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β-Hexaalkylporphycenes: Positional Effect of Alkyl Groups toward Design and Control of Structural and Photophysical Properties in Isomeric Hexaethylporphycenes

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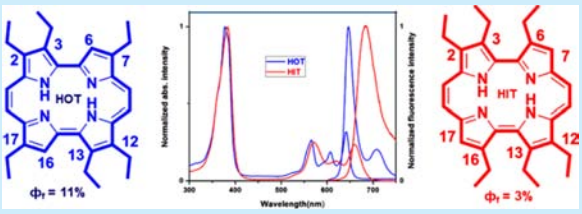
Ⓢ *Supporting Information*

ABSTRACT: Two novel β-hexaalkylated porphycenes, i.e., 2,3,7,12,13,17- (**HOT**) and 2,3,6,12,13,16-hexaethylporphycenes (**HIT**) were introduced for the first time in porphycene chemistry. These were synthesized through McMurry coupling reactions of new isomeric unsymmetrically substituted triethylbipyrrole dialdehydes. The positional effects of alkyl groups could be manifested through significant alteration in structure of porphycene cores and, as a consequence their photophysical properties, not noticed in β-octaethylporphycene. **HOT** displays significant fluorescence accompanied by reasonable singlet oxygen generation ability.



Porphyrin(2.0.2.0), commonly known as porphycene, is the first constitutional isomer of the much revered "pigment of life"; i.e., porphyrin(1.1.1.1), discovered by Vogel in 1986.[1] It was prepared from 5,5′-diformyl-2,2′-bipyrrole via a self-McMurry-type reductive coupling reaction. As it is abiotic in nature, its initial chemistry was mostly developed by following that of porphyrin. Its molecular symmetry is lower than that of porphyrin and hence has a relatively smaller HOMO−LUMO difference in energy.[2] Although the absorption bands in porphycene appear to be qualitatively similar to those of porphyrin, its Q-bands are both red-shifted and intensified. This attribute led to its emergence as a better photosensitizer than the latter for PDT application.[3] In addition, the effect of substituents is found to be more pronounced in porphycene than its parent isomer porphyrin. For example, not only the nature of the substituents but also their positions were found to induce a significant effect on the structure, complexation, and photophysical properties of the former.[4] These properties attracted various research groups to investigate their application in quite diverse fields such as photoinactivation of viruses and bacteria,[5] protein mimicry,[6] near-IR theranostic agents,[7] catalysis,[8] nonlinear optics,[9] thin-film organic solar cells,[10] and functional materials.[11]

Owing to the synthetic challenges involved, growth of porphycene chemistry is relatively much slower than that of its parent isomer porphyrin. Despite the hurdles, porphycene has lately emerged out of the shadow of the latter by exhibiting characteristics having no precedence in porphyrin chemistry, viz. double hydrogen transfer, adsorption of cis tautomers over metal surfaces, and formation of a stable cis tautomer and, very recently, a cis bimetallic complex with interacting metal ions.[12] It is worth mentioning that calculations show that among freebase porphyrin and all of its isomers porphycene is the most stable. Its greater stability is attributed to the presence of two exceptionally strong intramolecular NH⋯N hydrogen bonds in this rectangular ligand.[13] Therefore, intramolecular hydrogen bonding in porphycene is of great fundamental research interest because it regulates NH tautomerism, and as a result, the double-hydrogen-transfer processes and these attributes are found to be quite sensitive to the nature and position of the substituents.[14]

In the last three decades, several kinds of substitutions have been reported in porphycene chemistry, but mostly they are derived from symmetrically substituted bipyrroles, leading to a symmetric porphycene.[3,13,15] Recently, Srinivasan's group reported the synthesis of symmetrically substituted *meso*-arylporphycenes via oxidative coupling of bipyrrolylethane moieties, and subsequently, Ravikanth and co-workers optimized the same strategy.[16] Very recently, Hayashi's group synthesized *meso*-benzo-fused porphycenes by using Suzuki−Miyaura coupling followed by an intramolecular McMurry coupling reaction.[12c] Substitution is a key factor to control the core size as well as complexation ability with metal ions and photophysical properties. Therefore, a large number of porphycenes have been reported in literature endowed with tetra to dodeca substituents on their periphery, with major emphasis on the tetra- and octasubstituted analogues (Figure 1).[17] Interestingly, hexa- and dodecasubstituted porphycenes have not been explored in detail. The latter types proved difficult to aromatize, except for tetrabenzotetraalkylporphycene.[18] On the other hand, few β-

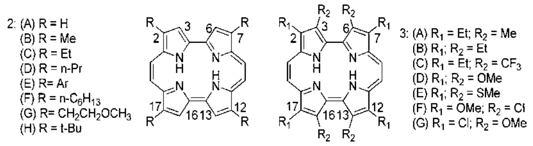


Figure 1. Selected β-substituted porphycenes.

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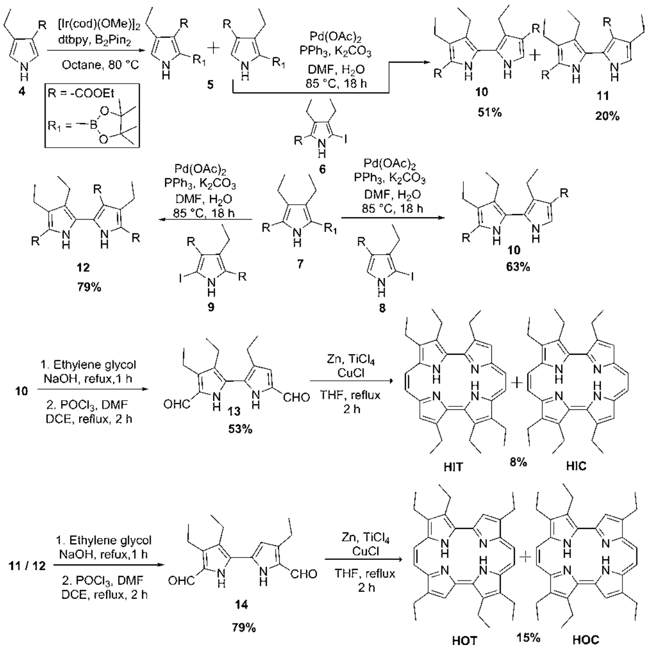
hexasubstituted porphycenes have been reported that have been synthesized either via post-difunctionalization of 2,7,12,17-porphycenes or through mixed McMurry coupling of tetra- and disubstituted bipyrrole dialdehydes.[19]

Recently, asymmetry-induced tautomerism has emerged as a fundamental research objective in porphycene systems as it sometimes leads to dual fluorescence.[13] This asymmetry could be introduced via post-modification of symmetrically substituted porphycenes.[20] Although Lucchesini and Neidlein opened the door to synthesizing unsymmetrical bipyrrole-derived core-modified porphycenes via thiophene and thiazole systems, their poor solubility, failure in the oxidation of their cis isomers, and additionally, lack of stability in solution led to dwindling interest in these type of systems.[21]

To the best of our knowledge, so far there is no report of hexasubstituted porphycene, where both of the pyrrole units of the bipyrrole moiety employed for their synthesis are different in terms of substitution. Toward this, herein, for the first time, we report the synthesis of new stable isomeric β-hexaethylporphycenes from two unsymmetrically substituted triethylbipyrrole dialdehydes. For the same type of substituents, two possible types of β-trisubstituted bipyrrole dialdehydes can be envisaged. Subsequently, their McMurry coupling reactions raise the possibility of formation of four types of hexa(**H**)-substituted porphycenes. For example, the singly substituted pyrrole can have the β-substituent outside (**O**) or inside (**I**), whereas the same types of pyrroles can reside on the same side, i.e., cis (**C**) or opposite, i.e., trans (**T**), leading to our nomenclature 2,3,7,12,16,17-(**HOC**), 2,3,7,12,13,17-(**HOT**), 2,3,6,13,16,17-(**HIC**), and 2,3,6,12,13,16-(**HIT**) for these hexaethylporphycene isomers. Among them, we were able to isolate **HOT** and **HIT** in pure form. They were thoroughly characterized, including their solid-state structures by X-ray diffraction analysis. These new porphycenes will be of great fundamental interest[3,14] while opening up a new vista for tailor-made macrocycles with altered chemical and photophysical properties for targeted application in different fields.[10,11]

The key to synthesizing these isomeric hexaethylporphycenes is the unsymmetrical diethyl 3,3′,4′-triethyl-1*H*,1′*H*-[2,2′-bipyrrole]-4,5′-dicarboxylate **10** and diethyl 3′,4,4′-triethyl-1*H*,1′*H*-[2,2′-bipyrrole]-3,5′-dicarboxylate **11**. In order to realize them, a different approach is needed, unlike the current strategy of Ullmann coupling or oxidative coupling of the same pyrrolic moieties.[15,16] Both bipyrroles were synthesized using a Suzuki–Miyaura coupling reaction (Scheme 1) between ethyl 3,4-diethyl-5-iodopyrrole-2-carboxylate **6** and an uncontrolled and inseparable mixture of borylpyrrole **5** (Figure S1).[22] Both mono-α-protected bipyrroles **10** (51%) and **11** (20%) were isolated through column chromatography (Figures S3–S7) from the same reaction mixture. It is noteworthy to mention that in order to design four porphycenes only two differently substituted pyrroles (ethyl 3,4-diethyl-1*H*-pyrrole-2-carboxylate and ethyl 4-ethyl-1*H*-pyrrole-3-carboxylate) were needed, establishing a unique strategy toward the design of tailor-made porphyrionoids in the future with an altogether different perspective. However, due to very low yield of **11**, we followed a selective Suzuki coupling reaction between borylated pyrrole **7** and diethyl 3-ethyl-5-iodo-1*H*-pyrrole-2,4-dicarboxylate **9** to obtain **12** (79%) in good yield (Figure S8). Similarly, an analogous coupling reaction between borylpyrrole **7** and ethyl 4-ethyl-2-iodo-1*H*-pyrrole-3-carboxylate **8** raised the yield of **10** (63%). Base-mediated deprotection of the esters yielded the desired unsymmetrical bipyrroles, and subsequent Vilsmeier formylation of these bipyrroles resulted in the formation of the precursor bipyrrole dialdehydes **13** (53%) (Figure S10) and **14** (79%) (Figure S12). Both of the unsymmetric bipyrroledialdehydes were subjected to Ti(0) mediated McMurry coupling separately to obtain the desired products **HOT** and **HIT** along with their corresponding cis analogues **HOC** and **HIC**. Herein, we found the formation of both the isomers in almost similar yields (Figures S14 and S15). However, owing to their very similar polarity, the trans- and cis-isomers could not be separated by chromatographic techniques. Therefore, we attempted repeated recrystallization of the products. Interestingly, this led to isolation of the pure trans isomers **HOT** and **HIT** (Figures S16–S19). To date, all of our efforts to isolate corresponding cis isomers in pure forms have been unsuccessful.

Scheme 1. Synthesis of β-Hexaethylporphycenes



Both of the isomeric porphycenes were rigorously characterized by ^{1}H and ^{13}C NMR spectroscopy and mass analysis. Further, their solid0state structures were also ascertained by X-ray diffraction analysis. The ^{1}H NMR spectrum of **HOT** displays meso protons resonating in the range of 9.76 to 9.66 ppm, whereas inner β protons resonate at 9.42 ppm. Isomeric **HIT** shows slightly upfield-shifted resonances for meso protons (9.56–9.50 ppm) and outer β protons at 8.84 ppm. Interestingly, the NH signal of **HIT** is quite upfield shifted (0.39 ppm) compared to that of **HOT** (2.08 ppm). This indicates the presence of relatively stronger NH···N hydrogen bonding in **HOT** rather than its isomeric analogue **HIT**. Strikingly, the NH resonances in hexaethyl porphycene **HIT** were found to be relatively more upfield shifted than octaethylporphycene **3B** (0.65 ppm) reported by Vogel,[17b] indicating greater geometrical reorganization of the N$_4$ core in the former.

Single crystals of both isomers were obtained through slow evaporation of their chloroform:hexane (5:95) solutions. The molecular structure of porphycene **HOT** exhibited a perfectly planar rectangular core with N1···N2 and N1···N1′ distances of 2.797 and 2.670 Å, respectively (Figure 2), whereas that of isomeric porphycene **HIT** reveals a nonplanar rectangular N4 core (N1···N2:2.710 Å; N1···N1′: 2.805 Å) (Figure 2). The remarkable elongation of the N1···N1′ distance in the latter led to

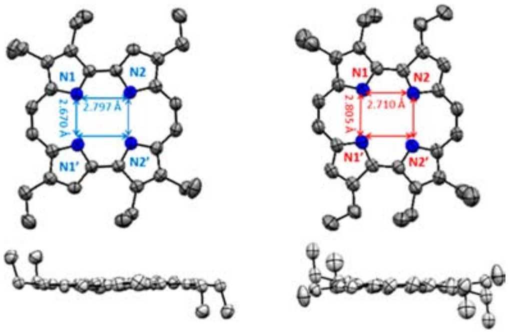


Figure 2. X-ray crystal structures of **HOT** (left) and **HIT** (right) (above front views and below side views) scaled at 35% probability level. Color code: C, gray; N, blue (hydrogens are omitted for clarity).

significant weakening of its N−H···N hydrogen bonds, which was reflected in its quite upfield shifted NH protons in the NMR spectrum. This is in contrary to our expectations as **3B** endowed with eight β-ethyl substituents was expected to exhibit greater elongation in its N1···N1′ distance (2.798 Å), owing to greater nonbonding interactions.[17b] In order to understand this apparent discrepancy, we analyzed the structures more carefully. Interestingly, we noticed while the ethyl groups at the 2,3- and 12,13-positions reside below and above the macrocyclic planes, those at 6,16- (**HIT**) and 7,17- (**HOT**) lie almost in the porphycene planes, which was not observed in **3B**. Further, greater angle contraction of the bond angles in the NCCN segments was found in **HIT** (117.98°) rather than **HOT** (119.87°), accounting for the former's deformation from planarity. This, in plane disposition of the ethyl groups at 6,16-positions, attributes to the greater van der Waals repulsions between the substituents at the 3,6- and 13,16-positions, not observed either in the isomeric **HOT** or even in β-octaethylporphycene **3B**. This highlights further how the porphycene core can be modulated not only by the nature of the substituents but also by their positions at its periphery.

The UV−vis spectra of isomeric porphycenes **HOT** and **HIT** were recorded in chloroform (Figure 3). Both of the porphycenes displayed characteristic intense Soret bands and three weaker Q-bands. Porphycene **HOT** showed a Soret band at 378 nm and Q-bands at 565, 607, and 641 nm, whereas **HIT** exhibited a Soret band at 383 nm and Q-bands at 571, 619, and 660 nm (Table S1). This clearly indicates the positional effect of the substituents (e.g., ethyl moieties), which in general is more evident in the lowest energy Q-band, with **HIT** displaying a 19 nm bathochromic shift with respect to **HOT**. Further, the absorption bands of **HIT** are very comparable with those of the β-octaalkyl analogues **3A** and **3B**. For example, while **3B** displayed a slightly red-shifted Soret band at 385 nm and a lower energy band at 665 nm, etioporphycene **3A** showed a marginal blue shift in its absorption bands with respect to **HIT**.[17b] From this we can conclude that the unusually stronger van der Waals repulsion noticed in **HIT** is due to the in-plane orientation of the ethyl moieties at the 6,16-positions in solution. Further, compared to **HOT**, the theoretical estimations of energies of the frontier orbitals obtained from the DFT-optimized structures (Figure 4) revealed that the HOMO and HOMO−1 is more degenerate in **HIT** owing to distortion in its macrocyclic core. This is further reflected in stabilization of the latter's LUMO by 0.06 eV, which is in accordance with the bathochromic shift in the absorption spectra of **HIT** compared to **HOT**.[23]

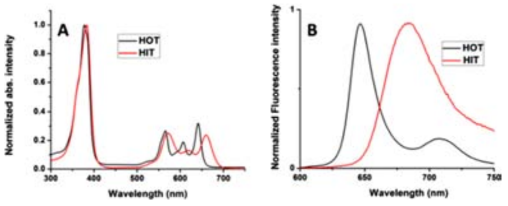


Figure 3. (A) UV−vis spectra of **HOT** (black line) and **HIT** (red line) and (B) fluorescence spectra of **HOT** (black line) and **HIT** (red line) in chloroform at 25 °C.

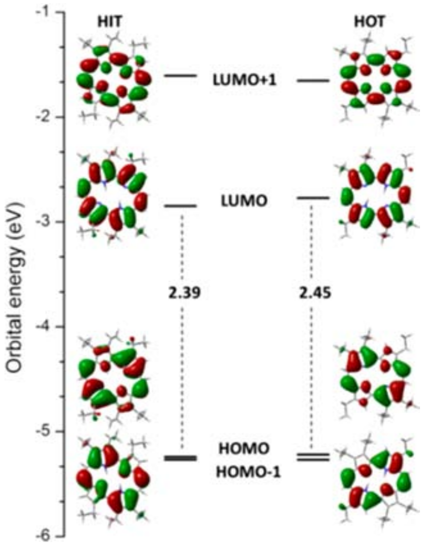


Figure 4. Frontier molecular orbitals and their corresponding energy levels of **HIT** and **HOT**.

Further, emission spectra of both isomers exhibited intense fluorescence (Φ_f 0.11) in **HOT** with a strong band at 647 nm accompanied by a weaker lower energy band at 707 nm and weaker fluorescence (Φ_f 0.033) with a relatively broad emission profile having maxima at 684 nm for **HIT** (Figure 3 and Table S1). This is again reflected in their fluorescence lifetimes: **HOT** (5.31 ns) and **HIT** (0.74 ns) (Figure S20). In order to evaluate their efficacies as potential photosenstizers for photodynamic therapy, steady-state luminescence spectra of singlet oxygen for **HOT** and **HIT** were measured in an air-saturated solution of toluene to find their singlet oxygen generation abilities. Both of them displayed weak emission bands ranging from 1240 to 1320 nm with maxima around 1280 nm (Figures S21−S22). The singlet oxygen quantum yields (ϕ_Δ) of **HOT** and **HIT** were 0.22 and 0.025 (Table S1). While the efficiency of the former is quite comparable to that of the much accomplished 2,7,12,17-tetraphenylporphycene,[24] that of the latter is more than that of the β-octasubstituted analogues.

In conclusion, we have demonstrated a simple strategy to synthesize a new class of isomeric hexaalkylporphycenes for the first time from unsymmetrically substituted bipyrroles, which in turn were derived through Suzuki−Miyaura coupling of differently substituted pyrroles. Interestingly, in the present systems, only six β-positions are substituted, making them a perfect hybrid class between the much explored tetra- and octasubstituted porphycenes. Further, the remaining two β-positions can be selectively functionalized for the desired application. The arrangements of ethyl groups at different positions completely altered their solid-state structure to photophysical properties,

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majorly owing to their orientation to the macrocyclic plane that significantly influenced the nonbonding interactions between the two pyrrolic moieties of the constituent bipyrroles. Further, the structure and photophysical properties demonstrate clearly that six appropriately substituted substituents on the porphycene periphery can inflict a much more drastic influence than that by eight substituents. This again highlights the greater sensitivity of these attributes of porphycene toward not only the type of substituents but also their positions at its periphery and has no precedence in porphyrin chemistry. This further justifies the uniqueness of porphycenes as a new class of functional material and, thus, requires sustained effort to unravel its structure and photophysical properties in detail. Efforts are currently underway in this direction in our group.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03428.

Experimental details, ^{1}H and ^{13}C NMR spectra, photophysical data, computational details and X-ray data for compounds **HOT** and **HIT** (PDF)

X-ray data for compounds **HOT** and **HIT** (CIF)

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Notes

The authors declare no competing financial interest.

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