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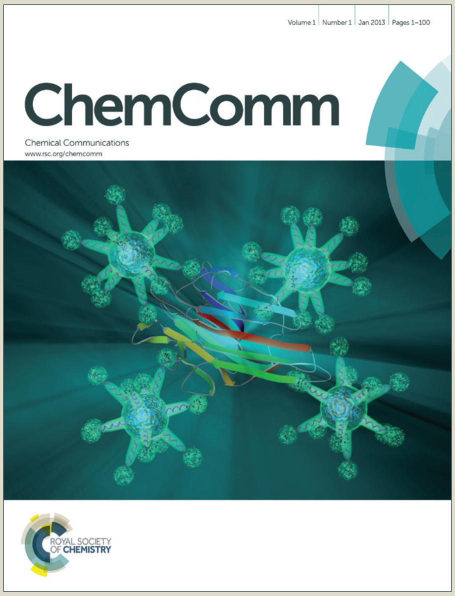

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The effect of π-conjugation in the macrocyclic ring on the photophysical properties of a series of thiaaceneporphyrinoids

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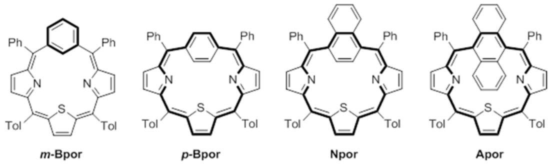
In a series of thiaaceneporphyrinoids, their conformers exhibit macrocyclic π-conjugation pathways controlled by a dihedral angle between the porphyrin framework and acene planes. Conformational equilibria significantly affect the photophysical properties of these macrocycles.

Porphyrinoids have attracted the interest of synthetic and physical organic chemists because of their potential applications in photovoltaic devices, photodynamic therapy, and photosensitizers.[1] In porphyrinoids, π-electron conjugation in the macrocyclic framework plays an important role in stabilizing the molecules and determining their chemical properties. In this regard, numerous studies on the synthesis of modified porphyrinoids containing different macrocyclic π-conjugation pathways such as thiaporphyrins and N-confused porphyrins have been conducted,[2] but only few studies have been performed to reveal the effect of macrocyclic π-conjugation on their photophysical properties.

In porphyrins, pyrrole rings can be substituted by thiophene, furan and benzene related moieties to modify the macrocyclic π-conjugation pathway.[1] In this regard, a series of thiaaceneporphyrinoids, 24-thia-*m*-benziporphyrin (*m*-Bpor), 24-thia-*p*-benziporphyrin (*p*-Bpor), 24-thia-1,4-naphthiporphyrin (Npor) and 24-thia-*meso*-anthriporphyrin (Apor) (Scheme 1) were recently synthesized (the synthetic methods are described in detail in the ESI).[3] In their ^{1}H-NMR spectra, *p*-Bpor and Npor exhibited aromatic features despite of the tilting of *p*-phenylene and naphthalene moieties with respect to the macrocyclic plane, whereas *m*-Bpor and Apor showed the limited macrocyclic π-conjugation (Figure S1).[3] We thought that the above series of macrocycles might reveal meaningful relationships between their macrocyclic π-conjugation and photophysical properties, providing further insight into the nature of π-conjugation in porphyrinoids. In this contribution we chose to explore these possibilities using various spectroscopic techniques, such as steady-state absorption and emission, time correlated single photon counting (TCSPC) and fs-transient absorption at different temperatures, in combination with quantum mechanical calculations.



Scheme 1. The molecular formulas of a series of thiaaceneporphyrinoids

Although the series of thiaaceneporphyrinoids contain acene moieties, their absorption features are qualitatively similar to those of regular porphyrins, in which they can be roughly separated into the B-type region (more intense, < 500 nm) and Q-type region (less intense, > 500 nm, Figure 1). In contrast, the absorption spectra of Npor which possess broad bands with similar intensity at 354, 462 and 623 nm are significantly different from those of typical aromatic porphyrinoids which exhibit an intense B-band with several weak Q-bands.[1]

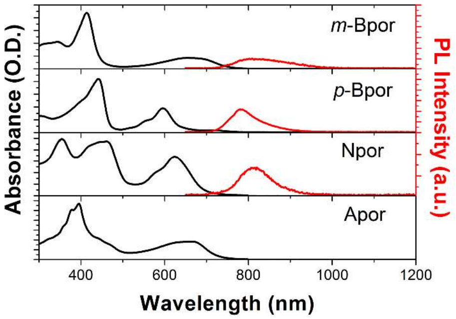


Figure 1. The steady state absorption and fluorescence spectra of a series of thiaaceneporphyrinoids in toluene (black line: absorption spectra, red line: fluorescence spectra)

To further investigate these absorption features of a series of thiaaceneporphyrinoids, we have calculated the optimized geometries and vertical transition energies by using their X-ray structures (Figure 2 and Figure S1).[3] The calculated vertical transitions are well matched with their absorption spectra. Even though the *m*-phenylene ring does not significantly participate in macrocyclic conjugation, it provides significant contributions to the frontier orbitals of *m*-Bpor (HOMO-3 to LUMO+3). The ring symmetric MOs of *m*-Bpor induce the porphyrin-like transitions which are represented by the B- and Q-like bands.[4] However, unlike typical porphyrinoids,[1] the degenerate states between HOMO and H-1, LUMO and L+1 are broken due to their reduced symmetry ($D_{2h} \rightarrow C_s$) and electron deficient part on the benzene ring of porphyrin framework in HOMO and L+1 (Figure S2). Similar to *m*-Bpor, *p*-Bpor also exhibits porphyrin-like MOs with broken degeneracy among four frontier orbitals which explains the porphyrin-like transitions with the relatively intense Q-like bands (Figure S3). Unlike *m*-Bpor and *p*-Bpor, Npor does not exhibit porphyrin-like MOs due to the perturbation by naphthalene on the porphyrin macrocyclic ring. The HOMO and LUMO show electron-poor MOs on the naphthalene ring and the H-1 and L+1 exhibit MO extended to the naphthalene ring, which breaks the degeneracy of four frontier orbitals and perturbs the vertical transitions to be different from the typical porphyrin transitions (Figure S4 and Table S5). Furthermore, Apor shows porphyrin-like MOs (H-2, HOMO, LUMO, and L+1) with electron deficient MOs on the part of macrocyclic ring (H-1, H-3, and L+2), which induces the transitions to be porphyrin-like transitions with several CT transitions (Figure S5). These results imply that the introduction of benzene, naphthalene, and anthracene into thiaaceneporphyrinoids affect their molecular geometry and electronic structures, significantly altering their absorption features.

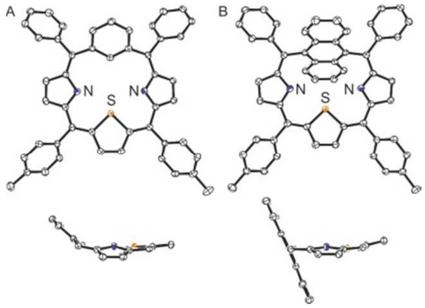


Figure 2. The X-ray molecular structures of *m*-Bpor (A) and Apor (B) (top: perspective view, bottom: side view with aryl groups omitted for clarity)

The fluorescence emission of a series of thiaaceneporphyrinoids except for Apor was observed in 700-1100 nm region (Figure 1). Although the macrocyclic π-conjugation of *m*-Bpor is negligible, the fluorescence was observed and its spectral position is similar to those of *p*-Bpor and Npor. To get more detailed information on the excited state dynamics, we have measured the excited state lifetimes by using TCSPC and fs-TA techniques. The excited state lifetimes of *p*-Bpor (3 ns), Npor (80, 850 ps) and Apor (2, 15 ps) decrease because their molecular structures show systematically increased number of fused phenyl rings (Figures S1, S6 and S7). Furthermore, the excited-state lifetime of *m*-Bpor was observed to be 285 ps, which is relatively shorter than that of *p*-Bpor. This fast excited-state dynamics of *m*-Bpor could be explained by its insignificant macrocyclic π-conjugation. While *p*-Bpor and *m*-Bpor exhibit a single exponential decay, Npor and Apor show a double exponential decay. Because the excited state optimized structure of Npor exhibits dihedral angle of 80˚ between the porphyrin framework and naphthalene plane, which is different from the ground state optimized structure having 60˚ dihedral angle (Figure S8), it is reasonable to assume that Npor can adopt several conformations having dihedral angles of 60-80˚ in the excited state. In the anisotropy of the current induced density (ACID) plot, which represents the 3D image of delocalized electron densities with a scalar field and illustrates the paramagnetic term of the current induced density, the ground state optimized structure shows well-defined macrocyclic ring current. Nevertheless, the macrocyclic ring current effect is not essential for excited state optimized structure having the tilting angle of about 80˚ (Figure 3). It seems likely that the existence of conformers with different contributions of macrocyclic π-conjugation in Npor gives rise to two excited state lifetimes in which the fast decay component comes from a nonaromatic conformation and the slow one from an aromatic macrocyclically conjugated conformer.[6] In the case of Apor, the fast lifetime component is considered as resulting from torsional relaxation because the TA results of Apor exhibit rise profiles in 2 ps and the fast excited state decay component is too fast to be the singlet excited-state lifetime of porphyrinoids (Figure S6).[1]

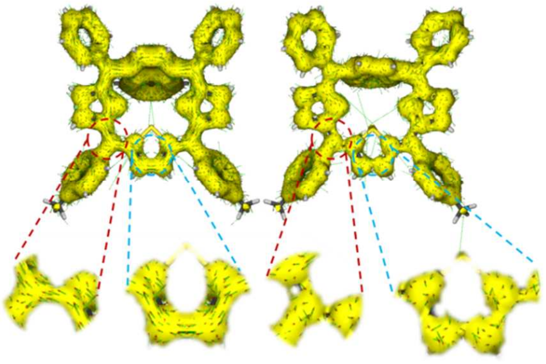


Figure 3. The ACID plots of Npor (left: optimized structure at the ground state, right: optimized structure at the excited state, isosurface value: 0.05)

To control the conformational changes of a series of thiaaceneporphyrinoids, we have measured the excited state lifetimes in a highly viscous medium.[7] The absorption spectra in paraffin oil exhibit nearly the same spectra as in toluene while the fluorescence spectra are blue-shifted compared with the spectra in toluene (Figure S10). Furthermore, the excited-state lifetimes have increased in paraffin oil (Figure S11 and S12). These results demonstrate that the decrease of Stokes shift in paraffin oil, which indicates that the structural flexibility in the excited state is restricted by the high viscosity of medium (Table

S2). The excited state dynamics of *p*-Bpor in paraffin oil exhibits double exponential decay giving rise to two lifetimes of 100 ps and 3 ns unlike the result of *p*-Bpor in toluene (Figure 4). The conformational flexibility of *p*-Bpor in the excited-state is restricted by paraffin oil, which suggests the existence of two sets of conformers with aromatic or nonaromatic macrocyclic conjugation. Furthermore, Apor shows a double exponential decay with increased lifetimes, which suggests the existence of two sets of conformers as well (Figures S10 and S11, Table S2). Interestingly the appropriate ACID plots do not show aromatic macrocyclic π-conjugation for any accessible dihedral angles between porphyrin framework and anthracene (Figure S19). Thus the origin of two excited state lifetime components of Apor is suggested to be induced solely by different tilting angles not by the macrocyclic π-conjugation effect.

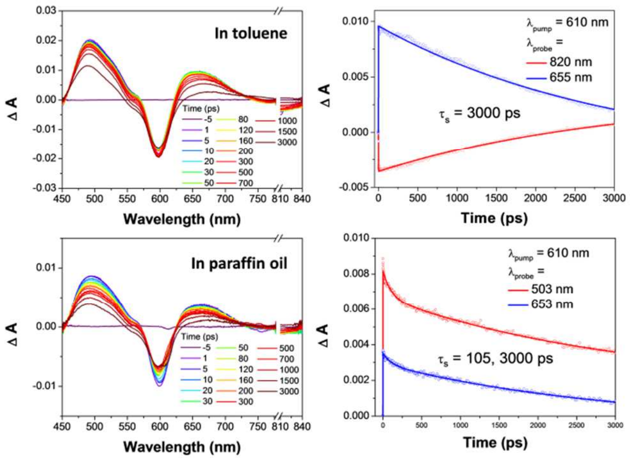


Figure 4. The TA spectra (left) and decay profiles of *p*-Bpor in toluene (top) and paraffin oil (bottom)

To analyse the conformational changes of thiaaceneporphyrinoids, we have investigated the photophysical properties by lowering the temperature.[8] Upon lowering the temperature, the absorption spectra of a series of thiaaceneporphyrinoids show intensified and red-shifted spectra with resolved structures. The fluorescence of thiaaceneporphyrinoids was blue-shifted at 77 K. Even for Apor, the fluorescence was detected at 77 K (Figure S13). The excited state lifetimes of a series of thiaaceneporphyrinoids at 77 K exhibit double exponential decay with increased excited-state lifetimes compared with those at room temperature (Figure S13 and S14). Interestingly, *m*-Bpor also shows double exponential decay at 77 K, indicating the contribution of multiple *m*-Bpor conformers, as discussed above for Apor. The excited-state lifetimes of *p*-Bpor (2.5, 7.5 ns) and Npor (2.3, 7 ns) are nearly the same. Furthermore, relatively fast decay components (~2.5 ns) of *p*-Bpor and Npor are similar to the averaged excited state lifetime of *m*-Bpor. Thus *p*-Bpor and Npor have two types of conformers revealing aromatic or nonaromatic π-conjugation in the macrocyclic ring. The second one induces the excited state dynamics of a series of thiaaceneporphyrinoids to become fast. Furthermore, the excited state lifetimes of Apor are relatively short compared to *m*-Bpor, which can be understood by taking into consideration the distorted structures and the increased density of states due to the increased number of atoms. From these results, we could conclude that the excited state dynamics of a series of thiaaceneporphyrinoids are significantly affected by the π-conjugation pathway which can be controlled by the torsional angle between porphyrin framework and benzene moiety in the macrocyclic ring.

In summary, a series of thiaaceneporphyrinoids show structural diversity giving rise to conformers with either aromatic or nonaromatic π-conjugation depending on their structures. The macrocyclic ring conjugation is limited at the dihedral angle among 80-110˚ between porphyrin framework and acene moieties. Furthermore, the conformational flexibility determines macrocyclic π-conjugation affecting the photophysical and chemical properties of the porphyrinoids.

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Electronic Supplementary Information (ESI) available: Synthetic procedures, and additional spectroscopic and crystallographic data together with computational details. CCDC reference numbers 1002418-1002419. For ESI and crystallographic data in CIF or other electronic format see DOI:

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