# New conducting composite material based on a platinum phthalocyanine charge transfer salt and poly(bisphenol A carbonate): electrochemical, optical, magnetic and structural properties

**Iakov L. Kogan***† **and Kyuya Yakushi**

*Institute for Molecular Science, Miodaiji, Okazaki, 444, Japan*

Electrochemical intercalation has been used to form a new conducting composite film $PtPc(PF_6)_x$—PBC [PtPc = platinum phthalocyanine, PBC = poly(bisphenol A carbonate)]. This material has specific conductivity 0.5–1 S $cm^{-1}$, a positive value of thermopower of *ca.*10 μV $K^{-1}$ at 300 K as well as an EPR signal with Pauli-like behaviour in the temperature range 100–300 K. The principal *g* values ($g_{\parallel} = 2.0165$ and $g_{\perp} = 1.989$) and lattice parameters are close to those of $PtPc(ClO_4)_{0.5}$. Three electrochemical oxidation–reduction peaks and optical absorption spectra at different potentials have been registered.

Platinum phthalocyanine (PtPc) charge transfer (CT) salts are well-known organic compounds with metal-like behaviour[1] and catalytic properties for oxygen reduction.[2] The general procedure for formation of these materials is electrochemical crystallization from 1-chloronaphthalene solutions at 120 °C.[1] It takes more than two weeks to accumulate a small amount of the conducting crystals, which is often not enough for characterization, never mind practical application. The method mentioned does not allow control of the degree of charge transfer and may lead to polymorphism‡.

Earlier, polycarbonate and some other polymers were applied to form so-called reticulate doped composites with organic CT salts.[3] However, a chemical oxidant was involved to convert the donor molecule to its cation-radical salt, which, again, did not permit simple control of the CT salt composition. A few attempts have been made to obtain high conducting phthalocyanine composites, *e.g.*, nickel phthalocyanine—poly(*p*-phenylene terephthalamide) (0.1 S $cm^{-1}$), which was prepared *via* dry jet-wet spinning.[4]

At the same time it is well known that conducting polymers[5] and thin films of MePc evaporated *in vacuo*[6] can be transformed into the oxidized state electrochemically. Thus, electrochemical intercalation of PtPc crystals encapsulated in the polymer matrix has been used in this work to form conducting films of $PtPc(PF_6)_x$—PBC. A new hexaphosphate anion salt has been chosen due to difficulties with crystallization by ordinary methods.

In contrast to vacuum evaporated films with a typical thickness of 40 nm,[7] the polymer composites allow the relatively large crystals (*ca.* 100 μm) to be maintained and can be released from the electrode after doping as free standing films. The porous and flexible matrix preserves the integrity of the film and is spacious enough to accommodate the volume changes of the CT salt during electrochemical intercalation.

## Experimental

PBC (Aldrich) was used without further purification. PtPc was synthesized[8] from $PtCl_2$ and phthalonitrile, sublimed three times and dispersed in $CHCl_3$ or $CH_2Cl_2$ in an ultrasonic bath together with PBC for 10 min. The suspension obtained was stable within a day, the final concentrations of PtPc and PBC being 1 mass%. Thin semi-transparent composite films of 1 μm thickness were obtained by spin coating at 500 rpm while thick layers (*ca.* 100 μm) were cast from suspension. Analysis by scanning electron microscopy (SEM) showed that the composite films were heterogeneous and consisted of 50–100 μm length crystals of PtPc dispersed in an amorphous polymer matrix.

Electrochemical experiments were performed in a vacuum-tight three compartment electrochemical cell. Glassy carbon or glass plates covered with ITO transparent films (surface resistance 10 Ω) were employed as current collectors. Propylene carbonate distilled *in vacuo* into a flask filled with 4 Å molecular sieves was mixed with 0.1 M tetrabutylammonium hexafluorophosphate (Aldrich) under argon atmosphere. Electrochemical measurements were performed in 0.1 M $Bu_4NPF_6$–propylene carbonate solution against a Ag/$10^{-3}$ M $AgClO_4$ + 0.1 M $LiClO_4$ in propylene carbonate reference electrode with a potential of +0.77 V with respect to the standard Ag/AgCl + 3 M KCl electrode. Spectroelectrochemical experiments were conducted in a three compartment cell with quartz windows installed in a Hitachi U-3400 spectrometer with a similar cell filled with electrolyte and placed in the reference beam. The thick composite film oxidized to 0.5 V was used for the measurement of electrical conductivity, thermopower, EPR spectra and X-ray diffraction.

The instruments used for the measurements were as follows. Potentiostat/Galvanostat: HA 501 (Hokuto Denko Ltd.); Physical Property Measurement System: Model 6000 (Quantum Design); EPR spectrometer: Bruker ESP-300 E; powder X-ray diffractometer: $MXP^3VA$ (Mac Science, Cu-Kα radiation); Energy Dispersive Analytical Electron Microscope (EDX): Hitachi S450/KEVEX.

## Results

### Electrochemical properties of PtPc–PBC thin films

The cyclic voltammogram (CV) of the composite film or, more exactly, the CV of the PtPc crystals in the electrochemically passive polymer matrix, gave the main oxidation states of the donor. Fig. 1 shows a typical CV and demonstrates that at least three oxidation states can be distinguished. The interrelation between anodic and cathodic peaks has been evaluated in experiments with the scan reversed at potentials of 0.4 and 0.18 V (Figs. 1 and 2). The cathodic peak a′ ($\varphi = 0.00$ V) is hidden by the more intense transition c′ and can be observed only when the limit potential is set at or below 0.18 V. Anodic and relevant cathodic potentials are as follows: a = 0.00–0.05,

---

† Permanent address: Institute of Chemical Physics in Chernogolovka, Chernogolovka, Moscow Region, 142432, Russian Federation.

‡ In the case of electrochemical crystallization of NiPc a triclinic modification $(NiPc)_3(AsF_6)_2(C_{10}H_7Cl)$ is sometimes obtained instead of an orthorhombic modification $NiPc(AsF_6)_{0.5}$.

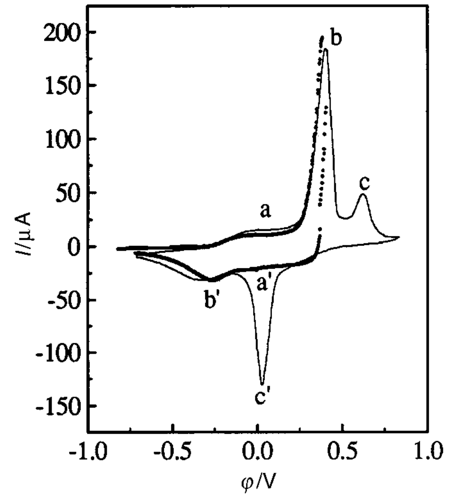

**Fig. 1** CV of a PtPc composite electrode in 0.1 M $Bu_4NPF_6$–propylene carbonate solution, scan rate 1 mV $s^{-1}$. The CV with the reverse potential at 0.4 V is indicated by circles. Peak a′ is hidden by c′.

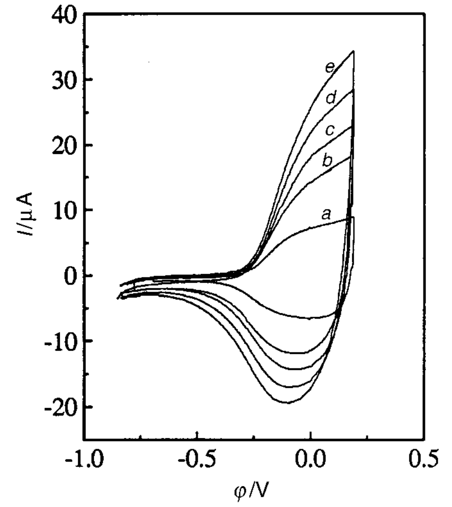

**Fig. 2** CV of a PtPc composite electrode in 0.1 M $Bu_4NPF_6$–propylene carbonate solution with reverse potential at 0.18 V; scan rates (*a*) 2, (*b*) 4, (*c*) 6, (*d*) 8 and (*e*) 10 mV $s^{-1}$

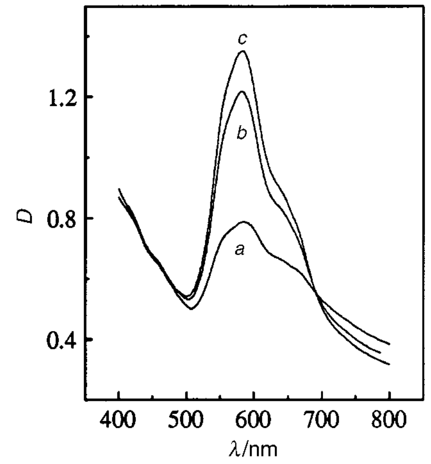

**Fig. 3** Optical absorption spectra of a PtPc composite electrode in 0.1 M $Bu_4NPF_6$–propylene carbonate solution during the first three scans: (*a*) first, (*b*) second and (*c*) third

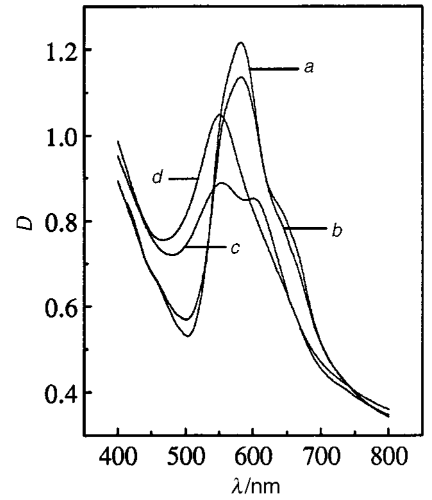

**Fig. 4** Optical absorption spectra of PtPc composite electrode in 0.1 M $Bu_4NPF_6$–propylene carbonate solution showing dependence on the potential of the electrode: (*a*) −0.8, (*b*) +0.2, (*c*) +0.4 and (*d*) +0.8 V

a′ = 0.00, b = 0.40, b′ = −0.33, c = 0.62, c′ = 0.028 V. The second (b, b′, Fig. 1) and third (c, c′) oxidation steps are characterized by very high potential differences (PD) of 0.73 and 0.59 V, in contrast to the first oxidation (a, a′) with PD ≈0–50 mV. The peak currents are approximately proportional to the square roots of the scan rates. Previous estimations made by comparison of the charge required for full oxidation of the PtPc crystals and their mass showed that at $\varphi = 0.8$ V the CT salt of composition $PtPcPF_6$ is formed.

## Optical properties of the composite film

Optical data obtained *in situ* for a semitransparent composite film is a good illustration of how properties of a CT salt can be characterized in the most general way for any donor–acceptor ratio. It is an important point that during cycling of the potential between the most reduced and oxidized states the degree of oxidation of each crystal of PtPc becomes larger and larger until it achieves a constant value. This effect is reflected in the enhancement of the peak heights in a cyclic voltammogram. The relevant changes in optical density are illustrated in Fig. 3. The optical spectra at different potentials were evaluated after several full cycles when the system had acquired reproducible behaviour. Fig. 4 shows the changes in optical absorption and its dependence on the degree of oxidation. The transformation of the reduced composite film at $\varphi = -0.8$ V to potential $\varphi = +0.2$ V leads to the disappearance of the absorption band at 650 nm. The next potential rise to +0.4 V is accompanied by the evolution of a new band at 550 nm, while the peak at 583 nm is substantially decreased and shifted to 600 nm. Full oxidation of PtPc to $\varphi = +0.8$ V results in the complete elimination of the absorption at 600 nm. The spectrum at $\varphi = +0.4$ V suggests a partially filled valence band, as we will discuss later.

## Structural changes

SEM pictures show that the electrochemically intercalated composite has a well defined crystalline structure. As a result, X-ray diffraction studies of the pristine powder and oxidized form have been undertaken. The pristine powder has the same diffraction patterns as α-PtPc[9] while the oxidized composite gives a pattern which is close to that obtained for $PtPc(ClO_4)_{0.5}$[1] CT salts§ with metal-like properties. This indicates that electrochemical intercalation results in the transform-

---

§ α-PtPc: *C*2/*n*, monoclinic, $a = 26.29$, $b = 3.818$, $c = 23.92$ Å, $\beta = 94.6°$, $Z = 4$.

$PtPc(ClO_4)_{0.5}$: *P*4/*mcc*, tetragonal, $a = b = 14.062$, $c = 6.510$ Å, $Z = 2$.

ation of the crystals from monoclinic to tetragonal symmetry, with lattice parameters $a=b=14.11(2)$, $c=6.491(8)$ Å.

The spectra obtained by EDX qualitatively confirm that phosphorus enters into the crystals, which suggests the formation of a CT salt with the possible formula PtPc($PF_6$)$_x$. Since the peak positions of Pt and P are almost the same, a Gaussian deconvolution was applied to separate the component originating from the phosphorus atom.

### Conductivity and thermopower measurements

It is not surprising that CT salt formation is accompanied by a dramatic conductivity growth up to 0.5–1 S cm$^{-1}$. Fig. 5 shows that the specific resistance of the composite film slowly increases down to 100 K with a subsequent steep rise at lower temperatures, in contrast to the single crystal of PtPc($ClO_4$)$_{0.5}$ with metal-like conductivity. Thermopower is positive at $T=$ 300 K (*ca.* 10 μV K$^{-1}$), but smaller than the value related to the single crystal of PtPc($AsF_6$)$_{0.5}$ (25 μV K$^{-1}$). However, a quasi-linear decrease of thermopower with temperature (Fig. 5) has been registered in the temperature range of 150–300 K.

### Electron paramagnetic resonance

EPR measurements have been used in this study as a most valuable technique for evaluation of the properties of the PtPc CT salt. Fig. 6 demonstrates that the EPR signal becomes narrower and shows well-defined uniaxial symmetry when the temperature falls. Principal $g$ values ($g_{\parallel}=2.0165$ and $g_{\perp}=1.989$) are close to those of PtPc($ClO_4$)$_{0.5}$ ($g_{\parallel}=2.0225$ and $g_{\perp}=1.992$) in the directions parallel and perpendicular to the normal of the molecular plane. The integrated intensity is almost constant down to 100 K, with subsequent growth in the range 100–3 K.

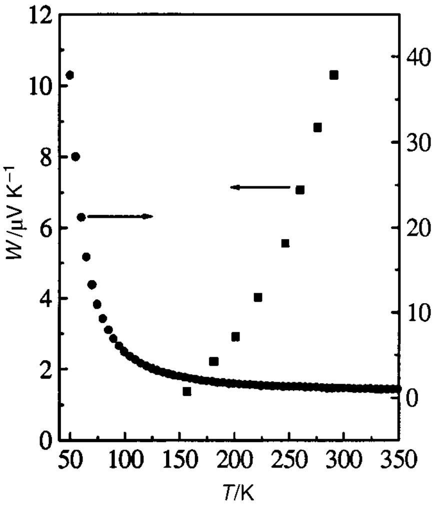

**Fig. 5** Relative resistance and thermopower *vs.* temperature

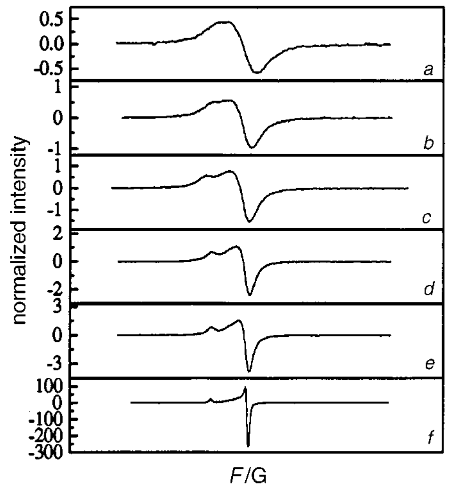

**Fig. 6** EPR spectra of PtPc($PF_6$)$_x$—PBC at (*a*) 300, (*b*) 270, (*c*) 240, (*d*) 210, (*e*) 190 and (*f*) 3 K

## Discussion

The most important point for discussion is the nature of the first peak (a) (Fig. 1). The amount of electricity required for this transition is about 15.6% of that necessary for full oxidation to PtPc$^{1+}$. Optical changes connected with this peak show that the shoulder at 650 nm resulting from the monoclinic symmetry of the reduced state has disappeared. To make clear the mechanism of electron transfer, the CV of the metal-free phthalocyanine ($H_2Pc$) was recorded. Two main anodic peaks at $\varphi=0.36$ (0.40) and 0.50 V (0.62 V), as well as associated cathodic peaks at $\varphi=-0.16$ ($-0.33$) and $\varphi=+0.10$ V (0.028 V) were registered. A third anodic peak at $\varphi=-0.18$ V (0.00 V) was also found, but its area is smaller in comparison with the PtPc composite electrode. The corresponding peak positions for PtPc are given in parentheses. It is clear that all the three oxidation–reduction transitions are linked with electron withdrawal from the Pc ring. The shift between the peak potentials of PtPc and $H_2Pc$ is due to the different position of the HOMO in these materials.

The main distinctive feature of the later peaks bb′ and cc′ is a large PD in contrast to the first one. There seems to be an overvoltage related to the sterical barriers during the migration (diffusion) of the relatively large anion into the PtPc crystal lattice. Recently, a relationship between PD and the Stokes radii of anions has been observed[5] in evaporated CuPc films. The authors found that the PD in the case of $NaPF_6$ electrolyte has the largest value. The main conclusion drawn is that the first peak relates to the process of doping with the anion transfer into the lattice of the reduced PtPc without sterical hindrance. The next oxidation encounters spatial difficulties and is characterized by a large PD between the anodic and cathodic peaks. An alternative explanation of the small PD between the aa′ peaks is based on the suggestion that only surface and small particle doping takes place during the first stage. In this case complete disappearing the absorption peak at 650 nm is connected with the fact that only small particles are semitransparent and thus responsible for absorption spectra in optical experiment (see below). Such an explanation was also supported by electrochemical experiments with a relatively large individual single crystal of PtPc($AsF_6$)$_{0.5}$ (1 mm length), where the aa′ peaks did not register at all (Fig. 7).

The peculiarities in the optical absorption spectra during electron withdrawal (Fig. 3) can be discussed from the viewpoint of structural transformations and changes in the degree

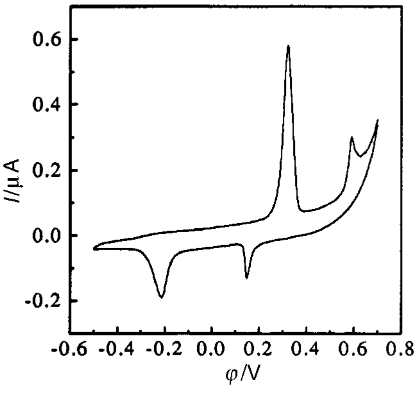

**Fig. 7** CV of a single crystal PtPc electrode in 0.1 M $Bu_4NPF_6$–propylene carbonate solution, scan rate 0.1 mV s$^{-1}$

of HOMO band filling.[10] The most reduced state has a strong maximum at 583 nm (Q band) and the above mentioned shoulder at 650 nm originated from Davidov splitting in the crystal system of low symmetry.[11] A potential shift to +0.2 V results in the disappearance of the latter. The next oxidation, to +0.4 V, leads to a new optical transition at 550 nm which is characteristic of the cation-radical of phthalocyanine. This absorption has been assigned to the optical transition from the lower lying valence band to the partly occupied HOMO band. This becomes dominant after full oxidation of PtPc composite (Fig. 6).

The increase of the optical density in the initial, most reduced state after several scans (see Fig. 2) originates from the change of the size of the CT salt crystals inside the matrix. As an approximation, the matrix contains a set of large (50–100 μm length) and small crystals, the latter being largely invisible to electron microscopy. Since the large crystals are not transparent, the semitransparent small particles of PtPc are responsible for the optical spectra. Full oxidation at +0.8 V leads to the disorganization of the large crystals, followed by their splitting into small crystals with a subsequent rise in optical density. The decrease of the apparent thickness of the crystals leads to higher peak currents in the CV at the same potential scan rates.

Both the decrease of the thermopower and the Pauli-like behaviour of the magnetic susceptibility indicates the metallic character of $PtPc(PF_6)_x$. The weak growth of the specific resistance in the temperature interval 100–300 K (apparent values of activation energy: 0.021 and 0.017 eV above and below 100 K, respectively) originates from the insufficient electrical contacts between the $PtPc(PF_6)_x$ crystals, which should be significantly improved by high pressure processing of the composite or use of a conducting polymer as the matrix.

The system 'donor molecule—polymer' can be utilized widely, not only for electrochemical synthesis and characterization of new conducting compounds, but also for practical applications such as antistatic and anticorrosion coatings, components of electrochromic indicators and rechargeable power sources, and as catalytic electrodes for fuel cells.

A number of important requirements must be satisfied to form a new CT salt polymer composite. The polymer used in such a system must (i) be electrochemically inactive and insoluble in the electrolyte in the potential range investigated, (ii) give a relatively stable suspension with PtPc and not interact with it, (iii) form films with good adhesion to the surface of the electrode, (iv) be permeable to the ions of the electrolyte, and (v) be transparent and not paramagnetic, so as not to interfere with optical and EPR measurements. The electrolyte should be chosen so that the donor molecule remains insoluble and does not interact with it at any level of oxidation.

In summary, a new conducting composite $PtPc(PF_6)_x$—PBC has been obtained. The electrochemical, structural, optical and magnetic properties of a new CT salt of PtPc have been characterized.

The authors are grateful to Y. Yonehara for providing PtPc and $Bu_4N(AsF_5)_{0.5}$ for the optical studies and J. Dong for his help with the EPR measurements. They thank the Ministry of Education, Science, Culture and Sports of Japan for financial support.

## References

1 H. Yamakado, K. Yakushi, N. Kosugi, H. Kuroda, A. Kawamoto, J. Tanaka, T. Sugano, M. Kinoshita and S. Hino, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2267.

2 A. K. Shukla, C. Paliteiro, R. Manoharan, A. Hamnet and J. B. Goodenough, *J. Appl. Electrochem.*, 1989, **19**, 105.

3 E. E. Laukhina, V. A. Merzhanov, S. I. Pesotskii, E. B. Yagubskii, J. Ulanski, M. Kryszewski and J. K. Jeszka, *Synth. Met.*, 1995, **70**, 797.

4 K. Beltsios and S. H. Carr, *Synth. Met.*, 1991, **41–43**, 941.

5 T. J. Marks, *Angew. Chem., Int., Ed. Engl.*, 1990, **29**, 857.

6 A. B. P. Lever, E. R. Milaeva and G. P. Speier, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1993, vol. 3, p. 1.

7 N. Toshima, T. Tominaga and S. Kawamura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 245.

8 P.A. Barret, C. E. Dent and R. P. Luistead, *J. Chem. Soc.*, 1936, 1919.

9 J. Brown, *J. Chem. Soc. (A)*, 1968, 2494.

10 K. Yakushi, T. Ida, A. Ugava, H. Ishii, H. Yamakado and H. Kuroda, *J. Phys. Chem.*, 1991, **95**, 7636.

11 Y. Iyechika, K. Yakushi and H. Kuroda, *Chem. Phys.*, 1984, **89**, 101.

*Paper* 7/02670F; *Received* 18*th April*, 1997