Communications in Computational Chemistry
Commun. Comput. Chem., Vol. 7, No.1 , 202–208
doi: 10.4208/cicc.2025.85.02

Regular Article

Insights into the Stability and Photophysical Properties of Expanded Porphyrins Through Theoretical Calculation

Wei Wei[1,*], Zeng-Xia Zhao[1], Xiao-Li Sun[1], Xi Chen[3], Bin Hu[1,*] and Wei Li[2,*]

[1] *College of Chemistry, Jilin University, Changchun 130012, P. R. China;*

[2] *School of Chemistry and Materials Science, Hunan Agricultural University, Changsha, China;*

[3] *College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing, 163318, China.*

[*] Corresponding authors: weiweiww@jlu.edu.cn; hubin_80@jlu.edu.cn; weili@hunau.edu.cn

Received on 25 March 2025; Accepted on 26 April 2025

Abstract: Expanded porphyrins serve as promising candidates for MRI contrast agents and sensitizers in photodynamic therapy. In this study, we theoretically designed a series of expanded porphyrins incorporating thiophene and selenophene moieties to investigate their optoelectronic properties. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to assess their aromaticity, stability, and photophysical characteristics. Our results reveal that all designed molecules exhibit superior optoelectronic performance, with enhanced aromaticity compared to conventional porphyrins. The absorption spectra of the molecules closely resemble that of porphyrins, suggesting potential applicability in related biomedical and photonic applications. Notably, molecule 4, featuring both a thiophene moiety and a conventional selenophene ring, demonstrates the highest stability, an increased energy gap highest between occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and a planar geometry, leading to strengthened aromaticity. These findings provide valuable insights for the rational design of next-generation porphyrin-based materials.

Key words: excited state, aromaticity, stability, optoelectronic properties, expanded porphyrins.

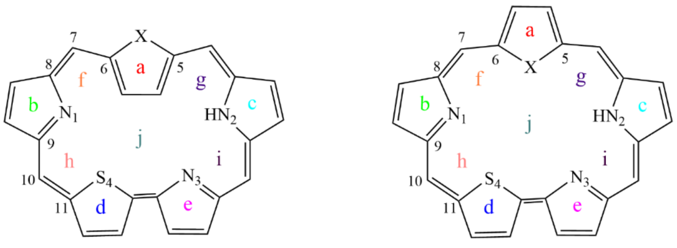
1. Introduction

Porphyrins, renowned for their fundamental roles in biological systems, have attracted significant interest in theoretical chemistry due to their well-defined electronic structures and diverse applications. In particular, 18 π-electron porphyrins have been extensively studied for their potential in material science, pigment development, and medicinal applications [1–5]. Structurally, these molecules consist of four pyrrole subunits connected in a coplanar arrangement via methine carbon bridges at their α-carbon positions.

As higher homologues of conventional porphyrins, expanded porphyrins have emerged as a major research focus over the past four decades [6–10]. These systems, characterized by enlarged cavities and extended conjugation, exhibit unique electronic properties and structural flexibility, making them promising candidates for various applications in theoretical chemistry. Their ability to bind diverse substrates depends on both the specific porphyrin framework and cavity dimensions. In neutral expanded porphyrins, aromatic conjugation primarily involves the imine-type nitrogen atoms, while the amino NH groups remain non-conjugated. Additionally, expanded porphyrins display distinctive Hückel and Möbius topologies compared to conventional tetrapyrrolic porphyrin macrocycles [11], enhancing their utility in biomedical applications such as MRI contrast agents and sensitizers for photodynamic therapy [12]. Several expanded porphyrins have garnered attention in contemporary research. Notably, sapphyrin [13,14], a pentapyrrolic expanded porphyrin with a 22 π-electron aromatic system, stands out due to its structural modifications. Unlike porphyrin, sapphyrin features an additional pyrrole inserted between a meso-carbon and an α-pyrrolic position. Other derivatives, including carbasapphyrin [15], benzosapphyrin [16], and dithiabenzisapphyrin [17], exhibit distinct aromaticity, stability, and absorption properties, contributing to their growing significance in optoelectronic applications [18].

Thiophene has emerged as a widely used π-conjugated building block, often replacing pyrrole units within the porphyrin framework [19]. Incorporating heterocyclic rings such as furan, thiophene [20,21], or selenophene [22,23] into expanded porphyrins enhances their aromatic stability and optoelectronic properties. These modified porphyrins, whether featuring normal or inverted thiophene/selenophene configurations, display remarkable photophysical characteristics [24]. Given this, it is crucial to explore how these structural modifications influence the aromaticity, stability, and electronic behavior of expanded porphyrins.

In this study, we theoretically design and analyze four macrocyclic molecules (coded as **1–4** in Scheme 1) incorporating thiophene and selenophene subunits. Using high-level quantum chemistry calculations, we systematically investigate their aromaticity, stability, and photophysical properties. Furthermore, we assess the impact of conventional versus inverted thiophene and selenophene configurations on their optoelectronic behavior. By elucidating the relationship between structural modifications and electronic properties, this work aims to advance the rational design of novel porphyrin-based materials with enhanced functionalities, contributing to the development of next-generation materials in theoretical chemistry and material science.



1=X=S
2=X=Se

3=X=S
4=X=Se

Scheme 1. Sketch structures of molecules of **1-4.**

2. Computational details

All calculations were conducted utilizing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. The full optimization of compounds **1-4** was executed using the DFT-B3LYP6-311G (d, p) level of theory [25-28]. To ensure structural stability, vibrational frequencies were computed for the optimized structures at the same theory level, confirming the absence of imaginary frequencies and validating that the obtained structures represent local energy minima. Vertical electronic excitations were determined via TD-DFT calculations using the range-separated CAM-B3LYP functional combined with a 6-311G (d, p) basis set. Additionally, aromatic stabilization energy (ASE) [29] values were computed employing a ring-opening isobond chemical reaction. Positive reaction energies indicate aromaticity, while negative values suggest antiaromaticity. The ASE was evaluated using the B3LYP functional alongside a 6-311G (d, p) basis set. All calculations were performed using the Gaussian 16 software package [30].

Critical points are analyzed at specific locations relative to the molecular structure. To avoid in-plane components, nucleus-independent chemical shifts (NICS) values are calculated at designated points, such as 1 Å above the thiophene/selenophene ring (point a), at the geometrical center of the pyrrole ring (points b, c, and e), above the thiophene ring (point d), and at various intramolecular positions (points f, g, h, and i), as well as at the molecular center (point j), using the GIAO method. In this study, calculations were performed using several functionals (CAM-B3LYP, M05-2X, M06-2X) to assess their performance. NICS (1) zz values obtained with the CAM-B3LYP functional closely match those from the M05-2X and M06-2X functionals. Therefore, CAM-B3LYP is selected as the optimal functional due to its widespread usage. Molecules are deemed aromatic if the NICS(1)zz value is negative, while a positive value suggests antiaromaticity. Illustrations of the different critical points are depicted in Scheme 1. The critical points were analyzed using the 'atoms in molecules' theory of Bader [31] via the AIM2000 package [32]. An NBO analysis [33] is also performed to calculate the second-order perturbation at the B3LYP/6-311G (d,p) theory level.

3. Results and discussions

3.1 Geometrical structures

The optimized ground-state structures of the designed molecules were obtained using the B3LYP/6-311G(d,p) level of theory, as shown in Figure 1. Notably, molecules **1** and **2** adopt inverted configurations, whereas molecules **3** and **4** feature conventional structures. These molecules were designed by substituting the pyrrole unit in the porphyrin core with either a thiophene or selenophene moiety. Specifically, molecules **3** and **4** incorporate the standard orientations of thiophene and selenophene, respectively. Structural interconversion between these configurations occurs via rotation of the thiophene/selenophene ring, transforming molecule **1** into **3** and molecule **2** into **4**. Table 1 summarizes the key optimized geometric parameters, providing insights into the structural characteristics of the designed molecules.

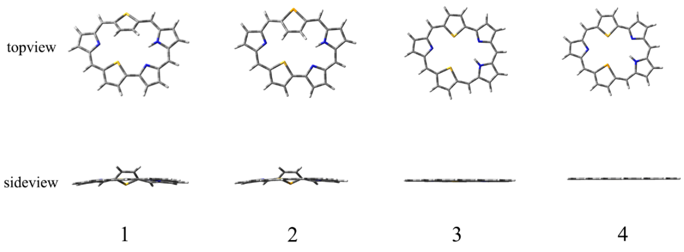


Figure 1. Optimized ground state structures of molecules **1-4.**

The N1-N2 bond lengths for molecules **1**, **2**, **3**, and **4** are 6.021, 6.084, 6.254, and 6.302 Å, respectively. Similarly, the C5-N3 bond lengths measure 4.835, 4.882, 5.271, and 5.312 Å, while the C6-S4 bond lengths are 4.349, 4.401, 4.838, and 4.857 Å. These values show a clear increasing trend in the order of **1** < **2** < **3** < **4**. Regarding bond angles, the C6-C7-C8 angles for molecules **1**–**4** are 121.7°, 122.4°, 127.5°, and 129.4°, respectively, with a similar trend observed for the