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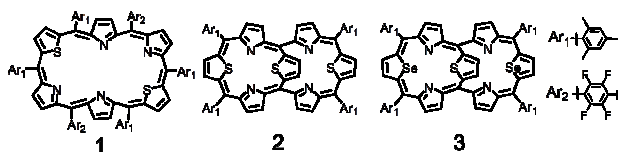
Photophysical Properties of Bridged Core-modified Hexaphyrins: Conjugational Perturbation of Thiophene Bridges

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The role of thiophene bridges in determining the photophysical properties of bridged core-modified hexaphyrins is investigated. Depending on the substituted chalcogen atoms and conjugational perturbation across the thiophene bridges, the bridged core-modified hexaphyrins reveal unique photophysical properties.

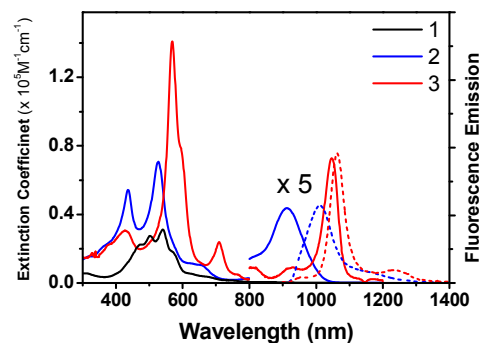
In recent years, increasing attention has been focused on synthetic modification to realize functional π -electronic structures in expanded porphyrins for their practical applications as optoelectronic devices, nonlinear optical (NLO), and photodynamic therapy (PDT) materials.^{1,2} There have been various approaches to control the electronic structures of expanded porphyrins such as core-modification,² *meso*-substituent changes,³ ring-fusion/confusion,⁴ and introduction of internal bridges.^{5,6} Among these, core modification by replacing pyrrole nitrogens with chalcogen atoms such as O, S and Se has been recognized as an easy and efficient method to modulate the molecular conformation and π -conjugation of expanded porphyrins.^{2,7} However, owing to the electrostatic forces and a change in hybridization of the group VI heteroatoms, the introduction of sulfur or selenium in the macrocyclic framework leads to asymmetric macrocyclic conformation with four inverted pyrrole rings as well as split multiple bands in the steady-state absorption spectra along with nonfluorescent features.⁸ In this regard, to realize a rigid and symmetric conformation, internal thiophene bridge between the two *meso*-positions is introduced to thiophene- or selenophene-substituted hexaphyrins.⁶



³⁵ Scheme 1. Molecular structures of dithiahexaphyrin **1**, thiophene-bridged dithiahexaphyrin **2**, and thiophene-bridged diselenahexaphyrin **3**.

Internally bridged core-modified hexaphyrins which have spectacle-like molecular conformation exhibit relatively intense UV/Vis- and NIR-absorption features and fluorescence signals. Moreover, the thiophene-bridged core-modified hexaphyrins exhibit unique photophysical features which are related to the

conjugation network across the thiophene bridge. For instance, while thiophene-bridged diselenahexaphyrin exhibits typical hexaphyrin-like spectroscopic features, thiophene-bridged dithiahexaphyrin reveals split absorption bands and broad fluorescence signals with a large Stokes shift. The most intense absorption band of thiophene-bridged dithiahexaphyrin at 527 nm is weaker and more blue-shifted than those of pyrrole-based and selenophene-substituted ones. And the thiophene-bridged dithiahexaphyrin exhibits a broad absorption transition in the Q-like absorption region without band splitting. These spectral features are not observed in typical hexapyrrolic macrocycles which have planar molecular conformations. Thus, in this work, we have investigated the photophysical properties of thiophene-bridged core-modified hexaphyrins with a particular focus on the conjugation effect of thiophene bridge and core-substituted sulfur or selenium atoms (Scheme 1). Although previous theoretical and photophysical observations infer the effect of thiophene bridge,⁶ a comparative spectroscopic study on the bridged hexaphyrins, which is expected to provide a key insight into the structure-property relationship in conjunction with the conjugational perturbation across the thiophene bridge, has not yet been performed. With these objectives in our mind, we have carried out a systematic spectroscopic study to characterize their unique photophysical features such as NIR fluorescence and excited-state dynamics in comparison with the parent molecule, dithiahexaphyrin **1**.



⁷⁰ Fig. 1 Steady-state absorption (solid) and fluorescence emission (dotted) spectra of dithiahexaphyrin **1** (black), thiophene-bridged dithiahexaphyrin **2** (blue), and thiophene-bridged diselenahexaphyrin **3** (red) in toluene.

Dithiahexaphyrin **1** exhibits broad and weak absorption spectra and nonfluorescence behavior (Fig.1). These spectral features are

in contrast with those of pyrrole-based [26]hexaphyrin and furan-substituted hexaphyrin which has planar and symmetric geometry with porphyrin-like absorption behaviors as well as NIR fluorescence emissions.^{2,9} Along with the nonaromatic (or weakly aromatic) ¹H NMR spectrum,⁸ we can indicate that **1** has a crumpled conformation where the configuration interactions among the degenerate frontier orbitals are restrained. In the case of thiophene-bridged core-modified hexaphyrins, notable absorption features in visible spectral region are observed (Fig. 1); while the absorption band at 433 nm of thiophene-bridged dithiahexaphyrin **2** is distinctive, thiophene-bridged diselenahexaphyrin **3** shows relatively weak and broad spectral features in the same spectral region. And the Soret-like band of **3** at 567 nm is more intense and sharper than that of **2** at 531 nm. In consideration of the Soret-like absorption bands of dithiaporphyrin and pyrrole-based [26]hexaphyrin appearing at 430 and 570 nm, respectively,^{9,10} the spectral differences between **2** and **3** indicate that the porphyrin-like conjugation network across the thiophene bridges and its hybridization effect on the hexaphyrin-like conjugation pathways are more prominent in **2** rather than **3**.

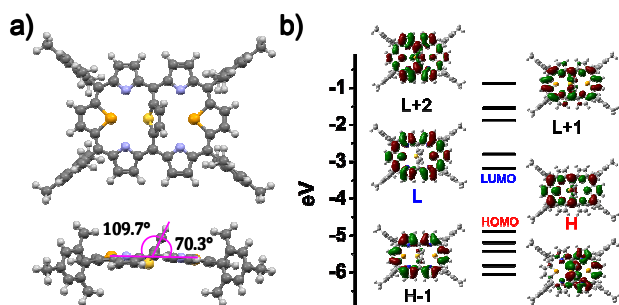


Fig. 2 Calculated molecular structure (a) and MO energy diagram (b) of thiophene-bridged selenophene-hexaphyrin **3**.

Additionally, it should be considered that there exist the conformational differences between **2** and **3** due to the repulsive forces between sulfur and selenium atoms. The optimized structures of **2** and **3** are spectacle-shaped, and especially, the former one has more bent conformation (ESI). The tilting angles of thiophene bridges in **2** and **3** are 22–44° and 70° with respect to the mean planes of porphyrin- and hexaphyrin-like macrocycles, respectively. In other words, owing to the difference in repulsive forces between selenium and sulphur atoms, while the thiophene bridge of **2** constitutes a porphyrin-like structure with surrounding thiophene and pyrrole rings, that of **3**, which is perpendicularly positioned with respect to the hexaphyrin-like macrocycle, only supports the planar molecular conformation. Thus, we expect that these structural features affect the differences in hybridization between porphyrin- and hexaphyrin-like conjugations in the bridged core-modified hexaphyrins.⁶ While the π -conjugation through the thiophene bridge of **3** is almost prohibited, the conjugation structure of **2** has a hybridized character of porphyrin- and hexaphyrin-like conjugation pathways. Furthermore, the conjugational differences between **2** and **3** are reflected in the fluorescence behaviors. The reduced Stokes shift of **3** (135 cm^{-1}) compared with **2** (1095 cm^{-1}) exhibits an enhancement of structural symmetry upon selenium substitution. Considering the Stoke shift of normal

[26]hexaphyrin (171 cm^{-1}),⁹ a large Stoke shift of **2** indicates a flexibility of thiophene bridge which may perturb the electronic structure of hexaphyrin-like macrocycle. However, interestingly, the fluorescence quantum yield of **2** was estimated to be 1.3×10^{-3} which is larger than those of **3** (1.5×10^{-4}) and normal [26]hexaphyrin (1.9×10^{-4}). In other words, despite of bent molecular conformation and flexible thiophene bridge, **2** exhibits more intense fluorescence signals than **3** which has planar symmetric conformation.

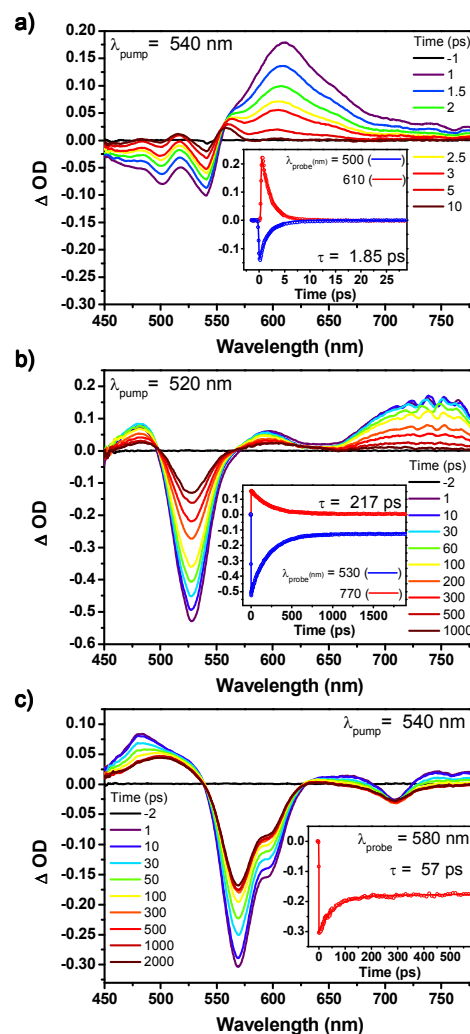


Fig. 3 Femtosecond transient absorption spectra and decay profiles of a) thiophene-substituted hexaphyrin **1**, b) bridged thiophene-hexaphyrin **2**, and c) bridged selenophene-hexaphyrin **3** in toluene.

In order to explain the interesting spectral features in the thiophene-bridged core-modified hexaphyrins, we have performed quantum mechanical calculations such as TD-DFT (B3LYP/6-31g(d,p)), Anisotropy of Induced Current Density (AICD) calculations for molecular orbital (MO) structures and vertical transitions as well as 3D image of delocalized electron densities.¹¹ Like aromatic porphyrinoids, there are configuration interactions among degenerated frontier molecular orbitals (FMO) in aromatic expanded porphyrinoids.¹² However, the calculated MO structures of **2** exhibit energetic degeneracies among HOMO/H-1 and LUMO/L+1 and the configuration interactions among FMOs are not manifest. On the other hand,

we should focus on the fact that the calculated vertical transitions of **2** mostly consist of the combination of transitions among MOs in which electron density distribution is localized on porphyrin-like moieties (H-1, H-2) and hexaphyrin macrocycle (LUMO) (ESI). Based on a comparison of the absorption spectra with the calculated vertical transitions (ESI), we could recognize that the peaks at 479 and 546 nm are mainly attributed to the transitions from porphyrin-like MO structures (H-1, H-2) to hexaphyrin-like ones (LUMO, L+1, and L+2), and one at 810 nm is the transition between hexaphyrin-like electronic structures (from HOMO to LUMO). In other words, the electronic structure of **2** is consistent with the complex combination of two conjugation pathways, porphyrin- and hexaphyrin-like ones. On the contrary, the calculated vertical transitions of **3** exhibit configuration interactions among FMOs which show electron densities mainly localized on hexaphyrin macrocycle. The energy gaps between HOMO/H-1 and LUMO/L+1 are reduced as compared with those of **2**. In this molecule, the conjugational contribution by the thiophene bridge is not so significant compared to that of **2**.⁶ And the AICD plots based on the calculated NMR shielding tensors with the Continuous Set of Gauge Transformations (CSGT) method support the conjugation effect of thiophene on the core-modified hexaphyrins. Both **2** and **3** reveal significant current densities through the hexaphyrin macrocycles and bridged thiophene moieties with aromatic, clockwise current density vectors (ESI). However, it should be noted that the thiophene bridge of **3** shows bisected current density in the middle of two beta-carbon atoms, indicating that the conjugational perturbation of thiophene bridge is prohibited in **3**.

To investigate the differences in conjugation structures and excited state dynamics in the bridged core-modified hexaphyrins, we have performed femtosecond transient absorption measurements. Consistent with the nonfluorescence behavior, the singlet excited state lifetime of **1** was estimated to be 1.85 ps (Fig.3). This ultrafast excited state dynamics is similar to those of highly distorted expanded porphyrins rather than normal [26]hexaphyrin which exhibits relatively long excited state lifetime (~100 ps).⁹ Thus, we infer that the very fast excited state decay is mainly due to its asymmetric molecular structure. In the cases of **2** and **3** which have planar conformation with enhanced molecular rigidity and symmetry, we have observed relatively long excited state decay profiles upon excitation at the most intense absorption bands at 531 and 567 nm, respectively. And, interestingly, the excited state lifetime of **3**, which has a planar symmetric molecular conformation and exhibits more intense absorption and reduced Stokes shift, is shorter than that of **2**; the transient absorption decay profiles of **2** and **3** are analyzed with the time constants of 217 ps and 57 ps, respectively. And there is no excitation wavelength dependency in the excited state dynamics of **2** and **3**. Along with the fact that the relative fluorescence intensity of **3** is weaker than **2**, the excited-state dynamics of **2** and **3** might be related to the conjugational effect of thiophene bridge on their electronic structures. In other words, the excited-state dynamics of **2** and **3** demonstrate that the two conjugation, porphyrin- and hexaphyrin-like, pathways do not exist independently, but are more efficiently hybridized in the electronic structures of **2** rather than **3** by conjugational perturbation of thiophene bridges. Additionally, it should be

considered that the residual transient species also indicate the enhanced contribution by the triplet excited state due to the heavy sulfur and selenium atoms effect.¹³

In summary, we have witnessed unprecedented photophysical properties in thiophene-bridged dithia- and diselenahexaphyrins. In contrast the previous observations on the relationship among molecular conformation, photophysical characteristics, and aromaticity of expanded porphyrinoids, thiophene-bridged dithiahexaphyrin **2** which has less planar and symmetric molecular conformation reveals relatively larger fluorescence quantum yield and longer excited state lifetime than thiophene-bridged diselenahexaphyrin **3**. As a consequence, our current investigations have demonstrated that the thiophene bridge not only has a role of molecular clamp to fix a macrocycle in planar and symmetric conformation but also constitutes a novel π -conjugation structure with tetra- and hexa-pyrrolic macrocycles.

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Notes and references

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- † Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
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