Russian Chemical Bulletin, International Edition, Vol. 50, No. 7, pp. 1299—1302, July, 2001

Synthesis and spectral and electrochemical properties of hexadecamethyl-substituted diphthalocyanines of rare-earth metals

I. P. Kalashnikova,[a] I. V. Zhukov,[b] T. V. Magdesieva,[b] K. P. Butin,[b] L. G. Tomilova,[a]★ and N. S. Zefirov[a]

[a]*Institute of Physiologically Active Compounds,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 913 2113
[b]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 0290. E-mail: tom@org.chem.msu.su

A new method for the preparation of 3,5-dimethyl-*o*-phthalodinitrile was proposed, and the substituted diphthalocyanine complexes of Lu^{III}, Tm^{III}, Er^{III}, and Dy^{III} were synthesized. The spectral and electrochemical characteristics of the complexes were found. The complexes can be used as materials for electrochromic devices with high contrast.

Key word: diphthalocyanines, rare-earth metals, electrochemistry, electronic absorption spectra.

An active search for the procedures for synthesis of substituted phthalocyanines with practically significant properties have recently being performed.[1—4]

The yield of phthalocyanine metal complexes can be increased when *o*-phthalodinitriles are used as the starting compounds instead of acids and anhydrides.[5] Cyanation of *o*-dibromobenzenes with copper cyanide in DMF (see, *e.g.*, Refs. 6 and 7) is the common method for the synthesis of substituted phthalocyanines. Other approaches to the synthesis of phthalodinitriles containing functional substituents at different positions of the benzene ring have been proposed in recent years.[8,9]

In this work, we synthesized 3,5-dimethyl-*o*-phthalodinitrile (**1**) with the purpose for preparation of 3,5-substituted diphthalocyanine complexes of rare-earth metals that possess simultaneously the photochromic properties and sufficient solubility to isolate them in the individual state.

Results and Discussion

Since the orientation effect of substituents in the aromatic ring of *m*-xylene does not allow the preparation of *o*-dibromo derivatives and, hence, 3,5-dimethylphthalodinitrile by bromination, it was necessary to search for another synthetic approach. 1-Amino-2-cyano-3,5-dimethylbenzene (**2**) prepared from compound **1** by Sandmeyer′s reaction was chosen as the starting compound.

Several 3,5-methyl-substituted diphthalocyanine complexes of rare-earth metals (${}^{3,5\text{-Me}}Pc_2Ln$) were synthesized for the first time from dinitrile **1**. Since the starting phthalodinitrile **1** has a nonsymmetric structure, a mixture of isomers can be formed, and they, as in the case of the earlier obtained 4-*tert*-butyl-substituted diphthalocyanine complexes[10] cannot be separated either on a chromatographic column or by TLC. Diphthalocyanines of Lu^{III}, Tm^{III}, Er^{III}, and Dy^{III} were synthesized in *n*-hexanol in the presence of diazabicycloundecene (DBU)[11] in high yields (Scheme 1).

The electronic absorption spectra of the obtained complexes contains bands in the region of 680—700 nm and the band at 450 nm characteristic of diphthalocyanines (Fig. 1). With an increase in the ion radius of

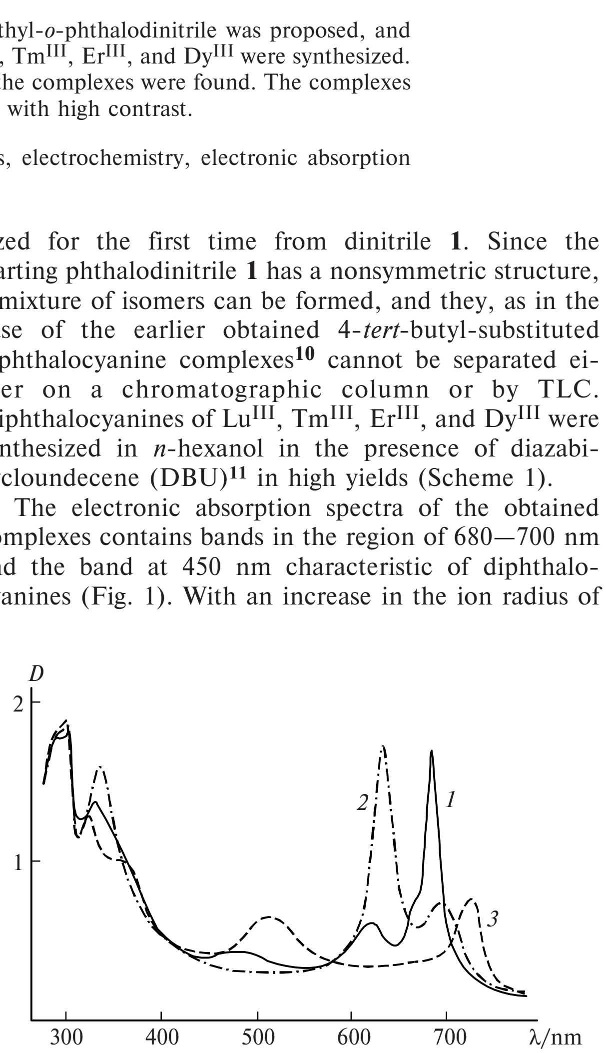
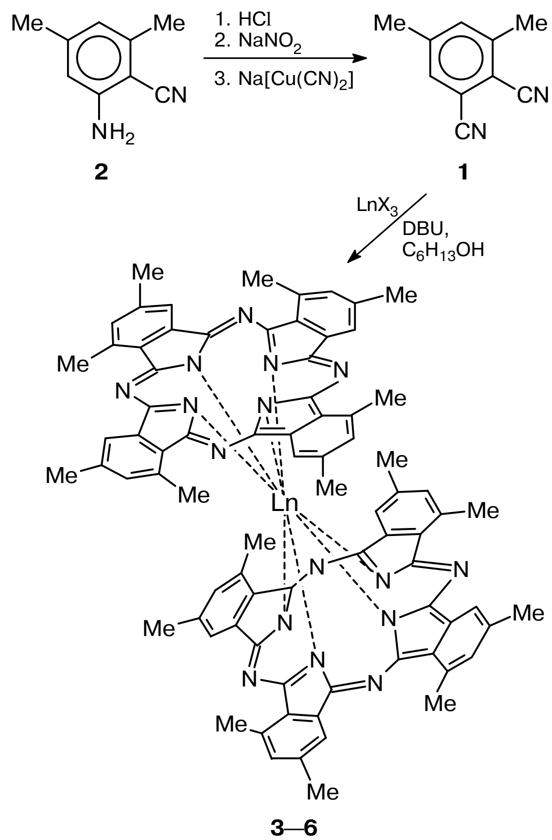


Fig. 1. Electronic absorption spectra of the neutral (*1*), reduced (*2*), and oxidized (*3*) redox forms of ${}^{3,5\text{-Me}}Pc_2Tm$ generated at potentials of −0.3 and +0.5 V (*vs.* Ag|AgCl|KCl) on the Pt electrode in DMF against 0.05 *M* $Bu^n{}_4NBF_4$.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1238—1241, July, 2001.

Scheme 1



Ln = Lu (**3**), Tm (**4**), Er (**5**), Dy (**6**)

the metal atom, the main absorption maximum is insignificantly shifted to the long-wave region (bathochromic shift) from 682 nm (for complex **3**) to 690 nm (**6**).

Compounds **3**—**6** are well soluble in chloroform and benzene, which differs them from symmetric analogs, 4,5-dimethyl-substituted diphthalocyanines,[12] and makes it possible to extent the possibilities of their chromatographic purification and application.

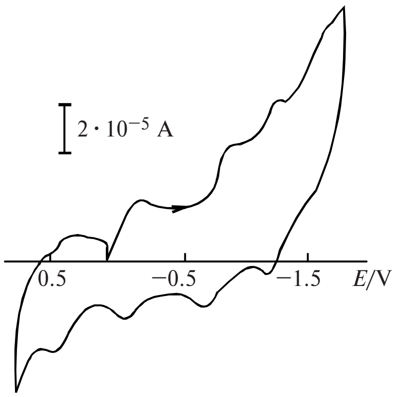


Fig. 2. Cyclic voltammogram of $^{3,5\text{-Me}}\mathrm{Pc_2Er}$ (graphite electrode; DMF; 0.05 *M* $\mathrm{Bu^n{}_4NBF_4}$; Ag|AgCl|KCl; $v = 200$ mV s^{-1}; 20 °C).

Table 1. Potentials of redox transitions[a] of $^{3,5\text{-Me}}\mathrm{Pc_2Ln}$ (Ln = Lu, Tm, Er)

Compound	*E* [b]/V	
	Oxidation	Reduction
$^{3,5\text{-Me}}\mathrm{Pc_2Lu}$	0.46	−0.06, −0.81, −1.23, −1.62
$^{3,5\text{-Me}}\mathrm{Pc_2Lu}$ [c]	0.42	0.01, −0.78, −1.21, −1.61
$^{3,5\text{-Me}}\mathrm{Pc_2Tm}$	0.46	−0.07, −0.76
$^{3,5\text{-Me}}\mathrm{Pc_2Er}$	0.47	−0.07, −0.75, −1.19, −1.58

[a] Graphite electrode; DMF; 0.05 *M* $\mathrm{Bu^n{}_4NBF_4}$; Ag|AgCl|KCl; $v = 200$ mV s^{-1}; 20 °C.

[b] Arithmetic mean of the potentials of the direct and inverse peaks in CVA.

[c] Pt electrode.

The electrochemical properties of 3,5-dimethyl-substituted diphthalocyanine complexes of Lu$^{\mathrm{III}}$, Tm$^{\mathrm{III}}$, and Er$^{\mathrm{III}}$ were studied by cyclic voltammetry in DMF. Five reversible redox transitions were detected in the accessible potential interval (from −2.0 to +1.1 V) (Fig. 2). The first anodic peak exists in the region of 0.42—0.47 V (*vs.* Ag|AgCl|KCl) (Table 1) and corresponds to the transition

$$^{3,5\text{-Me}}\mathrm{Pc_2Ln} \underset{+e}{\overset{-e}{\rightleftharpoons}} (^{3,5\text{-Me}}\mathrm{Pc_2Ln})^{+} (\mathrm{Ln = Lu,\ Tm,\ Er}).$$

Four peaks are present in the cathodic region of potentials (see Table 1), which correspond to the successive transfer of four electrons to $^{3,5\text{-Me}}\mathrm{Pc_2Ln}$

$$^{3,5\text{-Me}}\mathrm{Pc_2Ln} \underset{-e}{\overset{+e}{\rightleftharpoons}} (^{3,5\text{-Me}}\mathrm{Pc_2Ln})^{-} \underset{-e}{\overset{+e}{\rightleftharpoons}}$$
$$\rightleftharpoons (^{3,5\text{-Me}}\mathrm{Pc_2Ln})^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} (^{3,5\text{-Me}}\mathrm{Pc_2Ln})^{3-} \underset{-e}{\overset{+e}{\rightleftharpoons}}$$
$$\rightleftharpoons (^{3,5\text{-Me}}\mathrm{Pc_2Ln})^{4-}.$$

It is difficult to study the electrochemical properties of diphthalocyanine complexes of rare-earth metals due to their low solubility in most organic solvents suitable for electrochemical measurements. In the case of complexes **3**—**6**, DMF solutions with a maximum concentration of $1 \cdot 10^{-4}$ mol L^{-1} can be obtained. This concentration is not sufficient for the reliable detection of redox transitions by smooth platinum electrodes. Hence, we used the working electrode prepared from a graphite material (pyrolyzed polyacrilonitrile) with the highly developed surface (~$7 \cdot 10^3$ mm^2).

The potentials measured with this electrode and smooth platinum are very close (see Table 1), which enables a comparison of the data detected by these electrodes.

Redox processes were studied in a special cell, which allows the detection of spectral changes directly during electrolysis. Absorption maxima in the electronic spectra of the neutral, oxidized, and reduced forms of $^{3,5\text{-Me}}\mathrm{Pc_2Ln}$ are presented in Table 2. Figure 1 presents the electronic absorption spectra of the neutral, reduced, and oxidized forms of $^{3,5\text{-Me}}\mathrm{Pc_2Tm}$ obtained

Table 2. Electronic absorption spectra of the neutral, reduced, and oxidized forms of ${}^{3,5\text{-Me}}Pc_2Ln$ (Ln = Lu, Tm, Er) in DMF

Compound	Redox form	λ_{max}*/nm	Color of solution
${}^{3,5\text{-Me}}Pc_2Lu$	Neutral	330, 343 sh, 492 sh, 600 sh, 616, 653 sh, 685	Green
	Oxidized	295, 326, 358, 510, 611, 730	Pink
	Reduced	300 sh, 322, 336, 580 sh, 637, 708	Bluish-green
${}^{3,5\text{-Me}}Pc_2Tm$	Neutral	296, 330, 350 sh, 494 sh, 602 sh, 619, 652 sh, 687	Green
	Oxidized	296, 324, 346 sh, 514, 612, 734	Pink
	Reduced	296, 337, 586 sh, 639, 704	Bluish-green
${}^{3,5\text{-Me}}Pc_2Er$	Neutral	300, 328, 348 sh, 500 sh, 603 sh, 618, 651, 689	Green
	Oxidized	297, 324, 352 sh, 515, 617, 736	Pink
	Reduced	298, 338, 588 sh, 640, 703	Bluish-green

* The most intense absorption bands are underlined.

after preparative electrolysis at the potentials corresponding to the first reduction and first oxidation peaks. It is seen in Table 2 that the redox species differ strongly in color in each case, *i.e.*, 3,5-dimethyl-substituted diphthalocyanine complexes of rare-earth metals can be used as materials for electrochromic devices with high contrast.

Since direct electrochemical measurements of the number of electrons participating in redox processes of the diphthalocyanine complexes often give underestimated results,[13] spectral measurements can serve as the most adequate estimation of the number of electrons. The shape of electronic spectra of the neutral, reduced, and oxidized forms of the complexes studied is typical of diphthalocyanine complexes[14] and indicates that electrons are localized on the phthalocyanine rings. A comparison of the peak heights corresponding to the first anodic and first cathodic redox transitions and the peak heights for deeper reduction (see Fig. 2) suggests that all observed redox transitions are one-electron.

For this series of complexes (see Table 1), the metal nature only insignificantly affects the potential of the electrochemical transitions. We observed the same for the series of diamagnetic and paramagnetic octa-*tert*-butyl-substituted diphthalocyanine complexes of lanthanides.[13]

Substituents in the phthalocyanine ring have a much stronger effect on the potentials of redox transitions than the nature of the central metal atom. In the case of the 3,5-dimethyl-substituted and 4-*tert*-butyl-substituted Lu^{II} diphthalocyanine complexes, the oxidation potentials are shifted to the cathodic region compared to the nonsubstituted diphthalocyanine (Table 3). This is explained by the donor nature of alkyl substituents and agrees with electron localization on the phthalocyanine ligand. The potentials of the deeper reduction of the 3,5-dimethyl-substituted complex, unlike those of the 4-*tert*-butyl-substituted complex, are substantially shifted to the anodic region compared to the nonsubstituted derivative. Additional studies are required to explain these facts.

Table 3. Potentials of the redox transitions[a] of Pc_2Lu, ${}^{3,5\text{-Me}}Pc_2Lu$, and $Pc^t{}_2Lu$

Compound	E^b/V	
	Oxidation	Reduction
Pc_2Lu	0.53	0.14, −1.02, −1.37, −1.71
${}^{3,5\text{-Me}}Pc_2Lu$ [c]	0.42	0.01, −0.78, −1.21, −1.61
$Pc^t{}_2Lu$	0.35	0.01, −1.10, −1.41, −1.85

[a] Pt electrode; *o*-dichlorobenzene—MeCN (1 : 1); 0.05 *M* $Bu^n{}_4NBF_4$; Ag|AgCl|KCl; v = 200 mV s^{-1}; 20 °C.

[b] Arithmetic mean of the potentials of the direct and inverse peaks in CVA.

[c] Solution in DMF.

Experimental

Absorption spectra were recorded on a Specord M-800 UV spectrometer in the region of 200—800 nm. Spectra of the electrochemically generated forms of the diphthalocyanine complexes were obtained directly in a quartz cell on a Hitachi 124 spectrophotometer in the 200—800 nm region using 0.05 *M* $Bu^n{}_4NBF_4$ in the same solvent as the reference solution. ^1H NMR spectra were recorded on a Bruker AC-200 instrument (200 MHz, *vs.* Me_4Si).

1-Amino-2-cyano-3,5-dimethylbenzene (**2**) was prepared from mesityl oxide and malononitrile using a previously described procedure[15] in 80% yield (m.p. 60 °C). Compounds $Bu^n{}_4NBF_4$ (Merck) and DMF (Aldrich) were used as received. Formates or acetates of the corresponding lanthanides (analytically pure grade) were used for the synthesis of phthalocyanines.

3,5-Dimethyl-*o*-phthalodinitrile (1). Concentrated HCl (12 mL) was slowly added with stirring and cooling with ice-cold water to a solution of benzonitrile **2** (5.0 g, 0.034 mol) in water (30 mL). The reaction mixture was diazotized at 0—5 °C by adding dropwise a solution of $NaNO_2$ (3.44 g, 0.05 mol) in water (15 mL). The resulting solution of the diazonium salt was treated with stirring and cooling to 0 °C with a solution of $Na[Cu(CN)_2]$ prepared from CuCl (6.2 g, 0.062 mol) and NaCN (9.36 g, 0.15 mol). The reaction mixture was stirred for 2 h and stored for 12 h, and the precipitate that formed was filtered off. The solid residue was extracted with hot benzene, and the filtrate was extracted with chloroform. The organic extracts were combined and dried with $MgSO_4$. After removal of solvents, the combined crystalline product was recrystallized from CCl_4 and additionally purified by sublimation. Compound

1 was obtained as colorless crystals with m.p. 122 °C in 43% yield (2.30 g). Found (%): C, 76.39; H, 5.14; N, 17.88. Calculated (%): C, 76.89; H, 5.17; N, 17.94. $C_{12}H_8N_2$. ^1H NMR (DMSO-d_6), δ: 2.39, 2.49 (both s, 3 H each, Me); 7.65, 7.78 (both s, 1 H each, C_6H_2).

Bis(octamethylphthalocyanine)lutetium(III) (3). A mixture of compound **1** (500 mg, 3.2 mmol), $(HCOO)_3Lu \cdot 2H_2O$ (111 mg, 0.32 mmol), DBU (290 mg, 1.92 mmol), and *n*-hexanol (5 mL) was refluxed in an argon atmosphere. The solution was cooled, *n*-hexanol was distilled off *in vacuo*, and the residue was washed with MeOH and twice chromatographed on a column packed with SiO_2 (eluent $CHCl_3$). Compound **3** was obtained as a dark-green powder in 66% yield (310 mg), $R_f = 0.84$ (Alufol® plates, eluent $CHCl_3$), $\lambda_{max} = 682$ nm. Found (%): C, 67.54; H, 4.66; N, 15.58. $C_{80}H_{64}N_{16}Lu$. Calculated (%): C, 67.46; H, 4.53; N, 15.73.

Bis(octamethylphthalocyanine)thulium(III) (4) was prepared similarly to compound **3**, yield 68%, $R_f = 0.80$ (Alufol® plates, eluent $CHCl_3$), $\lambda_{max} = 683$ nm. Found (%): C, 67.92; H, 4.68; N, 15.63. $C_{80}H_{64}N_{16}Tm$. Calculated (%): C, 67.74; H, 4.55; N, 15.80.

Bis(octamethylphthalocyanine)erbium(III) (5) was prepared similarly to compound **3**, yield 72%, $R_f = 0.71$ (Alufol® plates, eluent $CHCl_3$), $\lambda_{max} = 685$ nm. Found (%): C, 67.94; H, 4.62; N, 15.65. $C_{80}H_{64}N_{16}Er$. Calculated (%): C, 67.82; H, 4.55; N, 15.82.

Bis(octamethylphthalocyanine)dysprosium(III) (**6**) was prepared similarly to compound **3**, yield 70%, $R_f = 0.68$ (Alufol® plates, eluent $CHCl_3$), $\lambda_{max} = 690$ nm. Found (%): C, 68.14; H, 4.65; N, 15.55. $C_{80}H_{64}N_{16}Dy$. Calculated (%): C, 68.05; H, 4.57; N, 15.87.

Electrochemical measurements were carried out on a PI-50-1.1 potentiostat, PR-8 programmator, and PDA-1 two-coordinate detecting instrument using the three-electrode scheme on a graphite electrode (pyrolyzed polyacrilonitrile) and on a disk platinum electrode with a working surface of 20.7 mm^2 against 0.05 *M* $Bu^n{}_4NBF_4$ at 20 °C. A Pt wire served as an auxiliary electrode, and a saturated Ag|AgCl electrode was used as the reference electrode. Dissolved oxygen was removed from the cell with a flow of dry argon. Voltammetric curves were detected by cyclic voltammetry at a sweep of 200 mV s^{-1}. The electrode was thoroughly polished after obtaining each curve. The measured potential values were recalculated taking into account ohmic losses. DMF was used as the solvent. The concentration of solutions of the compounds under study was $1 \cdot 10^{-4}$ mol L^{-1}.

Spectroelectrochemical studies were carried out at 20 °C in the potentiostatic regime in a special quartz cell connected to a P-5827M potentiostat using the three-electrode scheme. A Pt wire with a surface area of 120 mm^2 served as the working electrode, and 0.02 *M* $Bu^n{}_4NBF_4$ was used as the supporting electrolyte. The spaces of the auxiliary, working, and Pt electrodes were separated by a glass porous membrane. The potential values were measured *vs.* saturated Ag|AgCl electrode. DMF was used as the solvent. The concentration of solutions was $3.5 \cdot 10^{-5}$ mol L^{-1}. A solution was stirred during electrolysis and dissolved oxygen was removed during preparation using a flow of dry argon.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-33229 and 00-03-32658).

References

1. M. M. Nicholson, in *Phthalocyanines: Properties and Application*, Eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1993, **3**, 71.
2. P. Turek, P. Petit, J.-J. Andre, J. Simon, R. Even, B. Boudjema, G. Guillaund, and M. Maitrot, *J. Am. Chem. Soc.*, 1987, **109**, 5119.
3. M. Bouvet and J. Simon, *Chem. Phys. Lett.*, 1990, **172**, 299.
4. Z. Belarbi, C. Sirlin, J. Simon, and J.-J. Andre, *J. Phys. Chem.*, 1989, **93**, 8105.
5. V. D. Berezin, *Koordinatsionnye soedineniya porfirinov i ftalotsianinov* [*Coordination Compounds of Porphyrins and Phthalocyanines*], Nauka, Moscow, 1978, 280 pp. (in Russian).
6. E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, 1981, **20**, 3766.
7. R. Dieing, G. Schmid, E. Witke, G. Feucht, N. Dreben, J. Pohmer, and M. Hanack, *Chem. Ber.*, 1995, **128**, 589.
8. A. N. Cammidge, J. Chambrier, M. J. Cook, A. D. Garland, M. J. Heeney, K. Welford, *J. Porphyrins and Phthalocyanines*, 1997, **1**, 77.
9. D. S. Tereknov, K. J. Nolan, C. R. McArthur, and C. C. Leznoff, *J. Org. Chem.*, 1996, **61**, 3034.
10. L. G. Tomilova, E. V. Chernykh, N. T. Ioffe, and E. A. Luk´yanets, *Zh. Obshch. Khim.*, 1983, **53**, 2594 [*J. Gen. Chem. USSR*, 1983, **53** (Engl. Transl.)].
11. J. Jiang, R. C. W. Liu, T. C. W. Mak, T. W. D. Chan, and D. K. P. Ng, *Polyhedron*, 1997, **16**, 515.
12. M. A. Ovseevich, L. G. Tomilova, E. G. Kogan, and N. S. Zefirov, *Mendeleev Commun.*, 1998, 186.
13. T. V. Magdesieva, I. V. Zhukov, L. G. Tomilova, E. V. Chernykh, and K. P. Butin, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 2149 [*Russ. Chem. Bull.*, 1997, **46**, 2036 (Engl. Transl.)].
14. C. C. Leznoff and A. B. P. Lever, in *Phthalocyanines: Properties and Application*, Eds. C. C. Leznoff, A. B. P. Lever, VCH, New York, 1993, **3**, 85.
15. J. Sepiol, J. Mirek, and R. L. Soulen, *Pol. J. Chem.*, 1978, **52**, 1389.

Received July 21, 2000;
in revised form February 27, 2001