Diels–Alder Reaction of Tribenzo[*b,g,l*]thiopheno[*3,4-q*]porphyrazine as a New Path for Porphyrazine Core Modification

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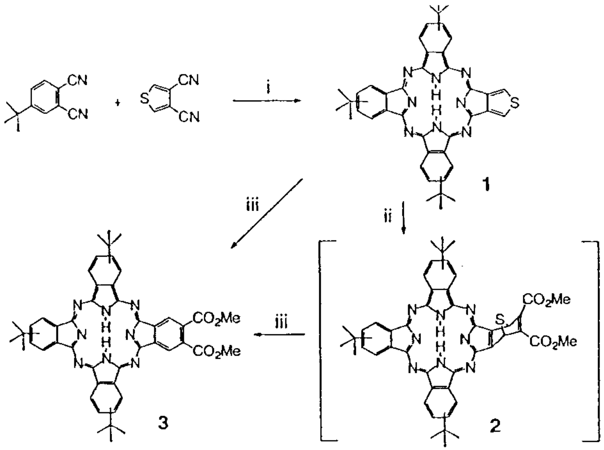
Diels–Alder reaction between tribenzo[*b,g,l*]thiopheno[*3,4-q*]porphyrazine and dimethyl acetylenedicarboxylate at ca. 200 °C produced a substituted tribenzo[*b,g,l*]porphyrazine and 3:1 unsymmetrically substituted phthalocyanine, which were characterized by UV-VIS, MCD, NMR, and mass spectroscopies.

Phthalocyanines (Pcs) and their analogues are useful compounds for the numerous applications.[1] The possibility of Pc or porphyrazine core modification leads to the synthesis of complexes with novel properties. However, most of the methods based on electrophilic or nucleophilic substitution reactions have no regio- or stereo-selectivity, and therefore usually give a mixture of all possible positional isomers.[2] A very recently developed method, based on Diels–Alder reaction of peripherally substituted Pcs, led to the formation of selective single products.[3] However, in these cases, the Diels–Alder reaction was carried out on a unit attached far away from the Pc center and accordingly, the shape of the π conjugation system and absorption spectrum was not altered. In this communication, we report a Diels–Alder reaction with aromatic substituents directly linked to the porphyrazine core, which changes the spectroscopic properties of Pcs significantly. Since the functions of Pcs are often related to their color, it is important to be able to obtain Pcs with different absorption spectra after reactions. From the viewpoint of low-symmetrical Pc synthesis, the present method is the fourth method following the mixed condensation, polymer support, and subPc ring-expansion method.[1]

Our key starting material was diene-containing tribenzo[*b,g,l*]thiopheno[*3,4-q*]porphyrazine (compound **1**) which can be readily prepared by a cross cyclotetramerization reaction of 4-*tert*-butylphthalonitrile and 3,4-dicyanothiophene obtained by Rosenmund von Braun reaction of 3,4-dibromothiophene[4] in refluxing 2-(dimethylamino)ethanol (DMAE) for 2 h. After evaporation of the solvent, the residue was separated on a silica gel column using $CHCl_3$/toluene (1:1 v/v) and the second blue fraction containing the desired compound **1** was collected and recrystallized from $CHCl_3$–MeOH (the first fraction was symmetrical metal-free tetra-*tert*-butylphthalocyanine and no other green–blue fraction was detected, which were in agreement with the earlier reports[4,5]).[6] Compound **1** then reacted with a 3-fold excess of dimethyl acethylenedicarboxylate as a dienophile (Scheme 1). When the reaction temperature was higher than 220 °C, the initial Diels–Alder reaction product (compound **2**) was aromatized via sulfur bridge elimination, and thus the only sulfur-eliminated unsymmetrical phthalocyanine compound **3** was detected in the reaction mixture, in addition to unreacted **1**, as Pc derivatives. Compound **3** was isolated from the reaction mixture by TLC on neutral alumina with toluene/MeOH (9:1 v/v) as eluent, followed by recrystalization from MeOH–$CHCl_3$.[6] On the other hand, a small amount of sulfur-containing substituted tribenzo[*b,g,l*]porphyrazine (compound **2**) was obtained when the reaction temperature was kept below 200 °C. This was isolated by TLC on neutral alumina with toluene/MeOH as eluent (95:5 v/v), followed by precipitation from $CHCl_3$–MeOH.[6,7]



Scheme 1. Reagents and conditions: i) Li/DMAE, 2 h, reflux. ii) decalin, dimethyl acethylenedicarboxylate (DMAC), 12 h, 180 °C. iii) decalin, DMAC, 2 h, 220 °C.

Figure 1 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of **1** – **3**. The spectra differ significantly from each other since their π systems differ in shape in the close proximity of the porphyrazine core. Thus, a multi-peak Q band is seen in the absorption spectrum of **1**, with the most intense component shifted to the near-IR region, characteristic of tribenzo[*b,g,l*]thiopheno[*3,4-q*]porphyrazines.[4,5] The well-split two-peak Q band in the absorption spectrum of **2** is characteristic of tribenzo[*b,g,l*]porphyrazine.[8] On the other hand, compound **3** showed a four-peak Q band, typical of metal-free Pcs.[9] Finally, the MCD spectra of **1** – **3** are characteristic of unsymmetrical (with C_{2v} effective symmetry of chromophores) metal-free Pcs or their analogues,[1] producing Faraday *B*-terms approximately corresponding to the absorption maxima or shoulders. From the inversion of the sign of the *B*-terms, two strong Q band peaks in **2** and **3** obviously belong to the Qx and Qy transitions. In **1**, the 1st and 3rd Q bands viewing from the longer wavelength belong to different components, while the assignment of the 2nd band is unclear since a dispersion type MCD curve was observed corresponding to this band.

Thus, as mentioned above, compound **1** is the first example of a Pc analog in which an aromatic ring directly linked to a porphyrazine core was used in a Diels–Alder reaction. The method shown here has general applicability, and the other Diels–Alder reactions of **1** leading to low-symmetrical Pcs are

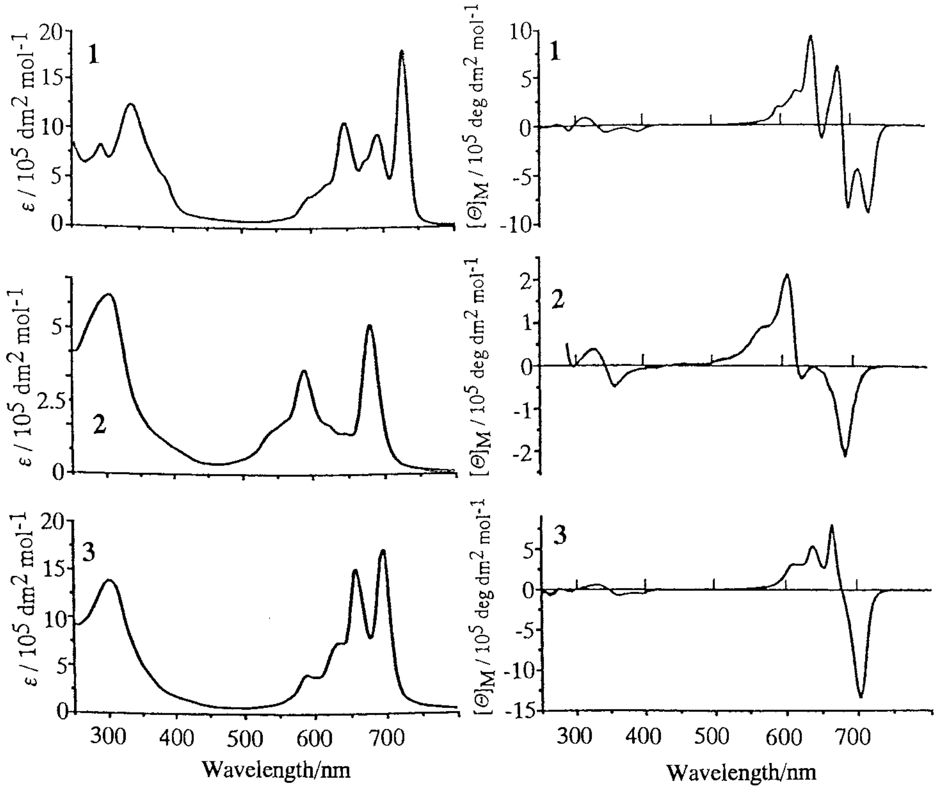


Figure 1. UV-VIS (left) and MCD (right) spectra of **1** – **3**.

in progress.

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6 Selected data for **1–3**. **1**: Yield: 11%. mp >250 °C. δ_H (400 MHz, $CDCl_3$): 8.65–9.15 (m, 6H), 8.0–8.25 (m, 5H), 1.8–1.92 (m, 27H), –2.30 to –2.05 (m, 2H). UV–VIS (λ,nm (log ε), $CHCl_3$): 337 (5.08), 648 (5.02), 692 (4.96), 727 (5.25). Found: C, 71.29; H, 5.82; N, 15.24%; Anal Calcd for $C_{42}H_{40}N_8S{\cdot}H_2O$: C, 71.39; H, 5.95; N, 15.86%; MS (MALDI-TOF$^+$, dithranol, *m/z)* M$^+$ 688; HRMS (FAB$^+$, *m*-nitrobenzyl alcohol, *m/z*) [M+H]$^+$ 689.3203 Calcd for [M+H]$^+$, 689.3175. **2**: Yield: 2%. mp >250 °C. UV–VIS (λ,nm (log ε), $CHCl_3$): 347 (4.8), 607 (4.54), 691 (4.72). Found: [M–1]$^+$, 829 (MALDI-TOF$^+$, dithranol). Calcd for $C_{48}H_{46}N_8O_4S$: M–1, 829. **3**: Yield: 26%. mp >250 °C. δ_H (400 MHz, $CDCl_3$): 7.6–8.05 (m, 11H), 4.61 (s, 6H), 1.8–1.92 (m, 27H), –0.42 (s, 2H). UV–VIS (λ,nm (log ε), $CHCl_3$): 345 (5.12), 609 (4.57), 671 (5.16), 707 (5.21). Found: C, 71.52; H, 6.22; N, 13.92%; [M+1]$^+$, 799 (MALDI-TOF$^+$, dithranol). Calcd for $C_{48}H_{46}N_8O_4$: C, 72.18; H, 5.76; N, 14.04%; M+1, 799.

7 Previously reported Diels–Alder reaction products[3] may be close to compound **2** in that they contain oxygen-bridges instead of the sulfur-bridge of this study, although their location is distant from the Pc center.

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