Synthesis and Spectral Property of Novel Phthalocyanines Substituted with Four Azo Group Moieties on Periphery of Phthalocyanine Ring

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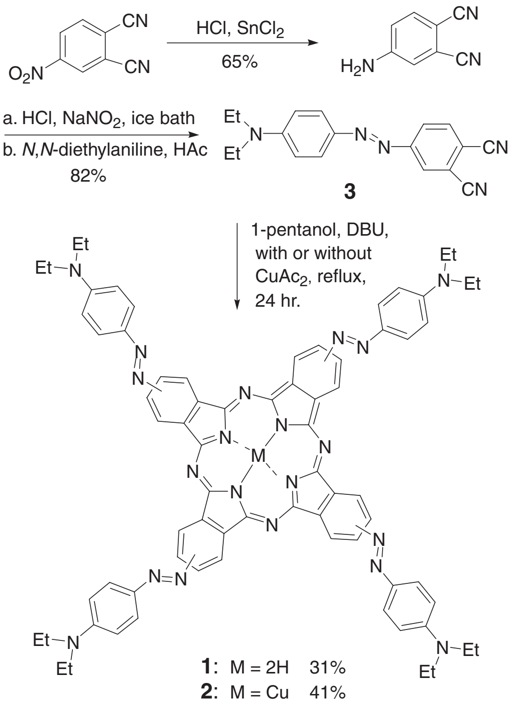
A novel class of phthalocyanines substituted with azo group moieties on the periphery of phthalocyanine ring was synthesized, and they show obvious, broad uncommon absorption band in the visible region compared to those normal phthalocyanines.

Phthalocyanines (Pcs) are known for their excellent chemical, light, and thermal stability, and especially for an intense absorption in the near-infrared region (NIR), leading to a wide variety of current and potential applications in many fields such as electrophotography, optical disks, photodynamic therapy of tumors, and so on.[1] Most of modern uses of Pcs are focused on the electronic properties of the π-electron system of the macrocycles.

Normally, phthalocyanines produce the most intense absorptions at 660–690 nm (Q-band).[2] A great deal of efforts have so far been made to shift the Q- and B-band of Pcs by extending the π-system of Pc ring for matching wavelengths of the used light sources. For this purpose, among approaches is ether that Pc molecules are benzoannulated[3,4] or that electron donors are introduced onto Pc rings.[5,6] In addition, direct attachment of Pc ring with chromophores through π-conjugated bridges tends to alter its electronic structures.[7,8] In that cases, the Q-band of Pcs, indeed, undergoes a red shift due to the extension of π-conjugated system, and but their absorptions in the visible region are too weak to be paid an attention. Michael J. Cook etc. has given indication of an absorption band, but still very weak, for the Pcs in the 450–600-nm region.[9]

Inspired by the approaches mentioned above, we made an attempt to attach electron donors through π-conjugated bridges onto the Pc ring to enlarge the absorption spectra of Pcs. To the best of our knowledge, there has been no report about Pcs with N,N double bond connected directly onto the Pc ring. Here we describe the preparation of the novel phthalocyanines containing *N*,*N*-diethylaminophenyl azo group on the periphery. The new compounds show obvious absorption band in the visible region besides the intense Q-band.

Compound **1**, tetrakis[4-(*N*,*N*-diethylamino)phenylazo]phthalocyanine, and compound **2**, tetrakis[4-(*N*,*N*-diethylamino)phenylazo]phthalocyaninato copper,[10] were conveniently prepared in three steps from 4-nitrophthalonitrile according to Scheme 1. Compound **1** and **2** are a black powder and a black-brown powder, respectively, and easily dissolved in THF.



Scheme 1.

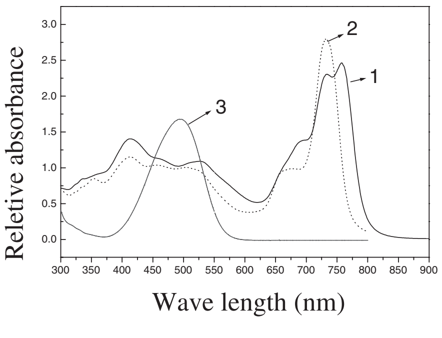


Figure 1. The absorption spectra of compound **1**, **2**, and **3** in THF.

Figure 1 shows the UV to near-IR spectra for **1** and **2**, as well as **3** for a comparison. The $\lambda_{\max}$ of the Q-band is about 759 nm ($\varepsilon_{\lambda\ 759\,\mathrm{nm}}$: $1.5 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for compound **1** and about 735 nm ($\varepsilon_{\lambda\ 735\,\mathrm{nm}}$: $1.6 \times 10^5\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for compound **2**, respectively. Compared to the normal Pcs,[2] the Q-band of the new Pcs with the azo moieties on the Pc ring has a significant red-shift, by about 90 nm for **1** and about 40 nm for **2**, respectively. In general, the red-shift of Q-band is a common feature for substituted Pcs.[1,9,11,12] It is noteworthy that the B-band absorption usually at about 350 nm for the normal Pcs[2] is not observed in the spectra of the new Pcs. Instead, a middle and broad new absorption band appears approximately at between 300 and 600 nm. The $\lambda_{\max}$ of the B-band is about 415 nm ($\varepsilon_{\lambda 415\,\mathrm{nm}}$: $7.5 \times 10^4\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for **1** and 415 nm ($\varepsilon_{\lambda\ 415\,\mathrm{nm}}$: 5.9 ×

$10^4\,M^{-1}\,cm^{-1}$) for **2**. As for as the IR is concerned, the compound **1** and **2** have a very similar pattern ranging from 3000 to $1000\,cm^{-1}$. But **1** has an additional middle and broad absorption at $\approx 3450\,cm^{-1}$ assigned to the N–H stretching vibration as compared to **2**.

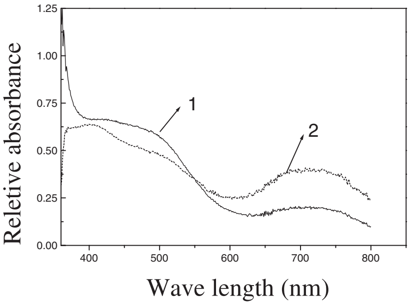


Figure 2. The absorption spectra of compound **1** and **2** adsorbed in thin TiO_2 film.

It is very interesting that **1** and **2** can easily and stably be adsorbed onto the surface of TiO_2. Their absorption spectra adsorbed onto thin TiO_2 film is shown in Figure 2. They show more intensive absorption in the visible region than the Q-band in the near-IR region, and the Q-band turns much broad compared to their spectra in THF solution.

Previous reports on Pcs were mainly focused on the near-IR absorption band and gave little indication of the absorptions in the visible region owing to their very weak absorptions compared to the Q-band. The notable red-shift of the Q-band as well as the shoulder is a common feature of Pcs' electronic absorption spectra, which can be assigned to an electronic transition to a higher energy level, and to the elongation of π-system of phthalocyanines.[12] The new and obvious absorption band appearing in the visible region for the new Pcs could be attributed to the combination of the red-shift of B-band and the absorption of the azo group introduced onto the Pc ring. It is well known that azo compounds usually show intense absorptions in the visible region (400–650 nm).[13] For instance, the precursor **3** produces an intense absorption from 450 to 550 nm (Figure 1). Obviously, here is the first observation of the new absorption band having effectively broadened the spectral absorption range of the Pcs. This kind of additional absorptions is really uncommon, and might entrust some novel opto-electronic properties to the Pcs.

In summary, we have prepared a new class of Pcs containing azo structure on the periphery and enriched categories of Pcs. The present result provides an important suggestion for enhancing the absorptions and enlarging the range of spectral absorptions for Pcs, which may entrust some new optical, electronic, and chemical properties to them. They are expected to find applications in organic opto-electronic conversion devices such as solar cells and photoconductors, in which research is currently under way.

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10 Compound **1** and **2** should be the mixture of their regioisomers.

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14 Preparation: Compound **3** was obtained by following normal method for synthesis of azo compounds. Compound **1**: 4′-*N*,*N*-diethylaminoazobenzene-3,4-dicarbonitrile (3.3 mmol), DBU (0.5 mL) and 1-pentanol (30 mL) were mixed in a 100-mL three-neck flask equipped with a mechanical stir and refluxed for 24 h. A black powder was filtered off, washed with ethanol and acetone, in turn, then extracted with ethanol in a Soxhlet apparatus thoroughly, and dried under vacuum, giving the product of 301 mg (yield: 31%). Compound **2**: According to the same conditions as synthesis of **1** except that $CuAc_2$ (2 mmol) was added in reaction mixture. A black-brown powder was filtered off, washed with ethanol, dilute hydrochloric acid, water, ethanol and acetone, in turn, then extracted with ethanol in a Soxhlet apparatus thoroughly, and dried under vacuum, giving the product of 440 mg (yield: 41%). Selected Data: Compound **3**: mp 116–118 °C; UV–vis λmax (THF) 495 nm; MS (EI) m/z (relative intensity) 303 [M^+, 65], 288 (100), 260 (15), 148 (25), 133 (28); ^1H NMR (300 MHz, CDCl3) δ 1.20 (t, 6H), 3.47 (q, 4H), 6.97–7.25 (m, 7H); Anal. Calcd for **3**: C, 71.29; H, 5.61; N, 23.10%. Found: C, 71.26; H, 5.67; N, 23.30%. Compound **1**: UV–vis (THF) λmax (log ε) 759 (5.176), 525 (4.775), 415 (4.876); IR (KBr, cm^{-1}) 3450 (m), 2970 (w), 1599 (s), 1513 (m), 1392 (m), 1351 (m), 1269 (w), 1139 (m), 1092 (w); MS (MALDI-TOF) m/z calcd for **1** 1215.4, found 1214.1 [$M^+ - 1$]; Anal. Calcd for **1**: C, 71.17; H, 5.77; N, 23.06%. Found: C, 70.62; H: 5.79; N, 22.70%. Compound **2**: UV–vis (THF) λmax (log ε) 735 (5.212), 510 (4.722), 415 (4.770); IR (KBr, cm^{-1}) 2970 (w), 1598 (s), 1512 (m), 1390 (m), 1346 (m), 1268 (w), 1140 (m), 1092(w); MS (MALDI-TOF) m/z calcd. for **2**: 1276.9, found: 1275.3 [$M^+ - 1$]; Anal. Calcd for **2**: C, 67.74; H, 5.33; N, 21.95%. Found: C, 67.34; H, 5.19; N, 21.45%.