A Phthalocyanine Producing Green, Ocher, and Red Colors Depending on the Central Metals

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Metal complexes of a highly deformed 1,4,8,11,15,18, 22,25-octaphenylphthalocyanine have been synthesized, and found to show various colors ranging from bright green, ocher, and red depending on the central metal employed.

Phthalocyanines (Pcs) are one of the most extensively developed industrial colorants. In the past few decades, they have been used as dyes and pigments but also in a variety of high technology applications such as photodynamic cancer therapy (PDT), nonlinear optics, as electrical conductors, and in high-density information storage disks.[1] Pcs typically have very intense blue or green colors due to the spectral bands associated with the lowest energy π-π^* transitions (Q-band) in the 650-750 nm region.[2] The color of Pcs can be altered substantially through the addition of peripheral substituents[3] or through extension of the π-conjugation systems.[4] The effect of the central metal on the energy of the Q band is usually relatively small except in the case of a few metals such as antimony and bismuth.[5] We have recently synthesized metal-free 1,4,8,11,15,18,22,25-octaphenyl Pc, **1** (Figure 1), whose Q band appears at ca. 790 nm (in toluene) due to a substituent effect associated with the eight phenyl groups. In addition, there is a remarkable degree of skeletal deformation due to the steric interactions.[6] A recent paper by Ghosh et al.[7] based on time-dependent DFT calculations of non-planar transition metal porphyrins predicted that a specific metal(d)-porphyrin(π) orbital interaction was responsible for sizable red shifts of the major electronic bands in the electronic spectra. On that basis we expect metal complexes of a highly non-planar Pc such as complex **1** also show substantial metal-ligand interactions, which would bring about marked color changes that would be detectable to the naked-eye. In the present study, we report colors ranging from bright green to ocher and then finally to red based on complexes synthesized with different central metals.

Nickel, zinc, tin, and lead were chosen as central metals since they can be readily inserted into metal-free Pcs. Tin[8] and particularly lead[9] complexes are expected to amplify the structural deformation since the central metal sits above the plane of the four pyrrole-nitrogen-coordination site. Metal insertion was performed by reacting **1** with the corresponding metal salt (ca. 160-190 °C).[10] Stable nickel, zinc, and lead complexes (**2**, **3**, and **5**, respectively) were obtained without additional axial ligands. In contrast, unlike normal unsubstituted SnPc, **4** was isolated only as a dihydroxo complex, despite the use of chloride salt ($SnCl_4$) as the starting material.

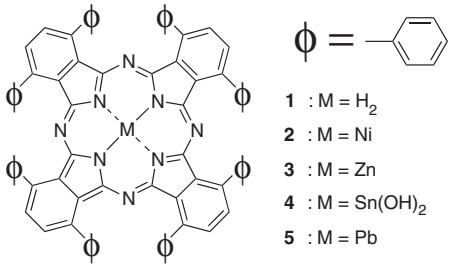

Figure 1. Structures and abbreviations of the Pcs in this study.

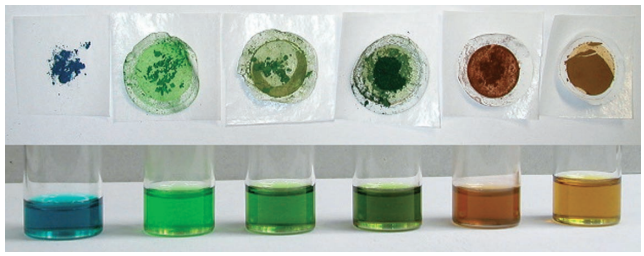

Figure 2. Color appearances in solid states (top) and in toluene solutions (bottom) for tetra-*tert*-butylated H_2Pc, **2**, **3**, **1**, **4**, and **5** (from left to right).

Figure 2 shows the color of **1**-**5**, together with that of tetra-*tert*-butylated H_2Pc as a reference. The color of each solution is reasonably similar to that of the corresponding solid. Compared to the normal blue H_2Pc, **1** has a dark green color due to the bathochromic shift of the Q band by ca. 100 nm. The difference of the color for each derivative can be clearly distinguished by the naked-eye. Nickel (**2**) and zinc (**3**) complexes show only slight color changes, but tin (**4**) and lead (**5**) complexes show drastically different colors from those of typical Pcs. Red and ocher colors appear in the case of **4** and **5**, respectively.

Electronic absorption spectra of **1**-**5** are shown in Figure 3. Those of **1**-**3** are typical for Pcs,[11,12] i.e. an unsplit Q band appears in the visible region and less intense Soret bands are located in the 300-500 nm region. There is almost no absorption between 500 and 600 nm of the spectra of **1**-**3**. The Q-band shifts slightly to the blue after nickel and zinc insertion. Nickel or zinc complexes of normal planar Pcs also show a hypsochromic shift of the Q band relative to that of the metal-free species. The spectra of planar, normal $SnPc(OH)_2$[13] and PbPc[14] exhibit Q band at 671 and 698 nm, respectively, indicating that tin or lead do not normally result in marked bathochromic shifts. In contrast, the Q bands of **4** and **5** shifted significantly to the red. The shift for **5** reached ca. 620 cm^{-1} (ca. 40 nm). This may be attributable to the interaction between the highly deformed Pc skeleton and the protruding central metals. Since the Q band of **4** and **5** shift to the near-IR region, blue or green colors could no longer be observed by the naked-eye. Compounds **4** and **5** gain intensity around 500 nm, which may contribute to their red and ocher colors, respectively. At the longer wavelength side of the Q band, shoulders are observed for **4** and **5**, though this is not the case for the corresponding planar Pcs. The origin of these shoulders and band broadening is unknown at present.

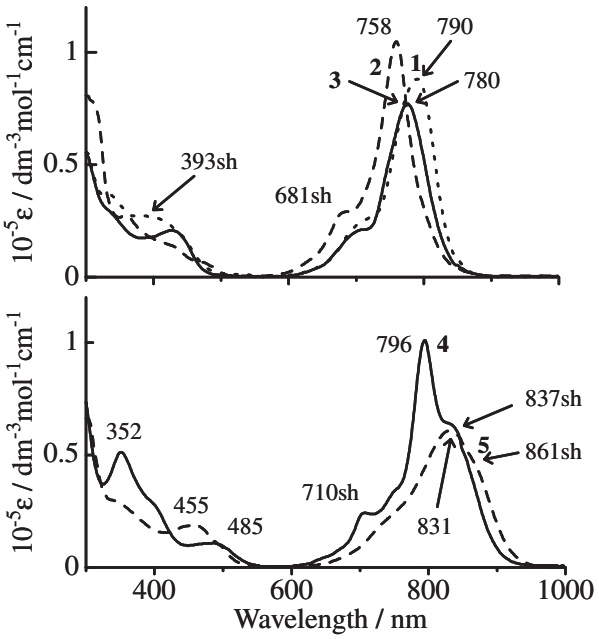

Figure 3. Electronic absorption spectra of **1** (dotted line), **2** (dashed line) and **3** (solid line) (top) and **4** (solid line) and **5** (dashed line) (bottom) in toluene.

High level molecular orbital calculations may be required to fully investigate this subject.

Table 1 summarizes the first oxidation and reduction potentials (vs ferrocene/ferrocenium) in *o*-dichlorobenzene (*o*-DCB). In general, the oxidation and reduction potentials depend on the polarizing power of the central metal.[15] This was found to be the case for **2**-**5**, i.e. the potential difference between the first oxidation and reduction per se correlates well with the most intense Q band energy, despite the fact that **4** is different from other Pcs in that it has two axial ligands, and therefore it has significantly different oxidation and reduction potential values from the other complexes. Since very limited data have been available on redox propeties of tin and lead Pcs,[16] it is difficult to draw more detailed conclusions from the data in Table 1.

In summary, we have outlined the drastic color changes that can occur for the metal complexes of highly deformed octaphenylated Pc. As shown in Figure 3, the Q band shifts from 758 nm for the nickel complex to 831 nm for the lead complex. This is the first example of complexes based on a specific modified Pc skeleton which show a systematic trend in color based on the difference of the central metal. Detailed structural and spectroscopic analyses will be reported in due course.

Table 1. The first oxidation and reduction potentials (vs Fc^+/Fc) in *o*-DCB containing 0.1 M tetrabutylammonium perchlorate

Compound	Metal	Ox./V	Red./V	Energy gap/V
1	H_2	−0.01	−1.39	1.38
2	Ni	+0.15	−1.46	1.61
3	Zn	−0.22	−1.81	1.59
4	$Sn(OH)_2$	+0.49	−0.95	1.44
5	Pb	−0.22	−1.43	1.21

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References and Notes

1 "Phthalocyanines: Properties and Applications," ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York (1989-1996), Vol. 1-4.
2 E. A. Luk'yanets, "Electronic Spectra of Phthalocyanines and Related Compounds," NIOPIK, Moscow (1989).
3 For example: N. Kobayashi, N. Sasaki, Y. Higashi, and T. Osa, *Inorg. Chem.*, **34**, 1636 (1995).
4 For example: N. Kobayashi and T. Fukuda, *J. Am. Chem. Soc.*, **124**, 8021 (2002).
5 H. Isago, Y. Kagaya, and S.-i Nakajima, *Chem. Lett.*, **32**, 112 (2003), and references therein.
6 N. Kobayashi, T. Fukuda, K. Ueno, and H. Ogino, *J. Am. Chem. Soc.*, **123**, 10740 (2001).
7 H. Ryeng and A. Ghosh, *J. Am. Chem. Soc.*, **124**, 8099 (2002).
8 a) R. Kubiak and J. Janczak, *J. Alloys Compd.*, **189**, 107 (1992). b) M. K. Friedel, B. F. Hoskins, R. L. Martin, and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, **1970**, 400.
9 a) Y. Iyechika, K. Yakushi, I. Ikemoto, and H. Kuroda, *Acta Crystallogr.*, **B38**, 766 (1982). b) K. Ukei, *Acta Crystallogr., Sect. B*, **29**, 2290 (1973).
10 **2**: A mixture of **1** and $NiCl_2 \cdot 2H_2O$ was reacted in DMF at 160 °C for 1 h to give **2** after alumina column chromatography (toluene-pyridine 10:1 (v/v)) to remove unreacted salt. Mass(ESI-TOF): *m/z* 1180 (M+2); Anal. calcd for $C_{80}H_{48}N_8Ni$: C, 81.43; H, 4.10; N, 9.50%. Found: C, 81.63; H, 4.72; N, 9.07%. **3**: A mixture of **1** and $Zn(CH_3CO_2)_2$ was reacted in DMF at 170 °C for 1 h to give **3** after alumina column chromatography (toluene-pyridine 20:1 (v/v)). Mass(ESI-TOF): *m/z* 1184 (M^+); Anal. calcd for $C_{80}H_{48}N_8Zn$: C, 80.97; H, 4.08; N, 9.44%. Found: C, 81.02; H, 4.53; N, 9.58%. **4**: A mixture of **1** and $SnCl_4$ was reacted in 1-chloronaphthalene at 190 °C for 45 min to give **4** after alumina column (toluene–pyridine 4:1 (v/v)) chromatography. Mass(ESI-TOF): *m/z* 1274 (M^+); Anal. calcd for $C_{80}H_{48}N_8Sn(OH)_2 \cdot H_2O$: C, 74.37; H, 4.06; N, 8.67%. Found: C, 73.93; H, 4.17; N, 8.17%. **5**: A mixture of **1** and $Pb(CH_3CO_2)_2 \cdot 3H_2O$ was reacted in DMF at 170 °C for 30 min to give **5** after alumina column chromatography (toluene–pyridine 9:1 (v/v)). Mass(ESI-TOF): *m/z* 1329 (M+1); Anal. calcd for $C_{80}H_{48}N_8Pb$: C, 72.33; H, 3.64; N, 8.43%. Found: C, 72.00; H, 4.15; N, 8.06%.
11 Although metal-free Pcs generally show clearly split Q-bands, the splitting energy decreases with shifting the Q-band to the red and finally they merge into an essentially unsplit band.[12]
12 N. Kobayashi, in "Phthalocyanines: Properties and Applications," ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York (1992), Vol. 2, Chap. 3.
13 B. N. Diel, T. Inabe, J. W. Lyding, K. F. Schoch, Jr., C. R. Kannewurf, and T. J. Marks, *J. Am. Chem. Soc.*, **105**, 1551 (1983).
14 "Aldrich Handbook of Fine Chemicals and Laboratory Equipment," Aldrich (2003).
15 A. B. P. Lever, E. A. Milaeva, and G. Speier, in "Phthalocyanines: Properties and Applications," ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York (1989), Vol. 1, Chap. 1.
16 M. L'her and A. Pondaven, in "The Porphyrin Handbook," ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego (2003), Vol. 16, Chap. 104.

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