 34 and 86 nm bathochromic shift compared to those of **7**. This should be attributed to the increased  $\pi$ -conjugation in benzotexaphyrin.

The inset in Figure 1 shows the fluorescence spectra of **7** and **8** in methanol solutions. The fluorescence of **8** appears at 825 nm, which is ~90 nm red-shifted compared to that of **7**. The fluorescence quantum yield ( $\Phi_{\text{f}}$ ) of **8** is slightly higher than that of **7**. For both complexes, the lowest singlet excited-state lifetimes are



**Figure 2.** Time-resolved triplet transient difference absorption spectra of **7** and **8** in methanol. The excitation wavelength was 355 nm.

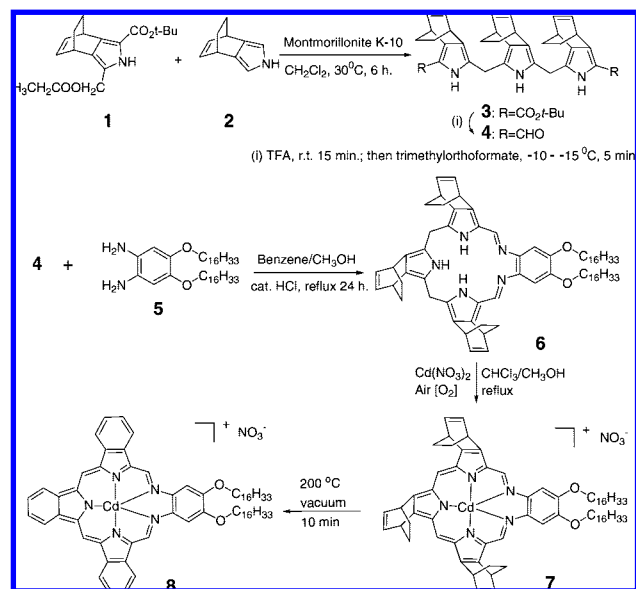
hundreds of picoseconds (Table 1), which are of the same order as that for Cd-Tex.<sup>6a</sup>

To understand the triplet excited-state ( $T_1$ ) characteristics of **7** and **8**, heavy-atom induced fluorescence quenching experiments<sup>13</sup> and time-resolved transient difference absorption measurements were conducted to estimate the energy level of the lowest triplet excited state and obtain the lifetime and quantum yield of the lowest triplet excited state, respectively. Fluorescence quenching experiments in the presence of different concentrations of  $\text{CH}_3\text{I}$  gave rise to an  $E_{T1}$  of 138 kJ/mol for **7** and 119 kJ/mol for **8**. Consistent with the trend observed in the UV–vis and fluorescence spectra, the triplet excited-state energy of **8** also decreases compared to those of **7** and other texaphyrins.<sup>6a</sup> Figure 2 shows the triplet transient difference absorption spectra of **7** and **8**. The features of these spectra are quite similar, composed of two bleaching bands between 450 and 500 nm and 700–800 nm, which corresponds to the B-like and Q-like bands of the UV–vis absorption, respectively, and a positive band at 475–570 nm for **7** and 505–590 nm for **8**. The triplet excited-state absorption coefficients were measured using the singlet depletion method.<sup>14</sup> The quantum yield of the triplet excited-state formation ( $\Phi_T$ ) is then deduced from the comparative method by using SiNc as the reference.<sup>15</sup> The resultant  $\Phi_T$ 's of **7** and **8** are comparable to those of reported texaphyrins.<sup>3b</sup> In addition, from the decay of the transient absorption, the triplet excited-state lifetime was obtained to be  $\sim 2 \mu\text{s}$  for both complexes. All these parameters are in line with the photophysical parameters of other cadmium texaphyrins reported in the literature.<sup>3b,6a</sup>

Due to the low-lying  $T_1$  state and high quantum yield of  $T_1$  formation as well as the long lifetime of  $T_1$ , efficient energy transfer from the  $T_1$  states of **7** and **8** to the ground-state oxygen is expected to occur. By monitoring the singlet oxygen emission at 1270 nm and using SiNc as the reference,<sup>16</sup> the quantum yield of singlet oxygen generation for **7** and **8** was obtained to be 0.11 for **7** and 0.65 for **8**. The energy transfer efficiency ( $S_A = \Phi_A/\Phi_T$ ) from  $T_1$  to the ground-state oxygen is obviously higher for **8** than **7**. This could possibly be attributed to the lower triplet excited-state energy of **8**, which matches the energy level of the ground-state oxygen better. The higher  $\Phi_T$  of **8** could also play a role.

In summary, a highly conjugated aromatic complex benzotexaphyrin **8** was successfully synthesized and fully characterized. It shows a red-shifted Q-like absorption band and NIR fluorescence with respect to the corresponding Cd-Tex. Photophysical studies indicate that **8** possesses low triplet excited-state energy, high triplet quantum yield, and singlet oxygen generation efficiency. These characteristics make benzotexaphyrin **8** a promising NIR photosensitizer and emitter. In addition, due to the extended  $\pi$ -electron system, **8** is expected to exhibit an enhanced third-order nonlinearity, which is currently under investigation. For future photodynamic therapy and biomedical imaging applications, Zn, Lu, or Gd

### Scheme 1. Synthetic Route for Benzotexaphyrin (**8**)



benzotexaphyrins that are more suitable for biomedical applications will be synthesized.

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**Supporting Information Available:** Synthetic details for **3**, **4**, and **6–8**,  $^1\text{H}$  NMR spectra of **7**, HRMS spectra of **7** and **8**, and photophysical measurements details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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