Synthesis of chlorophyll derivatives directly conjugated with an aryl group at the C3 position and their photophysical properties

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Photosynthetically active chlorophyll-*a* is one of the naturally occurring porphyrinoids, which has a π-conjugated skeleton, called a chlorin. Its peripheral substituents affect the visible absorption spectra in a solution. Especially, the C3-substituents regulate the redmost Qy absorption bands[1]. The rotation around the C3-C3^1 single bond also controls the Qy maxima[2].

Two regioisomeric chlorophyll derivatives **1** and **2** directly conjugated with an aryl group at the C3 position (Fig. 1) were synthesized by chemical modification of chlorophyll-*a* extracted from a cyanobacterium, *Spirulina* species. The isomeric aryl-chlorins gave different Qy maxima in CH_2Cl_2 (Fig. 2). Aryl-chlorin **2** bearing a substituent at the *ortho*-position of the 3-phenyl group showed a bule-shifted Qy band, compared with that of **1**: from 667 to 664 nm in CH_2Cl_2. This blue shift was ascribable to the steric factor of the *ortho*-substituent, inducing π-disconnection of the 3-aryl group with a chlorins moiety through the rotation of the C3-C3^1 bond from the coplanar conformation.

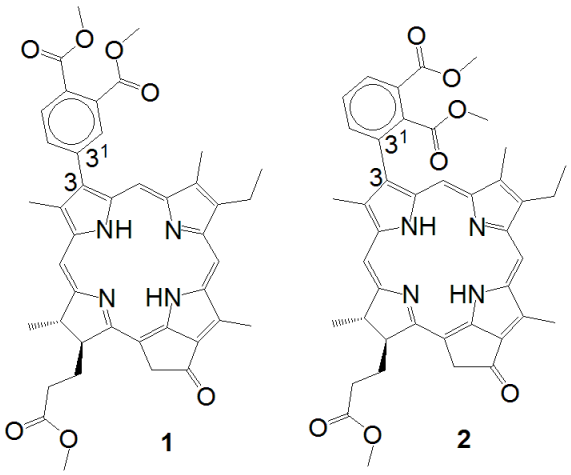

Figure 1. Synthetic chlorophyll derivatives directly conjugated with an aryl group

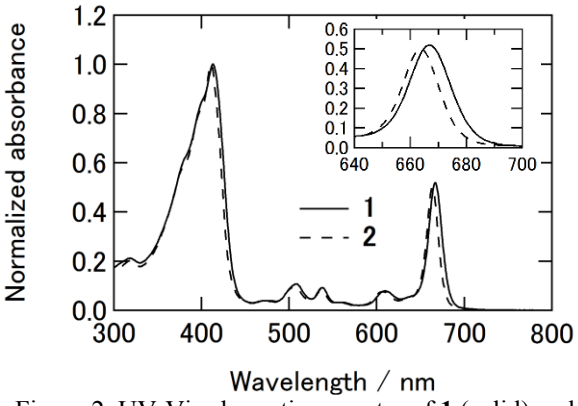

Figure 2. UV-Vis absorption spectra of **1** (solid) and **2** (broken) in CH_2Cl_2

References:

[1] H. Tamiaki, M. Kouraba, *Tetrahedron*, **1997**, 53, 10677-10688

[2] H. Tamiaki, K. Mizutani, S. Sasaki, T. Tatebe, *Tetrahedron*, **2016**, 72, 6626-6633