Prediction of magnesium tetraethynylporphyrin's solubility by theoretical calculation

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ABSTRACT: To investigate the solubility of porphyrin derivatives, their intermolecular interaction energies were calculated by the counterpoise method at the B97D3/6-31G(d) level. It was found that the calculated intermolecular interaction energies corresponded to the solubility measured by UV-Vis spectroscopy. This correlation was consistent with differences in substituents and in the metals in the porphyrin core.

KEYWORDS: porphyrin, solubility, theoretical calculation, intermolecular interaction

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INTRODUCTION

Porphyrin's unique properties derived from its planar π-conjugated system have attracted attention in many fields. Porphyrin is characterized by high stability, good light absorption efficiency, facile chemical modification, and the formation of supramolecular assemblies by π stacking [1-5]. As an organic semiconductor material, porphyrin has useful photoelectric conversion characteristics for organic solar cells and organic electroluminescence[6-10].

Organic solar cells are expected to serve as next-generation clean energy sources because of their cost performance, flexibility, light weight, and other beneficial features. Organic solar cells are classified into three types: dye-sensitized solar cells, which are a kind of wet solar cell using TiO_2[11]; organic thin-film solar cells, which can be scaled up by simple manufacturing methods[12]; and perovskite solar cells, which have rapidly advanced in recent years[13]. Porphyrin derivatives can be used as organic semiconductors with different roles in these various types of organic solar cells: a pigment in dye-sensitized solar cells[14-16], a donor or acceptor in thin-film organic solar cells[17-19], and a charge transport layer in perovskite solar cells[20-22]. The deposition of organic semiconductors in organic solar cells requires spin-coating, spray-coating, or screen printing, all of which are solution-based processes that require good solubility of organic semiconductor materials.

Porphyrin derivatives exhibit strong intermolecular interaction and good charge mobility due to π–π stacking. However, this also results in low solubility. Typical strategies for improving the solubility are to insert a metal that is compatible with coordinating solvents in the porphyrin core and to introduce long alkyl chain substituents onto the porphyrin core. Yet, by either approach, the target porphyrin derivatives must be synthesized and their solubility must be measured to confirm the improvement, and it is not uncommon to find, after considerable synthetic effort, that the desired increase in solubility has not been achieved. Therefore, an evaluation method that does not involve synthesis is needed to facilitate the development of porphyrin materials chemistry. In this paper, we propose that the intermolecular interaction energy calculated using density functional theory (DFT) can be used to evaluate the solubility of porphyrins. We demonstrate that the intermolecular interaction energy calculated by this method shows the same tendency as the solubility measured by UV-Vis absorption spectroscopy for various porphyrin substituents and metals.

EXPERIMENTAL

Materials

Materials were purchased from Tokyo Kasei (TCI) Co., SigmaAldrich Inc., and other commercial suppliers and used after appropriate purification. Anhydrous solvents (stabilizer-free) were purchased from WAKO Pure Chemical.

Theoretical calclations

The Gaussian09 package was used as a computational method. To calculate of the optimized structures of porphyrin dimers, we employed the polarized split-valence 6-31G(d) basis set and B3LYP function. In the calculation of the intermolecular interaction energies, the route section was # B97D3 /6-31G(d) counterpoise=2. Furthermore, in the estimate of energies of the optimized monomer, the route section was # sp B97D3 /6-31G(d).

RESULT AND DISCUSSION

Synthesis and measurement

Magnesium tetraethynylporphyrin derivatives, which have been synthesized for organic solar cells, were selected as the target compounds[23]. Compounds **1a–c** were obtained from a TIPS porphyrin derivative by deprotection and Sonogashira coupling to add two diketopyrrolopyrrole (DPP) units (Figure 1). Compound **1a** had 4-n-hexyl-phenyl substituents to improve solubility, **1b** had 4-trifluoro-phenyl substituents installed as electron-withdrawing groups, and **1c** had 4-dimethylamino-phenyl group installed as an electron-donating group. Furthermore, to investigate the difference of heterometals in the porphyrin core, we synthesized zinc tetraethynylporphyrin derivative **1d** from **1a** by removing magnesium and inserting zinc (Figure 2).

To measure solubility, we performed UV-Vis absorption spectroscopy using standard samples. The standard samples were prepared by diluting saturated solutions of compound **1a–d** 100-fold in tetrahydrofuran (THF). We compared the absorbance of the Q band (Figure 3).

Theoretical calclations

All calculations were carried out using the Gaussian09 program. In these calculations, we used isobutyl groups instead of 2-ethylhexyl groups in the DPP units to avoid the issue of chirality and to reduce the computational cost. We also replaced the n-hexyl groups in compound **1a** and **1d** with methyl groups. The intermolecular interaction energies were estimated by single-point calculation of optimized porphyrin dimers. In the calculation of intermolecular interaction energy, the supermolecule method was used. However, the supermolecule method causes basis set superposition error (BSSE), which overestimates the intermolecular attraction due to excessive stabilization of association[24]. The intermolecular interaction of a porphyrin dimer is a $\pi-\pi$ interaction that is mainly due to dispersion forces. BSSE cannot be ignored when a weak interaction such as dispersion force or hydrogen bonding is considered. There are several ways to correct for BSSE. One is to use Dunning's correlation-consistent basis functions considering electron correlation effects. A second approach is to use functions of higher order than triple zeta basis functions in order to include the molecular orbital extending outside the dimer. Along the same lines, a third method is to add diffuse functions[25]. Here, we employed Pople's split-valence 6-31G(d) basis set to reduce the large computational cost for porphyrin dimers. Taking into account the basis set, we corrected for BSSE by using the counterpoise method[26], which works by using basis functions of the dimer in the calculation of the monomer.

Figure 4 shows the optimized structures of the dimer of **1a′** and the dimer of **1d′**. In both cases, the dimer was stabilized with the upper and lower compounds twisted 90 degrees. While the distance between the magnesium atoms in the dimer of **1a′** was 5.83Å, that between the zinc atoms in the dimer of **1d′** was 5.32 Å. This difference could be explained by the atomic radii of these metals.

Generally, to estimate the energy of intermolecular interactions composed mainly of $\pi-\pi$ interactions, the Møller-Plessrt method (MP) or the configuration cluster method (CC) is employed. However, each of these methods is limited to small molecules. Tsuzuki and co-worker proposed model chemistry calculations combining MP2 and CCSD(T) in order to reduce the computational cost. However, this model chemistry is applicable to only dimers of small molecular compounds such as toluene, naphthalene, and thiophene[27-29]. Therefore, we employed DFT as a molecular orbital method. First, we calculated the optimized dimer of **1a′** using two types of DFT methods (Table 1).

B3LYP, which is the most common method for computations in organic chemistry, gave a positive value for the intermolecular interaction energy, even though the dimer should be stable. This inconsistent result indicated that B3LYP was not suitable for calculating the $\pi-\pi$ interaction energy because it could not consider the dispersion. Second, we used B97D3, which is based on the hybrid functional B97 reported by Becke in 1997 [30-32] and is able to consider the dispersion. B97D3

showed a stable dimer with an intermolecular interaction energy of –44.89 kcal/mol. Hence, we employed B97D3 in the following calculation.

Table 2 shows intermolecular interaction energies of dimers of **1a′**-**1d′** estimated by single-point counterpoise calculation using B97D3/6-31G(d). The order of intermolecular interaction energy was **1a′ < 1b′ < 1d′ < 1c′** from lowest to highest stability. By contrast, the order of solubility estimated from the Q band absorbance in Figure 3 was **1a′ > 1b′ > 1d′ > 1c′**. This result consequently meant that intermolecular interaction energy and solubility were correlated. Moreover, this correlation was consistent with differences in substituents on the aryl units and in the metal in the porphyrin core. The separation energies of association were calculated as the difference between the energy of the optimized dimer and that of the optimized monomer (Table 3). The energy of association was also correlated with the measured solubility.

CONCLUSION

In this paper, we focused on intermolecular interaction energy to evaluate porphyrin solubility. We estimated the intermolecular interaction energy by the counterpoise method at the B97D3/6-31G(d) level to reduce the computational cost. Although this calculation method was simple, the calculated interaction energies corresponded well to the measured solubility. In conclusion, this calculation method was meaningful as an approach for comparing the relative solubility of porphyrins without synthesis and measurement.

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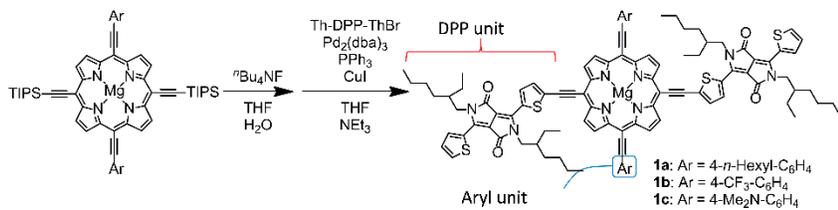32. Grimme S. *J. Comp. Chem.* 2006; **27**: 1787_1799.

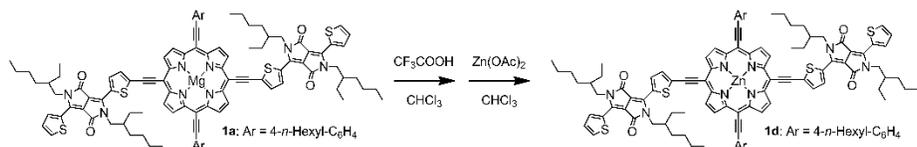**Fig. 1.** Synthetic route to magnesium tetraethynylporphyrin derivatives **1a–c**.

Fig. 2. Synthetic route to zinc tetraethynylporphyrin derivative **1d**.

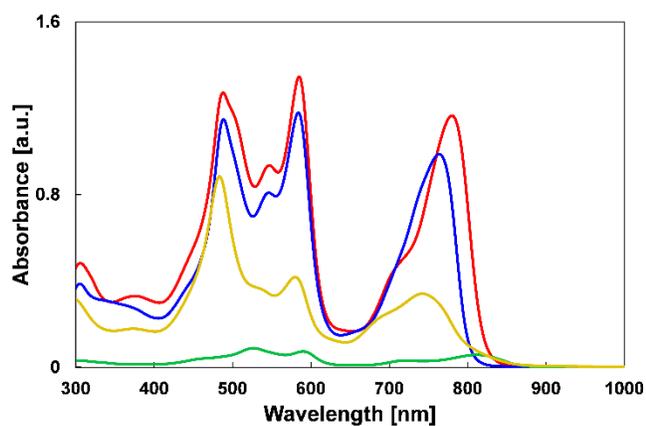**Fig. 3.** UV-Vis spectra of compound **1a–d** in THF for comparison of solubility: **1a** (red), **1b** (blue), **1c** (green), and **1d** (yellow).
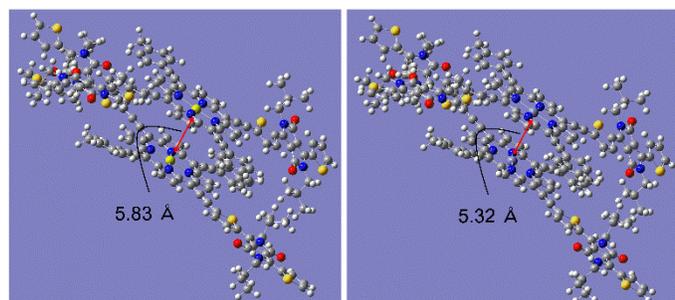

Fig. 4. Optimized structures of the dimer of **1a′** (left) and the dimer of **1d′** (right).

Table 1. DFT calculation of the optimized dimer of **1a′** (kcal/mol).

DFT method	Intermolecular interaction energy	BSSE
B3LYP	2.38	0.022
B97D3	−44.89	0.016

Table 2. DFT calculation of optimized dimers of **1a′-1d′** (kcal/mol) and measured solubility.

Compound	Intermolecular interaction energy	BSSE	Q band absorbance in Figure 3
1a′	–44.89	0.016	1.17
1b′	–49.47	0.028	0.99
1c′	–59.47	0.023	0.058
1d′	–52.06	0.021	0.34

Table 3. Separation energies of association (kcal/mol).

Compound	Energy of optimized dimer	Energy of optimized monomer	Separation energy of association
1a′	–7338446.43	–3669202.16	–42.11
1b′	–8085377.60	–4042665.43	–46.74
1c′	–7575898.94	–3787921.72	–55.50
1d′	–9321180.52	–4660565.62	–49.28

Prediction of Magnesium Tetraethynylporphyrin's Solubility by Theoretical Calculation

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We focused on the intermolecular interaction energy to evaluate the porphyrin's solubility. We estimated intermolecular interaction energy by counterpoise calculation using B97D3/6-31G(d) to reduce computational cost. Although this calculation method was simple, the calculated interaction energies substantially corresponded measured solubility. In conclusion, this calculation method was meaningful as the relative comparison approach of porphyrin's solubility without synthesis and measurement.