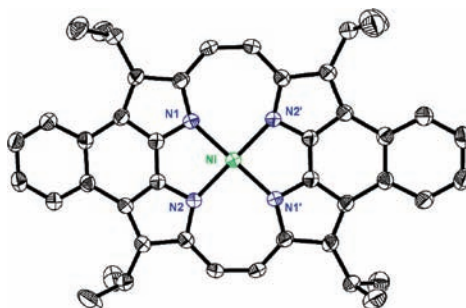# Dinaphthoporphycenes: Synthesis and Nonlinear Optical Studies

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ABSTRACT

Naphthobipyrrole-derived porphycenes are synthesized for the first time via McMurry coupling of the β-alkylated 2,9-diformylnaphthobipyrrole derivatives, which in turn were prepared easily from 2,3-naphthalene bishydrazine in four steps. Insertion of nickel into the porphycene core results in transformation of the rectangular N4-core into a square type geometry owing to the fusion of naphthalene moiety onto the bipyrrole entities. These porphycenes show large, intensity dependent three-photon absorption.
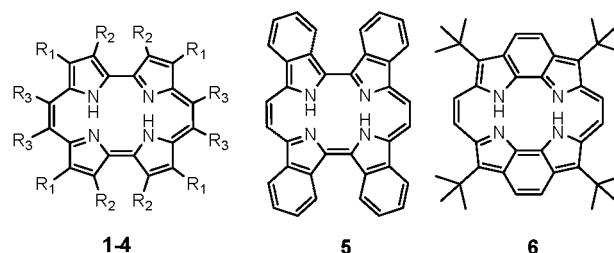
Porphycene **1** is the first constitutional isomer of porphyrin reported by Vogel and co-workers in 1986.[1]

1-4   **5**   **6**

1. $R_1 = R_2 = R_3 = H$
2a-b. R_1 = Et, R_3 = H; a: R_2 = Me, b: R_3 = Et
3a-b. R_2, R_3 = H; a: R_1 = *n*-Pr., b: R_1 = Ph
4a-b. R_1, R_2 = H; a: R_3 = *n*-Pr, b: R_3 = Ph

Since its initial disclosure many porphycene derivatives and their metal complexes have been reported.[2] Predominantly these derivatives contain alkyl substituents at the β-pyrrole or *meso* positions. Substituents play a more major role in modulating both the physical (e.g., solubility) and chemical properties (e.g., fluorescence, rate of metalation) of porphycenes than porphyrins.[2] For example, only 2,7,12,17-

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tetrapropylporphycene **3a** could provide the desired solubility as compared to its methyl or ethyl counterparts.[2b] However, insertion of Zn(II) in **3a** proved to be futile.[2b] On the other hand, the β- octaalkylporphycenes **2**, while proving to be better candidates for Zn(II) insertion, were found nonfluorescent in nature,[2c] unlike isomeric octaethylporphyrin (Φ_F 0.13).[3] Moreover, *meso*-tetra-*n*-propylporphycene **4a** shows extremely weak fluorescence,[4] whereas *meso*-tetraphenylporphycene **4b**[5] displays strong fluorescence (Φ_F 0.23). Porphycenes, owing to their structural resemblance to porphyrins, have been explored as possible photosensitizers in photodynamic therapy (PDT) and found better than the latter.[6]

Third-order nonlinear optical (NLO) materials possess tremendous potential in applications such as two-photon PDT, optical limiting, 3D-optical memory.[7] Recently large enhancement of a two photon absorption (2PA) cross section ($\sigma^{(2)}$) was observed in the case of conjugated porphyrin dimers, directly linked fused porphyrin dimers, and expanded porphyrins.[8a−c] Particularly, aromatic core-modified porphyrins display very large values of $\sigma^{(2)}$.[8d,e] However, reports on three photon absorption (3PA) are scarce, in spite of its advantages in deep-site PDT, optical limiting, and 3D nanofabrication leading to terabyte-level data storage.[9] Moreover, NLO studies on isomeric porphyrins are rare. To our knowledge, there is only one report on 2PA studies of porphycene.[10] It has been observed, in the case of benzosapphyrins, extending the π-systems by fusing the bipyrrole

moiety with an aromatic ring has a very dramatic effect on the electronic properties of the macrocycle than a multiple fusion of benzene rings through the β-positions of respective pyrrole units.[11]

Keeping in view the above perspective, we delve into a porphycene system where two bipyrrolic units are involved in macrocycle formation. Therefore, fusion of these entities with aromatic rings is expected to have a much greater effect on the photophysical properties including the NLO behaviors. Recently reported tetrabenzoporphycene **5b**[12] has a major problem regarding its solubility. Dibenzoporphycene **6**[13a] reported earlier by Vogel and co-workers exhibits interesting photophysical properties,[13b,c] but the synthesis and characterization of this macrocycle are yet to be reported in the public domain. However, the synthesis of one of the building blocks 2,7-diformyl-3,6-dimethylbenzodipyrrole was reported recently.[11] In this context, we found a convenient method to synthesize naphthobipyrrole, which can be employed as a building block for porphycene synthesis.[14a] This has an added advantage of extending the aromatic π-conjugation further, thereby, imparting better photophysical and NLO properties. Keeping these views in mind, we designed our target dinaphthoporphycenes and planned to introduce alkyl chains of at least 3 carbon units at their remaining four β-pyrrole positions presumably, to obtain better solubility of the resultant porphycene derivatives.

Here, we report a convenient and efficient route to the synthesis of dinaphthoporphycenes **7a−c** and their Ni(II)-derivatives **8b−c** and their multiphoton absorption studies.[16] Though the Vilsmeier−Haack formylation of unsubstituted naphthobipyrrole is reported to yield the corresponding 3,8-diformyl derivative,[14b] the modified acylation reaction with various *N,N*-dimethylamide derivatives resulted in 2,9-diketone derivatives exclusively. These diketones when subjected to McMurry type coupling did not yield any macrocycles. As a consequence, we revisited the reaction scheme for the synthesis of naphthobipyrrole and found that reaction of 2,3-naphthalene bishydrazine with suitable α-keto esters **9a−c** formed the corresponding bishydrazones **10a−c** in nearly quantitative yield, which, upon polyphosphate ester (PPE) mediated cyclization, led to the easy introduction of β-alkyl groups in the resultant naphthobipyrrole diesters **11a−c** (Scheme 1) in 26−67% yield from the combined two steps. However, Sessler's group adopted *p*-toluenesulfonic acid mediated cyclization to obtain the diesters (R =

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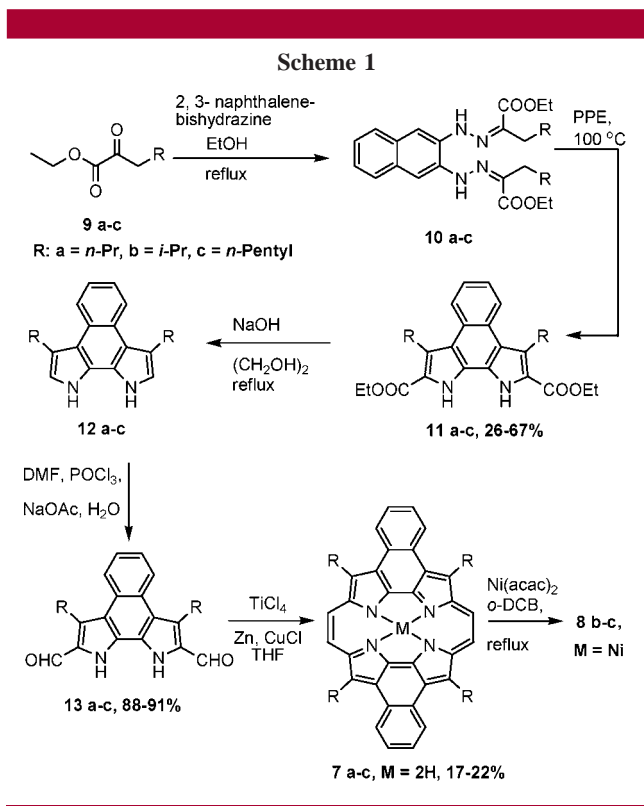(11) Panda, P. K.; Kang, Y.-J.; Lee, C.-H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4053–4055.

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Scheme 1

UV–vis, ^{1}H and ^{13}C NMR spectroscopy, mass, and elemental analysis. The absorption spectra of **7a–c** has large red-shifted absorption bands compared to **1**, where the lowest energy band appears at ~715 nm.[1] These porphycenes show well-defined Soret bands, near 400 nm unlike **6**,[13b] and the lowest energy Q-band is relatively more intense (~0.49) compared to the Soret band than other porphycenes.[1,2] Again there are few UV bands with maxima at 265 nm, which is attributed to the naphthalene moieties in the macrocycle (Figure 1).
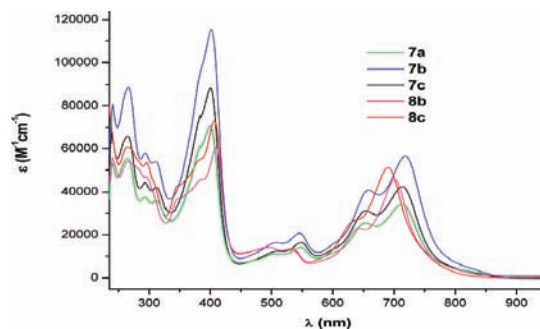

Figure 1. UV–vis spectra of **7a–c** and **8b–c** in CHCl$_3$.

1-ethylpentyl, isopropyl, and n-pentyl).[16] This method results in a marginal increase in yields except for **11b** (two step 62% vs 26%). Subsequent base mediated hydrolysis and decarboxylation resulted in α-free bipyrrole derivatives **12a–c** in almost quantitative yield, which upon Vilsmeier–Haack formylation resulted in the formation of desired dialdehydes **13a–c** in good yields (88–91%). The method implemented for the above two steps are quite general in nature and followed by us as well as by Sessler et al. and resulted in similar yields.[16]

All the above steps are quite straightforward and could be carried out in gram scales. The bishydrazones were supposed to form three geometrical isomers as the result of the two C=N double bonds in the product moiety, but their separation is not warranted as the subsequent product is not at all affected by this isomerism. However, for analytical purposes, the fastest moving isomer was separated in small quantity. With the required dialdehydes in hand, McMurry coupling reactions were performed to obtain the desired porphycenes. Unlike, in the case of **6**, where unoxidized product was isolated after McMurry coupling and oxidized further to obtain the dibenzoporphycene,[13a] we obtained **7a–c** directly in 17–22% yield. This is attributed to the easy reorientation of the ring current for the naphthalene moiety during oxidation of the McMurry coupled product, which was not possible in the case of the fused benzenoid ring leading to **6**. However, Sessler's group presumed[16] that we have isolated the dihydroporphycene and hence carried out DDQ oxidation to obtain the desired porphycenes (yield for **7b** is 15% vs 22% by us). The reason behind the unusually high yield (52%) obtained for the 1-ethylpentyl derivative is not discussed.[16] These porphycenes were characterized by

Sessler et al. reported only up to 300 nm, and there is no mention about ε-values at the absorption maxima. The proton NMR spectra of **7a–c** reveal highly deshielded NH protons appearing around 9 ppm that could be unequivocally assigned after deuterium exchange experiment. This may be attributed to strong intramolecular N–H...N hydrogen bonding in a rigid macrocyclic framework (due to the fused naphthalene rings), and a similar trend was observed for **6** (10.6 ppm).[15,16] The solid state structure of **7b** could be derived explicitly from the single crystals obtained via slow evaporation of a chloroform/hexane mixture by X-ray diffraction (XRD) analysis, revealing a near-planar geometry (Figure 1). The average deviation of nitrogen atoms from the mean porphycene plane (excluding the isopropyl substituents) is ±0.15 Å[16] which is similar to that for **2a**.[2] The shortest N–N distance in **7b** is 2.49 Å, much shorter compared to that of **1**.[1] Like **6**, porphycenes **7a–c** did not show any fluorescence at room temperature (<10^{-4}).[13b] However, Sessler's group observed weak fluorescence for **7b**.[16]

The metal insertion reactions were investigated for **7a–c** with several metal ions, viz. Zn(II), Cu(II), Ni(II), and Pd(II). However, only Ni(II) could be inserted successfully by refluxing the free bases with Ni(acac)$_2$ in the presence of o-dichlorobenzene and pyridine to yield the desired metal complexes **8b–c** in almost quantitative yield (**8a** could not be characterized due to the lack of solubility). These complexes were characterized by UV–vis, ^{1}H and ^{13}C NMR spectroscopy, mass, and elemental analysis. The absorption spectra of **8b–c** show a general trend of red-shifted Soret bands and blue-shifted Q-bands for porphycenes (Figure 1). However, the four-banded Q-bands were observed, where the relative intensity of Q$_{III}$ and Q$_{IV}$ interchanged upon metalation and the relatively broad Soret bands resolved with
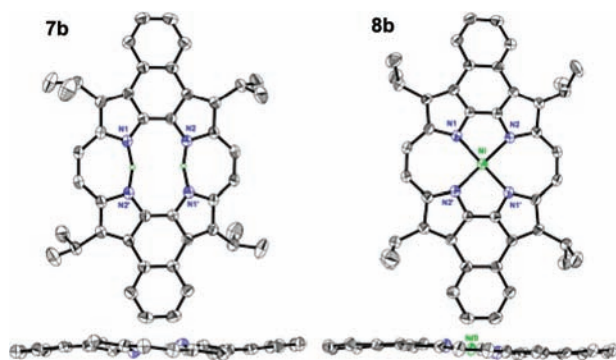
Figure 2. X-ray structure of **7b** and **8b**. Top: front view, Bottom: side view. Ellipsoids are scaled to 50% probability level. For clarity all H-atoms and *i*-Pr group have been omitted from side view; in front view all H-atoms bound to carbon have been removed.

the appearance of resolved shoulders on the higher energy side. The crystal structure of **8b**, derived via XRD analysis, showed a more planar core with Ni sitting in the same plane of the porphycene, and the nitrogen atoms are slightly less deviated (± 0.12 Å) from the mean porphycene plane compared to **7b** (Figure 2). However, the N4-core shows a dramatic change compared to the other metalated porphycenes.[2] Here the N1−N2 distance decreases from 2.95 to 2.64 Å upon metalation, whereas the N1−N2′ undergoes a concomitant increase from 2.49 to 2.67 Å, thereby resulting in an almost square type core, which is unprecedented in porphycene chemistry.

Nonlinear absorptions (NLA) of **7a−c** and **8b−c** were measured by the open aperture Z-scan method using the chirped pulse amplified Ti:sapphire laser system delivering nearly transform-limited (~ 2 ps, 1 kHz repetition rate) pulses at 800 nm as an excitation source.[17] All the measurements were performed with 10^{-4} M solutions in chloroform, and the solvent did not show any 2PA/3PA absorption (Experimental details in Supporting Information). Our intensity dependent studies reveal that they exhibit two photon absorption (2PA) at low peak intensities and three photon absorption (3PA) at higher peak intensities (Figure 3). This can be explained by the presence of two resonances in the absorption spectra of these porphycene molecules, one near 400 nm (Soret band) and another near 265 nm (naphthalene moiety), that may be responsible for the two possible excitation mechanisms. Since 3PA cross sections are weaker, it requires higher peak intensities to be observed. This kind of behavior is observed for the first time, to our knowledge, in these molecules. From Table 1 it can be observed that the $\sigma^{(2)}$ values obtained for the porphycenes at lower laser intensities are moderate (7930−21500 GM), whereas the $\sigma^{(3)}$ values obtained at higher intensities are quite large. In fact the $\sigma^{(3)}$ values are at least an order of magnitude higher

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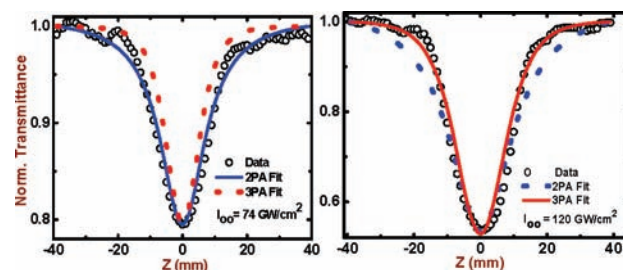
Figure 3. Open aperture Z-scan data of **8b** at two different intensities (in CHCl$_3$).

Table 1. Summary of NLO Coefficients Extracted from Data

sample	I_{oo} (GW/cm^2)	$\sigma^{(2)}$ (GM)	$\sigma^{(3)}$ (cm^{6}s^2/photon^2)
7a	78	8260	-
	118	-	1.44×10^{-75}
7b	98	11600	-
	132	-	3.69×10^{-75}
7c	74	14500	-
	117	-	1.03×10^{-74}
8b	74	21500	-
	120	-	8.01×10^{-75}
8c	120	7930	-
	407	-	4.52×10^{-75}

compared to the highest $\sigma^{(3)}$ values for the antiparallel prophyrin-phthalocyanine dimer reported very recently.[9f]

In conclusion, we have demonstrated a simple route for the synthesis of dinaphthoporphycenes.[16] β-Alkylated naphthobipyrroles can be used as synthetic precursors toward new porphyrinoids. The free base porphycene, **7b**, and its Ni(II) derivative, **8b**, were the first annulated porphycene derivative and its metal complex, whose solid state structure has been explicitly analyzed by XRD. Again, **8b** showed a hitherto unknown square type N4-core upon metalation. Nonlinear optical studies reveal that these simple systems show intensity dependent multiphoton absorbance possessing very high $\sigma^{(3)}$ values. Currently detailed photophysical and nonlinear studies are in progress along with the design and synthesis of new porphyrinoids.

Supporting Information Available: Synthetic procedures and characterization data of new compounds, Crystal data for **7b**, **8b**, and **11b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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