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Unexpected formation of benziphthalocyanine dimer: An easily synthesizable dimer of phthalocyanine analogue

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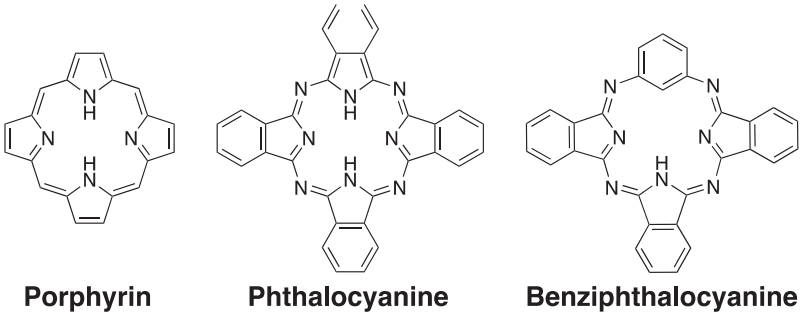
ABSTRACT

Methylene-bridged benziphthalocyanine dimer **2** was unexpectedly generated by the reaction of dihydroxybenziphthalocyanine **1** and formaldehyde in the presence of a catalytic amount of a base at room temperature. Single-crystal X-ray diffraction analysis of **2** revealed a V-shaped structure. Dimer **2** exhibited longer-wavelength absorption and fluorescence bands than monomer **1** in the near-IR region.

Phthalocyanines, which were fortuitously synthesized about a century ago, are extremely important chromophores with strong light absorption/emission in the visible/near-IR region. Extensive investigations of their basic molecular properties have led to applications in various fields, such as pigments, solar cells, and bioimaging.[1] Dimerization or oligomerization of porphyrins at peripheral positions enables electronic communication between the chromophores and modifies the photophysical properties, providing insight into the mechanisms of molecular wires and photosynthetic antenna models.[2] But, in contrast to numerous studies on dimeric and oligomeric porphyrins, there have been relatively few reports on phthalocyanine dimers and oligomers. Although dimeric phthalocyanines whose peripheral benzene units are annulated or linked through aryl, alkynyl, and alkyl units exhibit interesting optical properties,[3] these dimers are usually synthesized by statistical mixed condensation of two kinds of phthalonitriles, and this approach inevitably leads to low yields. This difficulty of preparation limits access to phthalocyanine dimers compared to porphyrin dimers, which can be obtained *via* late-stage selective chemical modifications at peripheral pyrrole rings and *meso* carbon atoms.[4]



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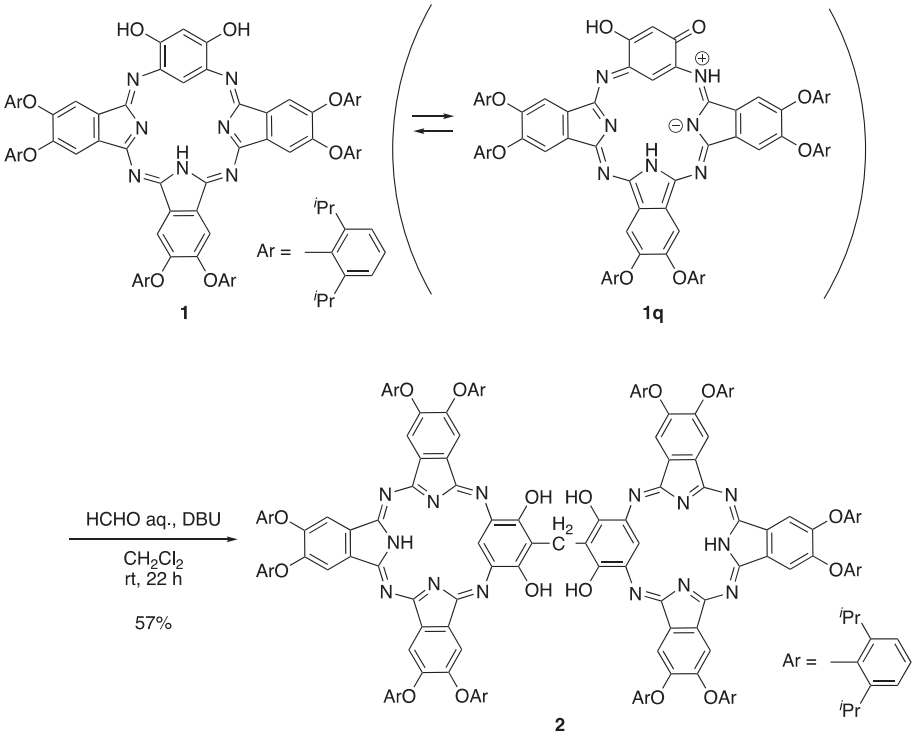

Scheme 1. Synthesis of benziphthalocyanine dimer **2**.

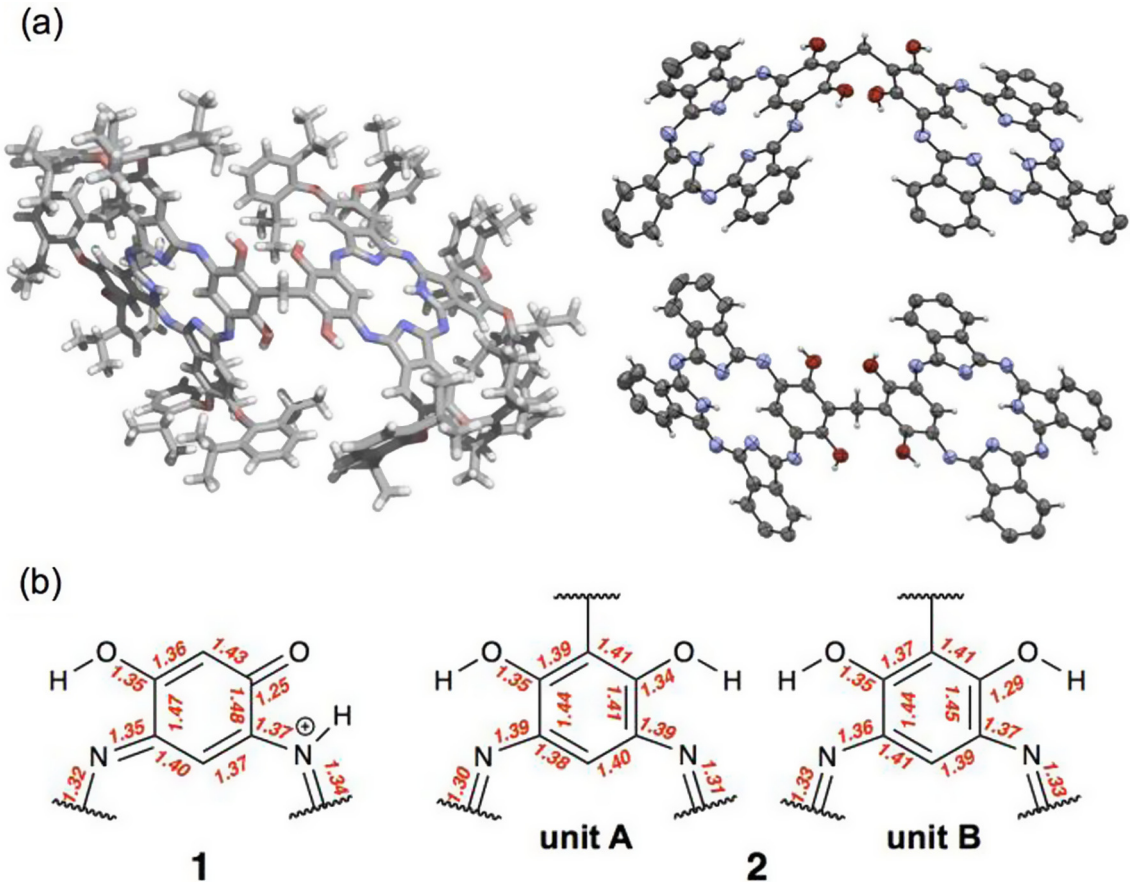

Fig. 1. (a) X-ray structure of **2** (left) and **2** without peripheral aryloxy substituents (right). The thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted and one of the disordered structures is shown for clarity. (b) Selected bond length (Å) in the crystals of **1**[6] (left) and **2** (right).