

# The synthesis of a symmetrically substituted $\alpha$ -octa(isopentoxy)anthralocyanine

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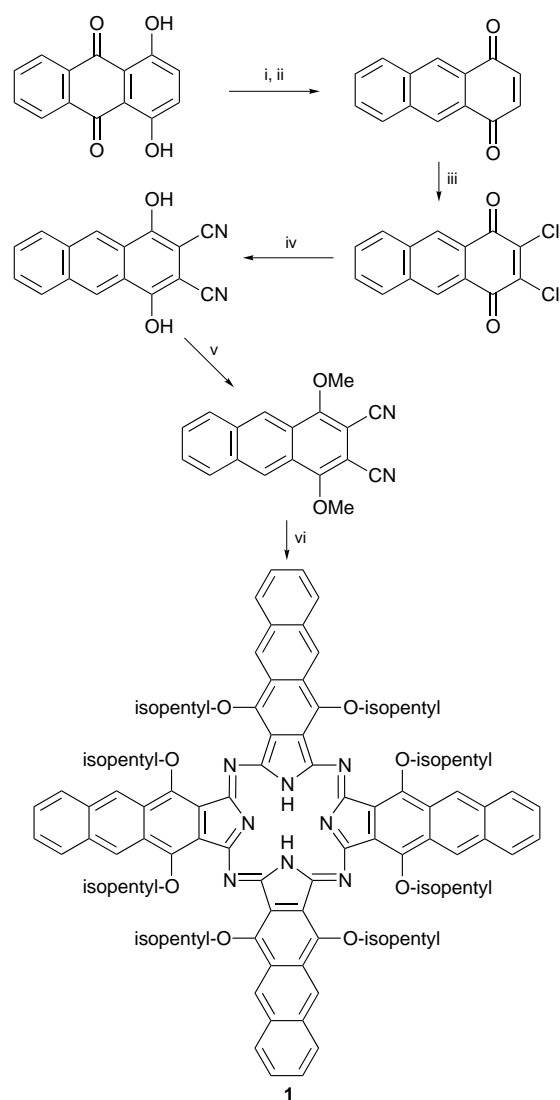
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**$\alpha$ -Octa(isopentoxy)anthralocyanine has been synthesized and is found to have an unprecedented low-energy Q-band absorption and a low first oxidation potential.**

In an effort to synthesize dyes that may find use in optical limiting devices<sup>1,2</sup> we have been investigating phthalocyanine complexes (Pcs). The Pcs have a region of relatively weak absorption from *ca.* 450–650 nm which falls between their Q and B bands. In addition, in this same spectral region they have strong excited-state absorption in their singlet manifold and even stronger absorption in their triplet manifold.<sup>1</sup> Consequently, in this spectral range the molecules are relatively transparent under weak irradiation, but under intense irradiation, such as from a pulsed laser source, it is possible to create a significant excited-state population that will be relatively opaque in the same spectral range. When the Pcs are functionalized with heavy atoms it is also possible to enhance the intersystem crossing rate so as to generate a large triplet population. Since the excited-states of these molecules are strongly absorbing, and it is possible to saturate the ground to excited-state transition, they are referred to as reverse saturable absorbers (RSAs) and are useful in optical limiting devices.<sup>1,3,4</sup> For certain applications where it is important to protect sensors from intense laser pulses in the 600–900 nm range, it is necessary to move the transparency window (the region between the high energy side of the Q band and the low energy side of the B band) to lower energy. It has been demonstrated that the transparency window of the phthalocyanines can be tuned by a number of structural modifications.<sup>5</sup> One approach is to benzannulate the phthalocyanine molecules and another is to substitute the rings with electron donors, thereby shifting the Q and B bands and therefore the transparency window to lower energy. We have also attempted to make these molecules soluble in common organic solvents despite structural features that would impart limited solubility. This is necessary in order to make dyes that are useful for many device configurations. Octaalkoxyphthalocyanines and octaalkoxynaphthalocyanines,<sup>5</sup> as well as a number of alkyl substituted anthralocyanines,<sup>6–9</sup> have been previously described. Here we describe the synthesis, linear optical properties and electrochemistry of  $\alpha$ -octaisopentoxyanthralocyanine **1**.

The synthetic pathway to octaalkoxyanthralocyanine **1** is shown in Scheme 1. The method is analogous to the synthesis of the octaalkoxynaphthalocyanines and tetra-*tert*-butylanthralocyanine.<sup>9</sup> The anthracene-1,4-dione was prepared by literature methods.<sup>10,11</sup> For 2,3-dichloroanthracene-1,4-dione, the method of Langa was modified. Chlorine gas was added in a vigorous stream to a solution of anthracene-1,4-dione in boiling acetic acid, which was interrupted for 20 min every 5 min, until the reaction was deemed complete as evidenced by <sup>1</sup>H NMR spectroscopy. The red solution with yellow crystalline precipitate was allowed to cool to ambient temperature and then filtered. The yellow crystalline solid was dried under vacuum (0.01 Torr) over KOH, to give the title compound in 75% yield.<sup>10,11</sup> 2,3-Dicyano-1,4-dihydroxyanthracene was prepared in moderate yield by treating 2,3-dichloroanthracene-1,4-dione with an excess of KCN in hot EtOH.<sup>12</sup> *O*-Methylation was accomplished with dimethyl sulfate in the presence of K<sub>2</sub>CO<sub>3</sub>.

The synthesis of **1** from 2,3-dicyano-1,4-dimethoxyanthracene was analogous to the synthesis of the corresponding  $\alpha$ -octaalkoxynaphthalocyanine to yield 15% of the desired product after purification. As was consistent with the reactivity of other alkoxy Pcs,<sup>13</sup> we observed complete *trans* alkoxylation of the methyl group by the isopentyl group from the solvent (there were no observable singlet methyl resonances by <sup>1</sup>H NMR spectroscopy) under the reaction conditions.<sup>13</sup> It is also important to note that **1** is fairly sensitive to silica gel. Thus, the isolated yield of **1** is significantly reduced if chromatography is performed at conventional flow rates and accordingly, flash



**Scheme 1** Reagents and conditions: i, NaBH<sub>4</sub>, MeOH; ii, H<sub>2</sub>O, HCl; iii, Cl<sub>2</sub>, AcOH, reflux; iv, KCN, EtOH; v, dimethyl sulfate, K<sub>2</sub>CO<sub>3</sub>, acetone; vi, lithium isopentoxide, isopentyl alcohol, reflux

chromatography techniques are necessary. All compounds gave satisfactory spectroscopic and analytical data.†

The UV–VIS/NIR spectrum of **1** (Fig. 1) shows a small splitting between the Q<sub>x</sub> and Q<sub>y</sub> bands and the bands are sharp, characteristic of phthalocyanines. The Q bands for **1** occur at 980 and 954 nm. These bands are red shifted about 110 nm compared to the analogous octaalkoxynaphthalocyanine and red shifted 80 nm compared to the tetra-*tert*-butylanthralocyanine.<sup>6</sup> The B bands of **1** are bathochromically shifted compared to the B bands of the octabutoxynaphthalocyanine, giving solutions of **1** a pleasant violet hue. The transparency window has moved about 100 nm bathochromically compared to the Npcs.<sup>6</sup>

The cyclic voltammogram of **1** (Fig. 2) shows four quasi-reversible redox events; those at  $E_{1/2} = -1279$  and  $-1039$  mV we attribute to sequential one electron reductions and those at 35 and 366 mV we attribute to sequential one electron oxidations. The separation of the inner-most redox events correlates well with the energy of the Q band. We have shown that through a systematic approach we have moved the transparency window of a Pc to a region centred about 700 nm. This will allow for the investigation of the utility of this compound and derivatives thereof as the active elements for optical limiters in a particularly important spectral range.

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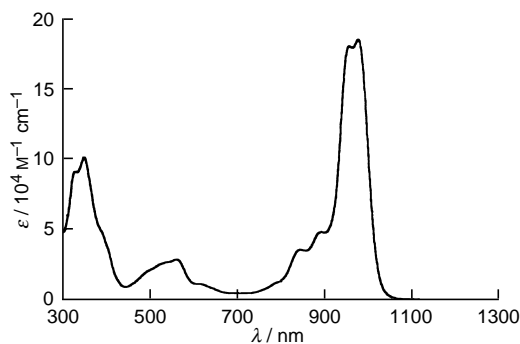


Fig. 1 The absorption spectrum of **1** in toluene

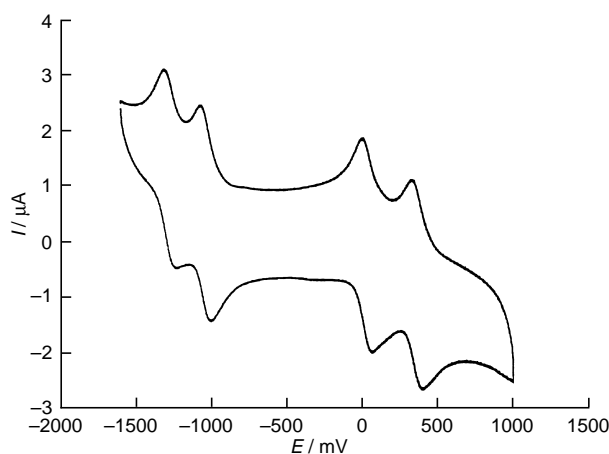


Fig. 2 Cyclic voltammogram of **1** in CH<sub>2</sub>Cl<sub>2</sub>, Ag/AgCl (aq.), 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>, 500 mV s<sup>-1</sup>, V<sub>init.</sub> = -600 mV. Four quasi-reversible redox events at  $E_{1/2} = -1279$ ,  $-1039$ , 35 and 366 mV are observed. The  $E_{1/2}$  of ferrocene was found to be 514 mV under these conditions.

## Footnotes

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† 2,3-Dicyano-1,4-dimethoxyanthracene. To a slurry of 2,3-dichloroanthracene-1,4-dione (50 g, 185 mmol) in EtOH (1 l) at 60 °C under argon was added a solution of KCN (61 g, 925 mmol) in water (240 ml). The mixture was stirred at 60 °C for 2 h then filtered. The solution was then cooled and neutralized with 3 M HCl (carefully in a hood with a sodium hypochlorite trap). The brown solid precipitate was collected and dried overnight over KOH under vacuum. To a mixture the crude 2,3-dicyano-1,4-dihydroxyanthracene (34 g) and K<sub>2</sub>CO<sub>3</sub> (76 g, 548 mmol) in acetone (150 ml) was added dimethyl sulfate (40 ml, 411 mmol). The mixture was heated to reflux for 3 h then poured into water. The brown solid residue was further washed with water then dried under vacuum over P<sub>2</sub>O<sub>5</sub>. The bright yellow product was collected by sublimation then recrystallized from MeOH to give 5 g of the title product. <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 8.85 (s, 2 H), 8.14 (4 line m, 2 H), 7.69 (4 line m, 2 H), 4.39 (s, 6 H); ν<sub>max</sub>(KBr)/cm<sup>-1</sup> 3062, 2949, 2226, 1452, 1351, 1029, 886, 749; λ<sub>max</sub>(CHCl<sub>3</sub>)/nm 404, 388, 370.

Compound **1**. To a slurry of 2,3-dicyano-1,4-dimethoxyanthracene (2 g, 6.9 mmol) in anhydrous isopentyl alcohol (40 ml) at 25 °C under argon was added lithium (5 mg). The mixture was heated to reflux for 1 h then allowed to cool to room temperature and acetic acid (10 ml) was added and stirred overnight at room temperature under argon. The mixture was neutralized with deoxygenated saturated aqueous NaHCO<sub>3</sub> and extracted with deoxygenated methylene CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with deoxygenated water then dried with Na<sub>2</sub>SO<sub>4</sub> (if MgSO<sub>4</sub> was used a considerable amount of AncMg was formed). The solvent was removed *in vacuo* and the residue was quickly chromatographed (solvent flow rate was about four times as fast as a standard flash column, if chromatography was run at a conventional rate the yield was greatly attenuated) on a short (125 × 45 mm) silica gel column with deoxygenated solvent (1:1, cyclohexane-CH<sub>2</sub>Cl<sub>2</sub>) to give 10% yield (0.29 g, 0.18 mmol) of the title compound; <sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 9.6 (br m, 8 H), 8.44 (br m, 8 H), 7.76 (br m, 8 H), 5.35 (m, 16 H), 2.19 (br q, *J* 7 Hz, 16 H), 2.26 (nonet, *J* 7 Hz, 4 H), 1.5 (br s, 24 H), 1.1 (br d, *J* 6 Hz, 36 H), 0.92 (br s, 12 H); <sup>13</sup>C NMR (75 MHz, [<sup>2</sup>H<sub>6</sub>]THF): δ 151.2, 133.4, 130.1, 129.9, 127.4, 124.8, 76.5, 40.5, 26.4, 23.4 (two quaternary carbons not observed); <sup>13</sup>C NMR DEPT 90 (125 MHz, [<sup>2</sup>H<sub>6</sub>]THF): δ 129.88, 127.36, 124.84, 26.43; FAB MS C<sub>105</sub>H<sub>116</sub>N<sub>8</sub>O<sub>8</sub>: Calc., 1602.87. Found (MH<sup>+</sup>), 1603.9. Elemental analysis C<sub>105</sub>H<sub>116</sub>N<sub>8</sub>O<sub>8</sub>: Calc., C, 77.94; H, 7.23; N, 6.92; Found, C, 78.00; H, 7.27; N, 6.84%.

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