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COMMUNICATION

## Unsymmetrically Functionalized Benzoporphyrins

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

**The synthesis of unsymmetrical *push-pull* benzoporphyrins has been realized. UV-Vis and fluorescence spectroscopy, cyclic voltammetry and DFT calculations reveal subtle substituent effects on the electronic and optical properties of these porphyrins.**

$\pi$ -Extended porphyrins in which one or more aromatic rings are fused to the porphyrin periphery at the  $\beta$ ,  $\beta'$ -positions have attracted considerable attention owing to their unique combination of photophysical, optoelectronic, and physicochemical properties, and their potential applications in various areas such as organic electronics, optic electronic and photomedicines.<sup>1</sup> Although known for decades, the investigation of  $\pi$ -extended porphyrins has been mainly restricted to symmetrical structures. Reports of unsymmetrical  $\pi$ -extended porphyrins are rare due to the limited synthetic methods to access these compounds.<sup>2</sup> In particular  $\pi$ -extended porphyrins with unsymmetrically substituted functional groups remain elusive in the literature. Unsymmetrically substituted porphyrins are expected to display different electronic and photophysical properties from their symmetrical counterparts due to a splitting of the frontier orbitals, and may hold promise for future broader applications. Herein, we report the synthesis of a series of unsymmetrically functionalized benzoporphyrins in which a *push* (electron-donating) group and a *pull* (electron-withdrawing) group are installed at the porphyrin  $\beta$ -positions, and characterized by UV-Vis and fluorescence spectroscopy, and cyclic voltammetry. DFT calculations of these porphyrins were performed to provide insights into their electronic and optical properties.

Design and synthesis of the unsymmetrically functionalized

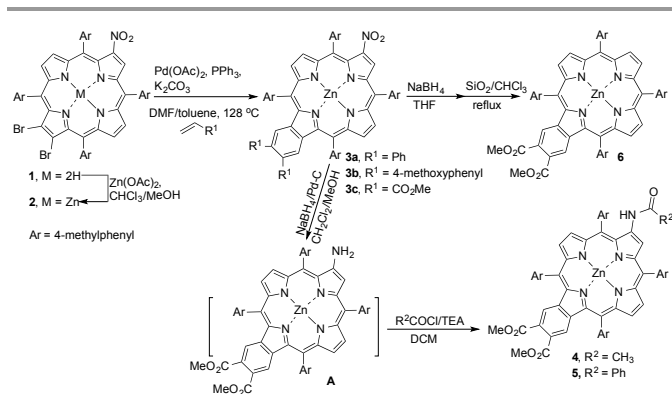
porphyrins (Scheme 1, **3-5**) takes advantage of a concise and versatile method developed in our laboratory for the synthesis of benzoporphyrins,<sup>3</sup> and the unique reactivity of 2-nitro-tetraarylporphyrins.<sup>4</sup> In this method, an alkene reacts with a  $\beta$ ,  $\beta'$ -dibromoporphyrin through a three-step cascade reaction involving a vicinal two-fold Heck reaction, 6- $\pi$  electrocyclization, and subsequent aromatization to afford the benzoporphyrin. We wished to design and synthesize unsymmetrical *push-pull* benzoporphyrins in which both an electron-withdrawing group and an electron-donating group were incorporated at the porphyrin periphery. The presence of a nitro group at the porphyrin  $\beta$ -position can serve as an anchor and direct the bromination of the free base porphyrin to the  $\beta$ ,  $\beta'$ -positions at the opposite pyrrole ring to afford the dibromoporphyrin **1**.<sup>4</sup> After metal insertion of free base porphyrin **1**, the resulting Zn(II) dibromoporphyrin **2** was reacted with substituted alkenes through the Heck-based cascade reaction leading to the benzoporphyrin **3**. The nitro group is a strong electron-withdrawing group. As such, we used styrene and 4-methoxystyrene in this reaction to introduce an electron-donating group at the opposite position of the porphyrin ring to afford the *push-pull* unsymmetrical porphyrins **3a** and **3b**. On the other hand, we used methyl acrylate to introduce two vicinal ester groups to the fused benzene ring, serving as moderate electron-withdrawing groups to give the unsymmetrical *pull-pull* benzoporphyrin **3c**. The nitro group was then reduced to an amine using NaBH<sub>4</sub> to give aminoporphyrin **A**. Aminoporphyrin **A** was not stable, and was further converted into an amide through acylation to generate another type of *push-pull* benzoporphyrin (**4** and **5**).<sup>5</sup> The carbonylamino group serves as “*push*” functionality. For comparison purposes, the symmetrical benzoporphyrin **6** was also prepared through denitration of **3**.<sup>4</sup>

UV-Vis and fluorescence spectra of these porphyrins are compiled in Fig. 1 and Fig S1 (see Supporting Information). As compared with the symmetrical benzoporphyrin **6**, the unsymmetrical benzoporphyrins **3-5** all display broadened and red shifted Soret and enhanced Q bands corresponding to the symmetry breaking of the structure. The unsymmetrical

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† The U.S. Department of Energy, Office of Science, Basic Energy Sciences (DE-FG02-13ER46976) supported research conducted at Miami University and the Robert A. Welch Foundation (K.M.K., Grant E-680) supported research conducted at University of Houston.

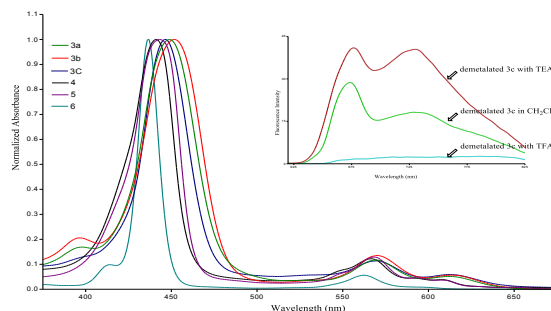
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**Scheme 1** Preparation of unsymmetrically functionalized benzoporphyrins.

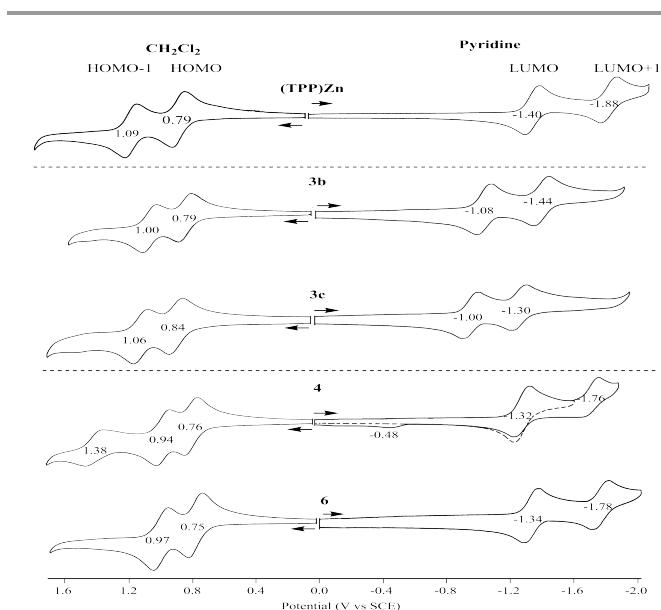
*pull-pull* nitroporphyrin **3c** exhibits a Soret band at 446 nm. Upon switching from a moderately electron-withdrawing ester group to an electron-donating phenyl group (**3a**), the Soret band is red shifted to 449 nm, while the Q bands remain mostly unchanged; installing a strong electron-donating methoxy group at the 4-position of the phenyl ring (**3b**) pushes the Soret band slightly further to the red region (452 nm). These data demonstrate the expected “*push-pull*” effect. Interestingly, the *push-pull* benzoporphyrins **4** and **5** show blue shifted absorptions relative to those of *pull-pull* **3c**. While the symmetrical benzoporphyrin **6** displays a strong fluorescence band at 664 nm with a weaker shoulder at 607 nm, the emission bands for the unsymmetrical porphyrins **4** and **5** are red shifted to 713/714 nm (main band) and 654/655 nm (shoulder), once again demonstrating the lack of symmetry and *push-pull* effects. On the other hand, porphyrins **3a-3c** exhibit similar emission bands regardless of the types of substituents at the porphyrin periphery (Fig. S1). These emission bands are much broader and red-shifted (740-743 nm), and are also much attenuated relative to those of **4-6**. This fluorescence quenching effect is likely related to the electronic perturbation of the directly conjugated nitro group to the porphyrins, which is a strong fluorescence quencher of fluorescent dyes.<sup>6</sup> Upon demetallation of **3a-3c**, their emission bands split and become more intense relative to those of **3a-3c** (Fig. 1 and Fig. S2 and S3); treatment of these free base porphyrins with trifluoroacetic acid (TFA) results in almost complete quenching of the fluorescence; in sharp contrast, when the demetallated **3a-3c** is treated with triethylamine (TEA), the emission bands are significantly enhanced instead. These interesting phenomena were not observed for free base porphyrin of **6** that does not contain a nitro group. The free base porphyrin of **6** exhibits expected enhanced fluorescence upon treatment of TFA, and remains unchanged in the presence of TEA (Fig S4).

The electrochemical properties of these mono-benzoporphyrins were investigated using cyclic voltammetry (CV) (Fig. 2 and Table S1 in SI). The reductions were measured in pyridine and the oxidations in  $CH_2Cl_2$  in order to obtain thermodynamically reversible electrode reactions for all processes. For comparison purposes, the CV of ZnTPP was also



**Fig. 1** UV-Vis spectra of **3a-3c**, and **4-6** in  $CH_2Cl_2$ . Inset: fluorescence spectra of demetallated **3c**, with TEA and TFA in  $CH_2Cl_2$  ( $\lambda_{ex} = 440$  nm).

measured under similar conditions. Several trends were observed in the electrochemical data. Porphyrin **6** displays two reversible oxidations and two reversible reductions, similar to (TPP)Zn. As compared with (TPP)Zn, both the first ( $E_{1/2} = 0.75$  V) and second oxidation ( $E_{1/2} = 0.97$  V) potentials of **6** are shifted negatively, while both the first ( $E_{1/2} = -1.34$  V) and second ( $E_{1/2} = -1.78$  V) reductions move in a positive direction. These shifts in redox potentials are anticipated for porphyrin **6** due to its extended  $\pi$ -conjugation upon fusion of a benzene ring to the porphyrin periphery. The reduced HOMO-LUMO gap of **6** is also reflected by its red-shifted and broadened absorption bands relative to those of (TPP)Zn. Two reversible oxidations and two reversible reductions were also observed for porphyrin **3a-3c**. The introduction of a strong electron-withdrawing nitro group influenced the reduction potentials more significantly than the oxidation potentials. While the oxidation potentials of **3a-3b** only shifted positively by 30-90 mV relative to those of **6**, the reduction potentials shifted by 260-480 mV. The *push-pull* porphyrins **3a** and **3b** display exactly the same the first oxidation and the first reduction potentials; the second oxidation and the second reduction potentials of **3a** and **3b** only deviate slightly from each other, and are negatively shifted by 20 mV and 10 mV, respectively in **3b**. These data suggest that the presence of a strong electron-donating group (-OMe) at the *para*-position of the phenyl ring in **3b** does not significantly influence the electrochemical properties of the porphyrin. This is likely due to the hindered electronic communication between the electron-donating methoxy group with the porphyrin ring. As shown in the calculated optimized geometry (Fig. S6), the aryl groups on the fused benzene rings of **3a** and **3b** preferably adopt a perpendicular position to the porphyrin plane; as a result, the  $\pi$ -conjugation of the porphyrin does not effectively extend to the attached aryl rings on the fused benzene unit. On the other hand, when the weakly electron-donating aryl groups in **3a** and **3b** are replaced with moderately electron-withdrawing ester groups of **3c**, oxidation and reduction potentials are positively shifted by 50 to 140 mV, showing a more pronounced substituent effect. Converting the strongly electron-withdrawing nitro group in **3c** into a moderate, electron-donating carbonylamino group in porphyrins **4** and **5** significantly shifts the reduction potentials negatively by 300 to 460 mV. The oxidation potentials of **4** and



**Fig. 2** Cyclic voltammograms of investigated porphyrins in  $\text{CH}_2\text{Cl}_2$  and pyridine containing 0.1 M TBAP at scan rate = 100 mV/s.

**5** also shift moderately in a negative direction. It is notable that an extra reversible oxidation (third oxidation) was observed for **4** at  $E_{1/2} = 1.38$  V, which likely results from oxidation of the carbonylamino group.

DFT calculations were performed to provide some insights into the electronic and electrochemical properties of the porphyrins (Fig S5 in SI). The frontier orbitals of these porphyrins display different electron density patterns. While both the HOMO and the LUMO of **6** mainly involve the porphyrin core, the electron density in the HOMO of **4** and **5** is extended to the fused benzene ring and the carbonylamino group. The HOMOs of **4** and **5** are destabilized and the LUMOs of **4** and **5** are stabilized as a result of the introduction of the moderately electron-donating carbonylamino group, leading to a smaller HOMO-LUMO energy gap relative to that of **6**. The electron density of the HOMOs for *push-pull* porphyrins **3a** and **3b** is mainly located on the porphyrin core with partial extension to the fused benzene ring. The involvement of the fused benzene ring in the HOMO of **3b** is slightly larger than that of **3a** due to the electron-donating methoxy group presence at the para-position of the attached phenyl ring. The electron density on the HOMO of *pull-pull* **3c** is distributed from the fused benzene ring through the porphyrin core to the nitro group. On the other hand, the LUMO of **3a-3c** shows a reversed trend in the electron density distribution. Both the HOMOs and LUMOs of **3a-3c** are stabilized relative to that of **6**. For the HOMO, the stabilization order is **3b** > **3a** > **3c**; for the LUMO, the stabilization order is **3c** > **3a** > **3b**. The HOMO-LUMO energy gap follows the order: **3b** < **3a** < **3c** < **6**, correlating well with their electronic and electrochemical properties. It is notable that the orbital splitting in the LUMOs of *pull-pull* **3a-3c** are more significant than that of **4** and **5**.

In summary, unsymmetrically functionalized benzoporphyrins, in which both an electron-withdrawing group and an electron-donating group are located at the porphyrin  $\beta$ -positions, were synthesized. Breaking the symmetry of the benzoporphyrin results in a significant broadening and red shifting of the

absorption and emission bands. The introduction of different types of substituents to the porphyrin periphery makes remarkable difference in the electrochemical and electronic properties of these porphyrins. The strongly electron-withdrawing nitro group appears to have a more pronounced impact on the properties of the benzoporphyrins than the electron-donating aminocarbonyl and aryl groups. Fluorescence quenching was observed for **3a-3c** and for their free base porphyrins, which display unusual fluorescence behaviour upon treatment with an acid or a base. These interesting results are apparently related to electronic perturbations of the nitro group on the porphyrin  $\pi$ -system, and are worthy of further investigation. This work provides useful information that is lacking in the field, and may open the door to functionalizing new benzoporphyrins for various applications.

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