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Tetrahedron Letters 48 (2007) 5687–5691

Tetrahedron Letters

Synthesis and crystal structure of 21,23-dithiaporphyrins and their nonlinear optical activities

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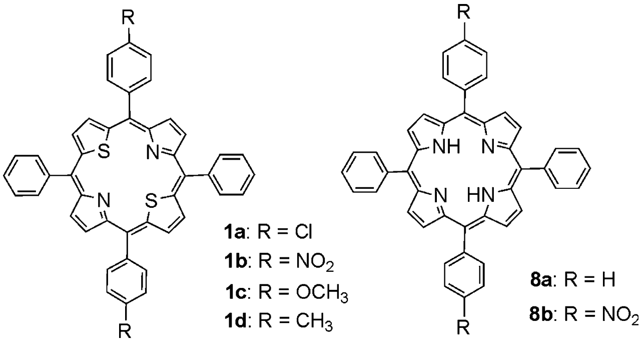
Received 9 March 2007; revised 29 May 2007; accepted 1 June 2007
Available online 5 June 2007

Abstract—A series of novel 21,23-dithiaporphyrins have been synthesized and determination of their optical nonlinearities demonstrated that they have much larger nonlinear refractive cross section than normal porphyrins and exhibit reverse saturable absorption.

There has been a great deal of interest in the nonlinear optical (NLO) responses of conjugated organic molecules during the past 20 years because of their potential utilities in optical switching, optical memory, optical power limiting and 3D microfabrication.[1,2] The nonlinear optical responses of organic molecules depend strongly on the molecular structure. Among the numerous molecules, porphyrins and their derivatives have exhibited great potential application due to their large and rigid π-conjugated structures and versatile modification.[3–7] Changing substituent groups on the *meso*- or β-positions of the porphyrin can result in different nonlinear optical properties;[8–10] however, outer rim modification can only affect the electronic structure of porphyrin slightly, core alteration will change the electronic structure of macroring more directly and remarkably.[11–13] Core-modified porphyrins, in which one or more internal nitrogen atoms are replaced with other heteroatoms or carbon, have shown some novel properties such as stabilizing unusual metal oxidation states, catalysis, and photodynamic therapy (PDT),[14–17] and are expected to be promising nonlinear optical materials. Up to now the optical nonlinear property of core-modified porphyrin is seldom reported.

To systematically exploit the distinctive properties of core-modified porphyrins requires the ability to locate not only the heteroatom in the core of the porphyrin, but also substituents arranged about the porphyrin perimeter.[18–22] We herein describe a rational synthetic strategy for 21,23-dithiaporphyrins (DSPs), bearing one kind of substituent groups at 5,15 positions and another kind of substituent groups at the 10,20 positions (Scheme 1). Such compounds could not be readily available through normal synthetic strategies or easily separated from their analogues.[22] This approach offers more feasibility and convenience to the porphyrin chemist to design and construct the unique units. We also report the crystal structure of **1a** and compare the nonlinear refractive cross section of compound DSPs with normal porphyrins.



Scheme 1. Structures of compounds **1** and **8**.

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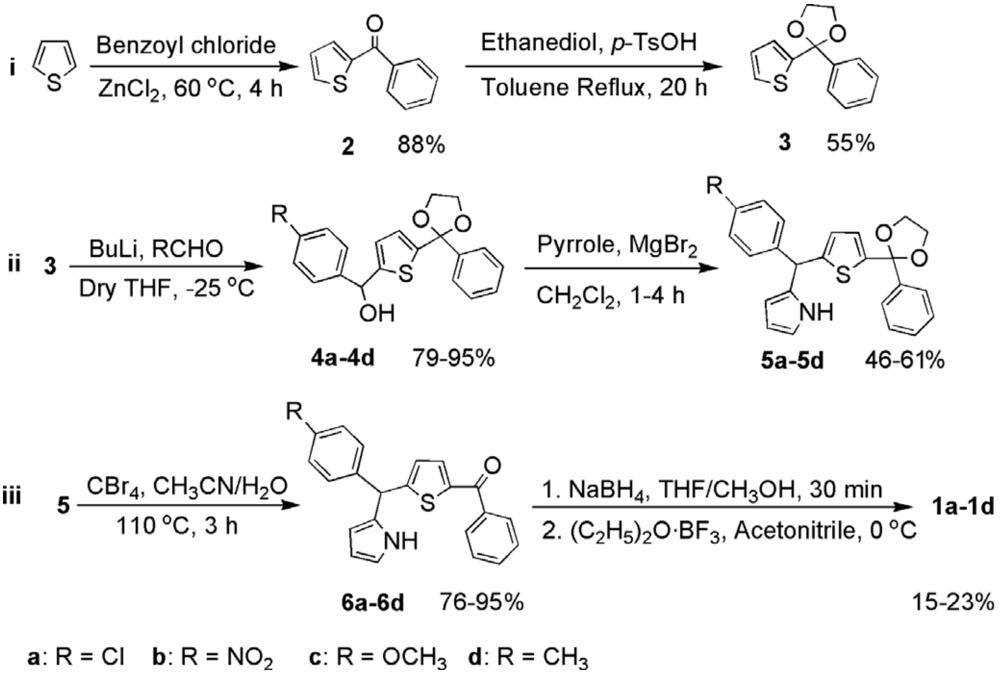
doi:10.1016/j.tetlet.2007.06.002



Scheme 2. Synthesis of 21,23-dithiaporphyrins **1**.

The synthetic strategy of DSPs is shown in Scheme 2. Compound **3** was obtained by treating thiophene with benzoyl chloride, and then protected by glycol. Treatment of **3** with *n*-butyllithium followed by an aromatic aldehyde afforded the corresponding compounds **4**.[18] To get compound **5**, the mild Lewis acid catalyst magnesium bromide was selected against trifluoroacetic acid and trifluoroborane, since the strong acid catalyst would destroy the protective group. As **5** was not stable enough, the hydrolyzation would also react under mild condition, and carbon tetrabromide was selected as the appropriate catalyst.[23] The ketone of **6** was easily reduced to alcohol by sodium borohydride,[16] then 10 equiv of ammonium chloride and 0.1 equiv of boron trifluoride etherate were added,[18] the reaction solution was stirred for 0.5–1 h under nitrogen atmosphere, then 2 equiv of DDQ was added. The crude compounds were purified by silica gel column chromatography and **1** was obtained as purple solids in 15–23% yields. The target compounds were characterized by ^{1}H NMR, ^{13}C NMR, HR-MS and ESI-MS. So it is a general route to synthesize such kind of 21,23-dithiaporphyrins whose 10,20 positions were phenyl and 5,15 positions contained electron-withdrawing or electron-donating groups.

The absorption spectra (Fig. 1 and Table 1) of DSPs show typical porphyrin character, with different substituents changing the observed wavelengths and deeply affecting the absorbency. The emission bands (Fig. 1 and Table 1) of DSPs are also red shifted relative to normal porphyrin. Fitting parameters of fluorescence decay curves (τ) for compounds **1** and **8** are shown in Table 2. They indicate that fluorescence lifetimes of **1** are shorter than normal porphyrins and they are not affected deeply by different substituents.

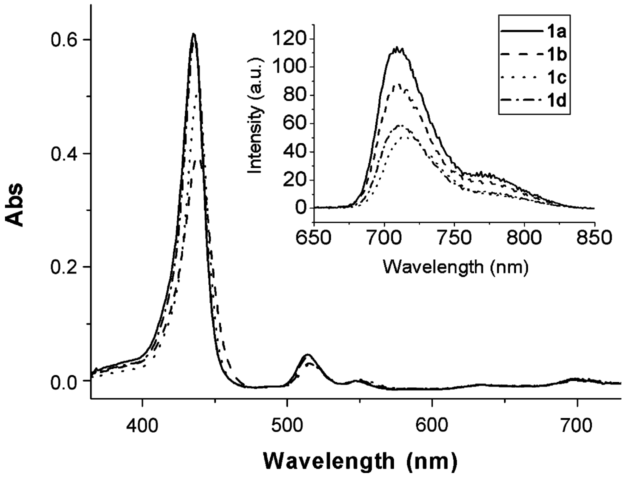


Figure 1. Absorption spectra and fluorescence spectra (inset, at $\lambda_{ex} = 435$ nm) of compound **1** (10^{-6} mol/l) (all in chloroform).

The structure of **1a** was elucidated by a single crystal X-ray diffraction (Fig. 2), and the structure is C_2 symmetrical. The deviations from planarity of the core, expressed as dihedral angles between the plane of the four *meso* carbons and the planes of the five-membered rings, are thiophene 0.2, pyrrole 7.5 of **1a**. The thiophene rings are almost in the plane of the core, so the substituents at *meso* carbons induce more planarity in our compounds compared to the parent dithiaporphyrins.[24] Meanwhile, distances between N,N′ and S,S′ are shortened. The nonbonded distances of N,N′ and S,S′ are 4.581 Å and 3.056 Å, respectively, in **1a**.

The optical nonlinear absorption and nonlinear refraction of the new 21,23-dithiaporphyrins have been

Table 1. Absorption and fluorescence data of coumpound **1** (all in chloroform)

Porphyrin	Soret band λ_{max} (nm) ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})	Absorption Q-bands, λ_{max} (nm) ($\varepsilon \times 10^{-3}$ M^{-1} cm^{-1})				Fluorenscence λ_{max} (nm) ($\lambda_{ex} = 435$ nm)
		IV	III	II	I	
1a	435 (612.2)	514 (34.3)	547 (8.8)	632 (2.2)	696 (5.4)	708
1b	438 (396.8)	515 (26.2)	550 (9.1)	633 (1.9)	696 (4.3)	708
1c	438 (506.0)	516 (24.8)	551 (9.5)	635 (1.5)	700 (5.4)	717
1d	436 (607.2)	516 (24.8)	551 (9.5)	635 (1.5)	700 (5.4)	711

Table 2. Optical nonlinearities (σ_0,σ_1,σ_{r1}/10^{-17} cm^2; β_{eff}/10^{-9} cm/W; n_{2eff}/10^{-14} cm^2/W; $|T|^{-1}$) and fluorescence lifetimes (τ/ns) of **1** and **8**

	σ_0	σ_1	σ_{r1}	β_{eff}	n_{2eff}	$\lvert T\rvert^{-1}$	τ
8a	2.63	6.85	−1.55	3.58	−1.40	0.037	4.885
8b	2.96	5.98	−1.45	2.86	−1.28	0.042	6.410
1a	3.38	5.92	−4.40	2.34	−3.35	0.135	1.039
1b	3.23	4.45	−4.60	0.83	−3.48	0.394	1.088
1c	3.02	5.74	−5.30	1.86	−3.64	0.184	1.044
1d	2.89	5.52	−4.50	2.02	−3.38	0.157	1.072

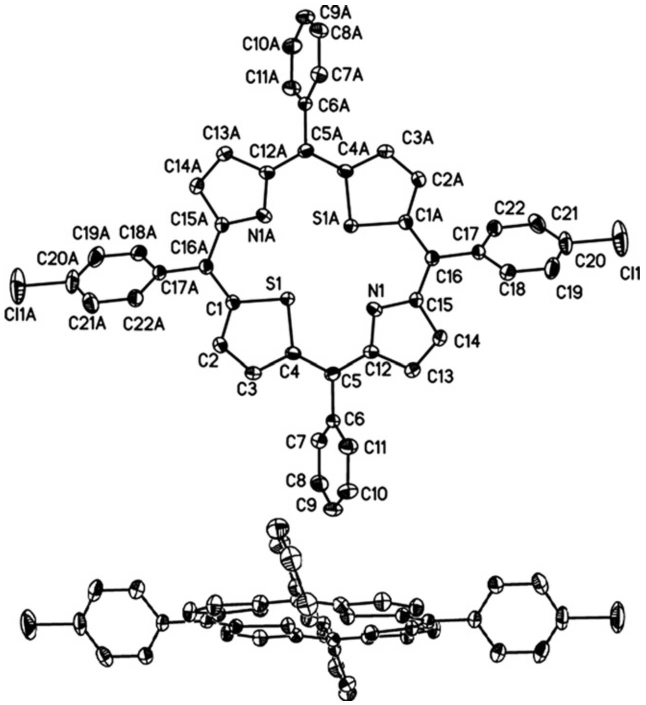


Figure 2. Crystal structure of **1a** (crystallographic data in Supplementary data).

measured by open- and closed-aperture Z-scan experiments performed with a picosecond laser source.[25] Table 2 gives the ground state S_0–S_1 absorption cross section σ_0 and the excited state S_1–S_n absorption cross section σ_1[26] and the excited state refractive cross section σ_{r1}[27] obtained by fitting the Z-scan results. We also performed the Z-scan experiments of **8a** and **8b** to compare the change of optical nonlinear absorption and nonlinear refraction with DSPs. TPP (**8a**) is well known to exhibit RSA at the wavelength of 532 nm,[3] which is identical with our experimental results. Furthermore, a negative nonlinear refraction was observed in TPP.

In a similar fashion to TPP, DSPs also exhibit RSA and negative optical nonlinear refraction. However, all the DSPs have about 3–4 times enhancements of excited state refractive cross section relative to TPP. Figure 3 depicts the Z-scan curves of **1b** and **8b** with the same substituent group. Although **1b** exhibits an obvious RSA, the ratio of σ_1 to σ_0 for **1b** ($\sigma_1/\sigma_0 = 1.38$) is much less than that of **8b** ($\sigma_1/\sigma_0 = 2.02$), which indicates decreasing of RSA for **1b**. The optical nonlinear refraction Z-scan curves depicted in Figure 3b are obtained from dividing the closed-aperture Z-scan data by corresponding open-aperture Z-scan data. Clearly we see that nonlinear refraction is negative for both **1b** and **8b**, and the large enhancement of nonlinear refraction can be observed for **1b**. The solid lines in Figure 3b show fits, giving $\sigma_{r1} = -4.60 \times 10^{-17}$ cm^2 for **1b** and $\sigma_{r1} = -1.45 \times 10^{-17}$ cm^2 for **8b**.

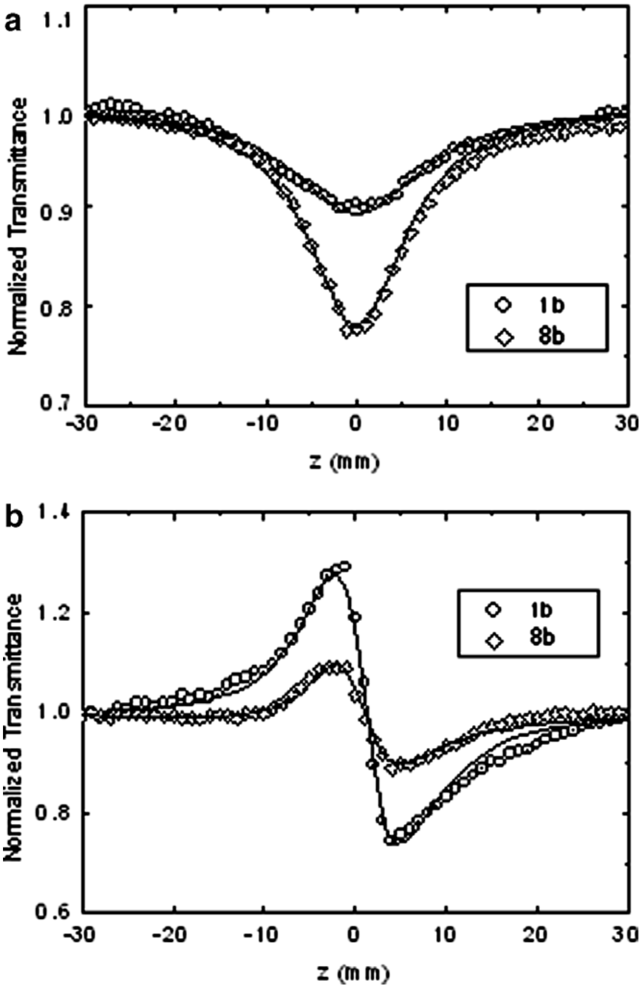


Figure 3. The Z-scan curves of **1b** and **8b** (top absorption and bottom refraction).

Just as the real and imaginary components of the linear susceptibility $\chi^{(1)}$ are associated with refraction and absorption, nonlinear refraction (NLR) and nonlinear absorption (NLA) can be described by the real and imaginary parts of third-order nonlinear susceptibility $\chi^{(3)}$. Usually, the third-order nonlinear refractive index n_2 and nonlinear absorptive coefficient β are used in nonlinear refraction and nonlinear absorption. The material's suitability for device fabrication can in most cases be estimated by considering a figure of merit (FOM) detailing the ratio of the nonlinear refraction to nonlinear absorption. The FOM is usually given as $|T|^{-1} = |n_{2\text{eff}}/(2\lambda\beta_{\text{eff}})|$.[28,29] When the nonlinearity is due to the population of excited state, what we observe is not a true $\chi^{(3)}$ effect but is a sequential $\chi^{(1)}$:$\chi^{(1)}$ process (effective third-order nonlinearities). Here, the first $\chi^{(1)}$ is associated with the ground state absorption, the second with the resulting excited state absorption or refraction. In order to determine the FOM of DSPs, we have also fitted the data of *Z*-scan experiments with effective third-order nonlinear absorptive coefficient β_{eff} and effective third-order nonlinear refractive index $n_{2\text{eff}}$.[30,31] The values of β_{eff}, $n_{2\text{eff}}$ and the FOM $|T|^{-1}$ of DSPs are given in Table 2. Among the porphyrin compounds used in our experiments, **1b** had the largest FOM: $|T|^{-1} = 0.394$, which is about 10 times larger than that of **8b** ($|T|^{-1} = 0.042$).

In conclusion, we have developed a general synthetic strategy of a series of novel 21,23-dithiaporphyrins bearing one kind of substituent group at 5,15 positions and the other kind of substituent group at 10,20 positions. It not only provides a reasonable route to synthesize core-modified porphyrins with especial symmetry using facile precursors and catalysts, but also offers more feasibility in the design and construction of porphyrin units. We determined the optical nonlinear behavior of these dithiaporphyrins, and found that DSPs had larger enhancement of nonlinear refractive cross section than normal porphyrins. Changes of nonlinear refraction were mainly attributed to sulfur atoms introduced to the central of porphyrin, and outer rim modification of porphyrin would alter the nonlinear absorption at the same time. We found 10 times larger FOM on **1b**, with large nonlinear refraction and small nonlinear absorption. Efforts are being undertaken to further enhance and characterize optical nonlinearities of core-modified porphyrins.

Crystallographic data of the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 630521 for **1a**. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or web: http://www.ccdc.cam.ac.uk). The time-resolved fluorescence measurements were carried out on Acton Research SpectroPro-300i spectrograph coupled with an ultrafast gated ICCD camera (LaVision, PicoStar). A frequency-doubled Ti:Sapphire laser system (Spectra Physics) performing at 1 kHz was used as an excitation source. The typical pulse width was less than 130 fs fwhm at 400 nm.

Acknowledgments

We thank the 973 Program (2006CB932900) and NSFC (Nos. 20572048, 20421202 and 10574075), Asia Research Center in Nankai University (No. AS0528) and the Preparatory Project of the National Key Fundamental Research Program (No. 2004CCA04400) for their generous financial support.

Supplementary data

Supplementary data (Experimental, NMR, mass, X-ray crystal structure data, absorption and emission spectral data of selected compounds.) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.002.

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