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Mendeleev Commun., 2019, **29**, 212–214

Mendeleev Communications

Electrochemical and spectroelectrochemical properties of tetra-*tert*-butylphthalocyanine indium(III)

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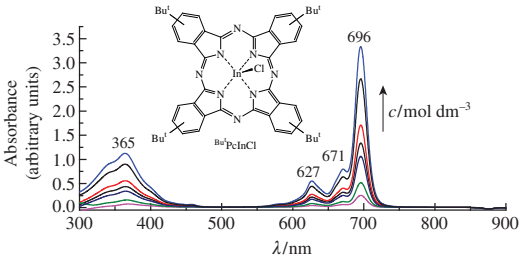
DOI: 10.1016/j.mencom.2019.03.033

The known tetra-*tert*-butylphthalocyanine indium(III) complex was obtained *via* a novel procedure based on the microwave-assisted synthesis, which made it possible to shorten the reaction duration to 5 min and to significantly increase the yield. Redox transitions of the obtained complex were characterized by cyclic voltammetry and square-wave voltammetry. The spectroelectrochemical data revealed the opportunity to utilize this complex as an electrochromic component in various devices.



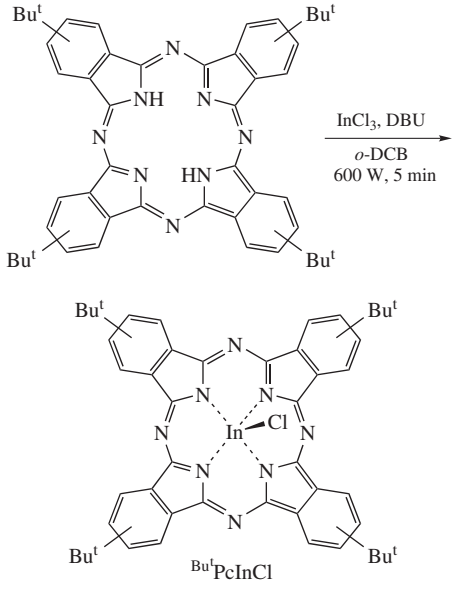
Investigations of physico-chemical properties of phthalocyanines have opened up broad prospects for practical applications of these compounds. They are widely used as photoconductors,[1,2] active media for optical information recording,[3] charge transporting material in light-emitting diodes.[4] Phthalocyanine complexes and their substituted analogs are known as capable of exhibiting electrochromism, which ensures their utilization as components of information displays.[5–9] Thus, their spectral and electrochemical properties are of special interest.

This work was focused at a substituted indium(III) phthalocyanine ($^{Bu^t}$PcInCl). The replacement of the axial ligand, as well as electrochemical stability of the complex, allows one to use it as a catalyst in various photocatalytic processes. The bulky *tert*-butyl groups were chosen due to the high solubility of *tert*-butyl-substituted phthalocyanines, and moreover, their presence prevents aggregation.[10,11] Although the synthesis of $^{Bu^t}$PcInCl by the classical method of cyclic tetramerization of *tert*-butyl-substituted phthalonitrile and its spectral properties have already been reported,[12,13] there are almost no data on its electrochemical properties.

Thus, the present work was aimed at the optimized synthesis of $^{Bu^t}$PcInCl, studies of its electrochemical properties, and spectroelectrochemical analysis of redox processes. The target compound was prepared *via* metallation of a *tert*-butyl-substituted phthalocyanine ligand with indium(III) chloride (Scheme 1). Our synthetic approach was based on utilization of microwave irradiation, which allowed us to significantly increase the yield from 49 to 85% and to shorten the reaction time from 5 h to 5 min as compared to the known procedure.[12] The obtained compound was characterized by a combination of high resolution mass spectrometry (MALDI TOF/TOF), UV-VIS-NIR spectroscopy, and thermogravimetry coupled to mass spectrometry (TG–MS). It is important to notice the high stability of this complex (up to 380 °C).

The MALDI TOF/TOF mass spectrum contained a peak of the molecular ion (*m*/*z* of 886.2729 corresponding to $^{Bu^t}$PcInCl). The UV-VIS-NIR absorption spectra recorded for solutions of $^{Bu^t}$PcInCl in toluene at different concentrations contained the characteristic absorption bands (Figure 1), while the maximum (696 nm) was linearly depended on the concentration with a molar extinction coefficient $\varepsilon = (1.32\pm0.04)\times10^5$ dm^3 mol^{-1} cm^{-1}.

The redox properties of complex $^{Bu^t}$PcInCl were estimated in *o*-dichlorobenzene (*o*-DCB) by cyclic voltammetry (CV) and square-wave voltammetry (SWV) using a platinum and glassy carbon (GC) disk electrodes in the potential range from –1.8 to



Scheme 1

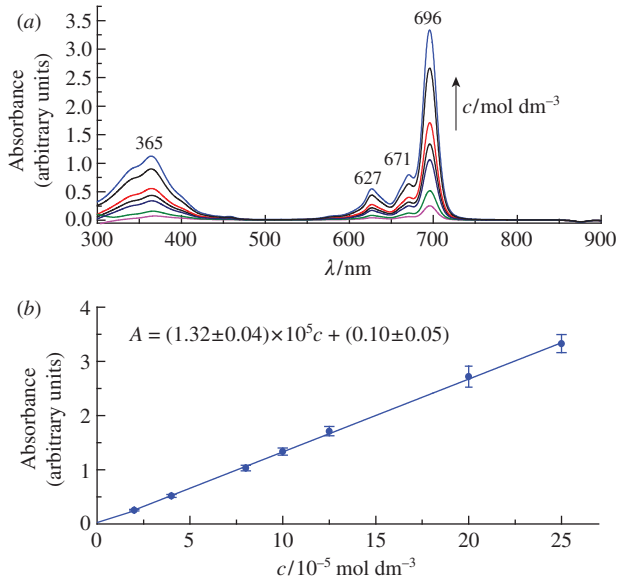


Figure 1 (*a*) Absorption spectra of $^{Bu^t}$PcInCl in toluene at different concentrations and (*b*) its absorbance at 696 nm as the function of concentration.

1.5 V *vs.* Ag/Ag$^+$ (Figure 2, Table 1). As one can see from Table 1, the influence of the electrode nature on the potential values was insignificant.

The complex demonstrated a quasi-reversible oxidation Ox_1 at 0.705 V with two well-defined peaks for the both scan directions, where the peak-to-peak separation (ΔE) was 0.12 V. The second oxidation at 1.30 V was irreversible likely due to a subsequent degradation of the aromatic ring similarly to other phthalocyanines.[14–16] The first and second reduction reactions (Red_1 and Red_2) were quasireversible (ΔE = 0.15 V) yet showing a small split that was visible in both CVs and SWVs, which could mean that the electrochemical reactions were complicated by an aggregation, side chemical reactions, or adsorption processes. It can be assumed that the reduced anion radical $^{Bu^t}$PcInCl$^{\bullet-}$ may partially dissociate to result in heterogeneous behavior during the

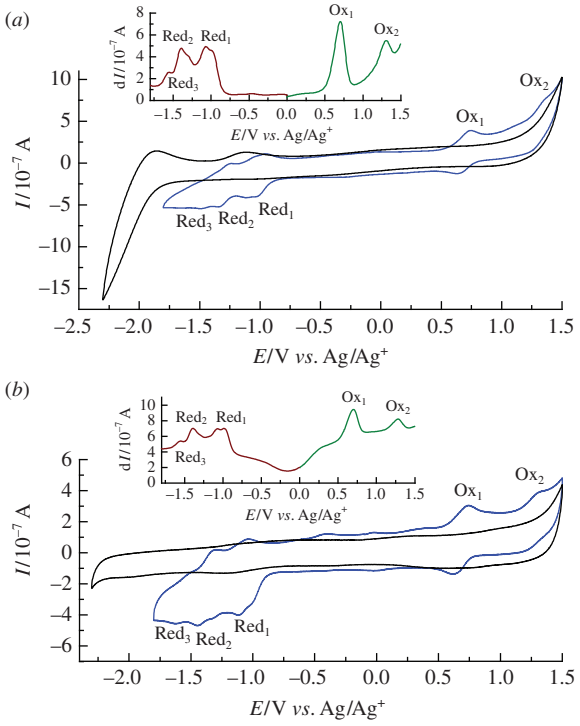


Figure 2 CVs of $^{Bu^t}$PcInCl (3.4×10^{-4} M) in *o*-DCB (0.05 M $TBAPF_6$) recorded on (*a*) Pt and (*b*) GC electrodes. Insets show SWVs data.

Table 1 Voltammetric data on complex $^{Bu^t}$PcInCl.

Electrode	$E_{1/2}$ (*vs.* Ag/Ag$^+$)/V				
	Red_3	Red_2	Red_1	Ox_1	Ox_2
Pt	–1.551	–1.395	–0.987	0.705	1.304
GC	–1.551	–1.390	–0.982	0.700	1.279

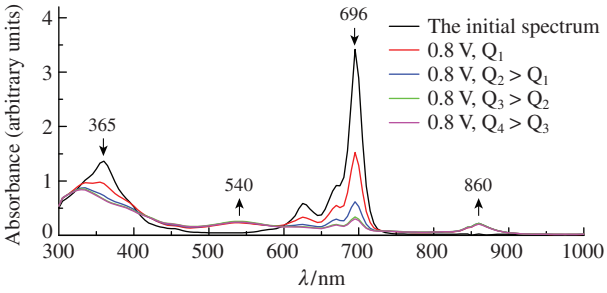


Figure 3 UV–VIS–NIR spectral changes for $^{Bu^t}$PcInCl (2.6×10^{-4} M) in DCB containing 0.1 M $TBAPF_6$ during its oxidation at the controlled potential (+0.8 V).

voltammetry experiments due to a small difference in reduction potentials and adsorption on the electrode surface. In summary, we have observed two traditional redox transitions and two additional ones, which was also consistent with the voltammetry data. One of these transitions is shown below:

$$InPcCl + e^- = InPcCl^{\bullet-}$$

$$InPcCl^{\bullet-} = InPc^{\bullet} + Cl^-$$

UV-VIS-NIR spectral changes for complex $^{Bu^t}$PcInCl during the controlled potential electrolysis at +0.8 V (Figure 3) reflect the transformation of the neutral phthalocyanine into the one-electron-oxidized form.

$$[In^{III}Pc^{2-}Cl]^0 \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} [In^{III}Pc^{1-}Cl]^{+\bullet}$$

green (neutral) red (oxidized)

During the oxidation of the neutral form, the Q band of the complex continues to decrease without a shift, while new broad bands of medium intensity appear at 540 and 860 nm, being characteristic exclusively of the electronic transitions inside the phthalocyanine ring.[14] An obsrved decrease in the intensity of the Soret (B) band was accompanied by a slight hypsochromic shift. This process gives well defined isosbestic points at 410, 600 and 730 nm, which indicates reversibility of the electronic transition. Noteworthy, the electrochemical reduction at 0.5 V fully recovers the initial character of the spectra thus confirming reversibility of the first oxidation process in agreement with the voltammetry data.

In conclusion, we have performed comprehensive electrochemical and spectroelectrochemical characterizations of tetra-*tert*-butylphthalocyanine indium(III) complex $^{Bu^t}$PcInCl and confirmed reversibility of the first oxidation process. Spectroelectrochemical analysis revealed a high color contrast of the redox forms of $^{Bu^t}$PcInCl, which allows one to use this complex as electrochromic material in a design of displays and as potential photosensitizers for different applications.[17–20] In addition, we have improved the known procedure for the preparation of this complex by carrying out a microwave-assisted synthesis, which resulted in the increased yield and shortened duration of the reaction.

The work was supported by the Russian Science Foundation (grant no. 17-13-01197). The spectroelectrochemical characterization was supported by the Russian Foundation for Basic Research (ERA, project no. 18-53-76006).

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Received: 31st October 2018; Com. 18/5731