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Synthesis, Structure, Spectroscopic Properties, and Electrochemistry of (1,8,15,22-Tetrasubstituted phthalocyaninato)lead Complexes

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Three (1,8,15,22-tetrasubstituted phthalocyaninato)lead complexes $Pb[Pc(\alpha\text{-}OR)_4]$ [$H_2Pc(\alpha\text{-}OC_5H_{11})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine; $H_2Pc(\alpha\text{-}OC_7H_{15})_4$ = 1,8,15,22-tetrakis(2,4-dimethyl-3-pentyloxy)phthalocyanine; $H_2Pc(\alpha\text{-}OC_{10}H_7)_4$ = 1,8,15,22-tetrakis(2-naphthyloxy)phthalocyanine] (**1**–**3**) have been prepared as racemic mixtures by treating the corresponding metal-free phthalocyanines $H_2Pc(\alpha\text{-}OR)_4$ (**4**–**6**) with $Pb(OAc)_2{\cdot}3H_2O$ in refluxing *n*-pentanol. The molecular structure of $Pb[Pc(\alpha\text{-}OC_5H_{11})_4]$ (**1**) in the solid state has been determined by single-crystal X-ray diffraction analysis. This compound, having a nonplanar structure, crystallizes in the monoclinic system with a $P2_1/c$ space group. Each unit cell contains two pairs of enantiomeric molecules, which are linked by weak coordination of the Pb atom of one molecule with an aza nitrogen atom and its neighboring oxygen atom from the alkoxy substituent of another molecule, forming a pseudo-double-decker supramolecular structure in the crystals with a short ring-to-ring separation, 2.726 Å, and thus a strong ring–ring π–π interaction. The decreased molecular symmetry for these complexes has also been revealed by the NMR spectra of **1** and **2**. The methyl protons of the 3-pentyloxy and 2,4-dimethyl-3-pentyloxy side chains of **1** and **2**, respectively, are chemically inequivalent. In addition to the elemental analysis and various spectroscopic characterizations, these compounds have also been electrochemically studied. Two one-electron oxidations and up to five one-electron reductions have been revealed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods.

Introduction

Phthalocyanines have been important industrial dyes and pigments since their early synthesis at the beginning of last century.[1] They have been employed as charge carriers in photocopiers and laser printers, as well as materials for optical storage in recent years.[2,3] Many potential applications are expected for these molecular materials which have a high thermal and chemical stability, for instance as oxidation catalysts,[4] solar cell functional materials,[5] gas sensors,[6] nonlinear optical limiting devices,[7] photodynamic therapy agents,[8] antimycotic material,[9] and corrosion inhibitors.[10]

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Phthalocyanines can form complexes with more than 70 elements, including virtually all the metals in the periodic table. The electrochemical and spectroscopic properties can be altered by changing the metal center. The other way to tune the properties of phthalocyanine compounds is to introduce different kinds of substituents onto the peripheral and nonperipheral positions of the phthalocyanine ring. Particularly, the optical and electrochemical properties of phthalocyanines can be significantly altered by incorporating substituents at the nonperipheral positions. This has been well demonstrated by our recent work on the 1,8,15,22-tetrakis(alkoxy)phthalocyanine-containing heteroleptic bis- and tris(phthalocyaninato) rare earth complexes M(Pc)[Pc(α-$OC_5H_{11})_4$] (H_2Pc = unsubstituted phthalocyanine; M = Y, Sm−Lu)[11a,b] and (Pc)M(Pc)M[Pc(α-$OC_5H_{11})_4$] (M = Sm, Gd, Lu).[11c] Furthermore, due to the C_{4h} symmetry of the Pc(α-$OC_5H_{11})_4$ ring and the sandwichlike structure, the molecules of these sandwich double- and triple-decker complexes are intrinsically chiral in nature, possessing a C_4 symmetry as revealed by the X-ray molecular structure analysis results.

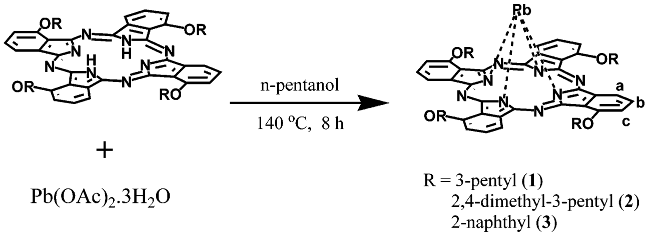
Among the various metal elements in the periodic table, lead has been relatively little studied for complexation with phthalocyanines despite the potential use of these complexes as nonlinear optical materials. Studies have been mainly focused on the unsubstituted analogues,[12−15] while only a few substituted (phthalocyaninato)lead(II) complexes have been reported so far.[16] We describe herein the synthesis and characterization of three lead phthalocyanines tetrasubstituted on the nonperipheral positions.

Similar to the situation of rare earth phthalocyaninato complexes, the lead ion is unable to completely enter the central cavity of the phthalocyanine ring but sits atop of the ligand due to its large ionic size. The resulting molecules having a C_4 symmetry thus also possess an intrinsic chirality. X-ray diffraction analysis of one of these complexes, namely PbPc(α-$OC_5H_{11})_4$ (**1**), has also revealed an unusual aza coordination of phthalocyanine, the examples of which reported thus far being very scarce.[17,18]

Results and Discussion

Synthesis of Pb[Pc(α-OR)$_4$] (1−3). Two synthetic pathways have been reported to prepare (phthalocyaninato)lead(II) complexes. The first method involves the cyclic tetramerization of phthalonitriles in the presence of metal salts such as $Pb(OAc)_2{\cdot}3H_2O$ or PbO.[16] The second pathway involves the treatment of Li_2Pc with $Pb(OAc)_2{\cdot}3H_2O$.[19] In this work, we performed the metalation of pure isomers of metal-free 1,8,15,22-tetrakis(3-alkoxy)phthalocyanine H_2Pc-(α-OR)$_4$ (**4**−**6**) with $Pb(OAc)_2{\cdot}3H_2O$ in refluxing *n*-pentanol (Scheme 1). The reaction yield of these compounds (91% for **1**, 80% for **2**, and 69% for **3**) seems to be smaller as the size of the α-substituents increases (from 3-pentyloxy group for **1**, to 2,4-dimethyl-3-pentyloxy group for **2**, and 2-naphthyloxy group for **3**). It is worth mentioning that to obtain pure metal-free 1,8,15,22-tetrakis(3-alkoxy)phthalocyanine single isomers as precursor to prepare corresponding lead complexes with C_4 molecular symmetry, phthalonitriles with bulky substituents such as 3-pentyloxy, 2,4-dimethyl-3-pentyloxy, or naphthyloxy groups have been selected as starting materials and the reaction temperature was strictly controlled to be lower than 120 °C; see the Experimental Section.

Scheme 1. Synthesis of (Phthalocyaninato) lead Complexes Pb[Pc(α-OR)$_4$] (**1**−**3**)



Spectroscopic Characterization. All the three new (phthalocyaninato)lead complexes **1**−**3** were characterized by elemental analysis and various spectroscopic methods. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the molecular ion $(M)^+$ or the protonated molecular ion $(MH)^+$. The diamagnetic lead(II) compounds **1** and **2** gave well-resolved ^1H NMR spectra in $CDCl_3$. Figure 1 shows the spectrum of **2**, in which two doublets at δ 9.07 and 7.70 and a triplet at δ 8.05 appear for the three sets of phthalocyanine ring protons. The aliphatic protons' signals can also be assigned unambiguously due to the well-resolved multiplicity and integration of all the signals. The virtual triplet at δ 4.67 and the multiplet at δ 2.57−2.67 are due to the OCH and CH protons, respectively. Interestingly, four instead of two doublets at δ 1.66, 1.35, 1.28, and 1.09 appear for the four sets of methyl groups, indicating their diastereotopic nature. The ^1H NMR spectrum of **1** shows similar spectral features in which the diastereotopic methylene protons resonate as two multiplets at δ 2.1−2.3 and 2.3−2.5 in 3:1 ratio, similar to that observed

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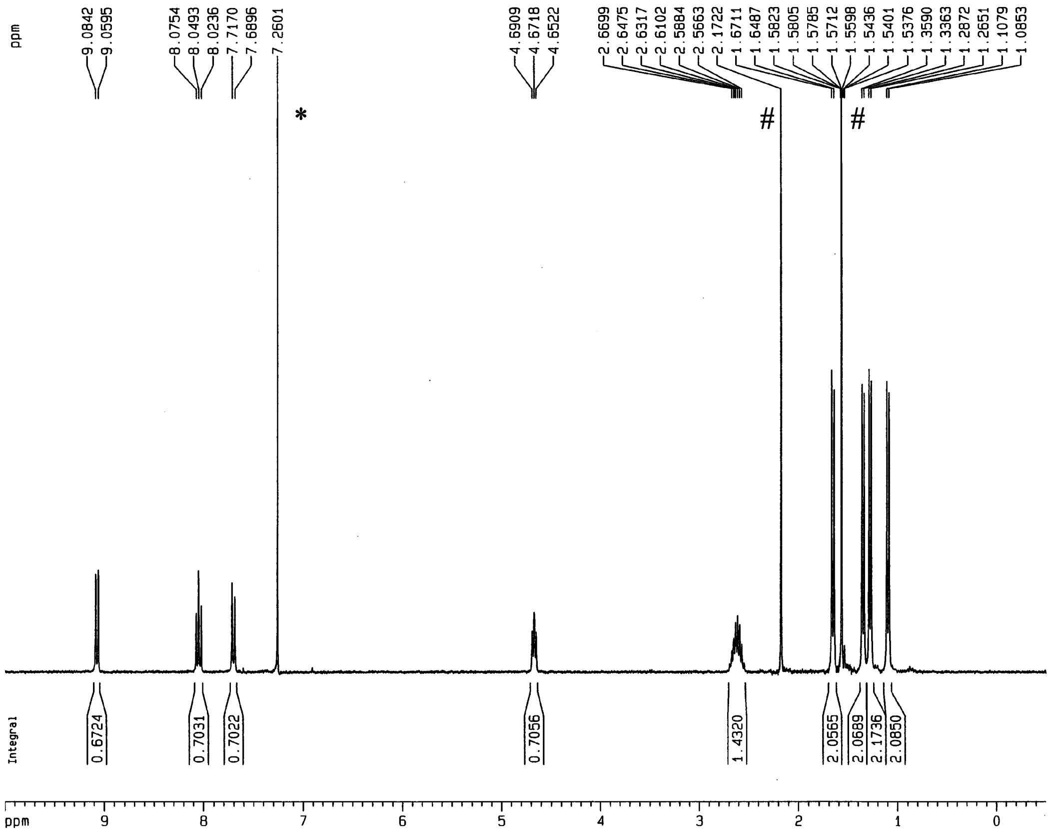

Figure 1. ^{1}H NMR spectrum of Pb[Pc(α-OC_7H_{15})$_4$] (**2**) in $CDCl_3$. The signals due to residue $CHCl_3$ and some impurities are denoted as * and #, respectively.

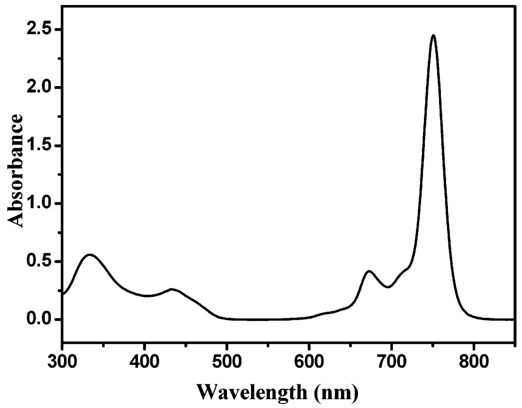

Figure 2. Electronic absorption spectrum of Pb[Pc(α-OC_5H_{11})$_4$] (**1**) in $CHCl_3$.

for the rare earth sandwich analogues.[11] As a result of the restricted rotation along the C(aryl)−O bond, two triplets are observed for the two methyl groups. These results are in accord with the C_4 symmetry of these complexes. Due to an extensive overlap of the signals, the ^{1}H NMR spectrum of **3** cannot be assigned readily.

The electronic absorption data for this series of compounds are analogous in general to those reported for normal monomeric (phthalocyaninato)metal compounds and, thus, could be assigned in the same manner. Figure 2 gives the UV−vis spectrum of PbPc(α-OC_5H_{11})$_4$ (**1**) as a typical example. All the spectra of **1**−**3** show a typical Soret band at 333 nm (for **1** and **2**) or 340 nm (for **3**). The Q-band appears around 741−755 nm as a very strong absorption with a weak vibronic band around 666−673 nm. The weak absorption band around 431−437 nm is common for alkoxy-substituted phthalocyanines, which may be attributed to an $n-\pi^*$ transition.

An intense IR band at 1329 cm^{-1} for **1** and **2** and 1324 cm^{-1} for **3** was observed. This band was the marker IR band for phthalocyanine dianion.[20] In addition, a group of absorption bands was also seen in the range of 2872−2962 cm^{-1} in the IR spectra of **1** and **2**. These can be attributed to the C−H stretching vibrations of the 3-pentyloxy or 2,4-dimethyl-3-pentyloxy groups.

Structural Studies. The molecular structure of the lead phthalocyanine Pb[Pc(α-OC_5H_{11})$_4$] (**1**) was also established by X-ray diffraction analysis. This represents the first structurally characterized (phthalocyaninato)lead(II) complex with nonperipheral tetrasubstitution. Single crystals suitable for crystallographic analysis were obtained by slow diffusion of MeOH into the $CHCl_3$ solution of **1**. The compound crystallizes in the monoclinic system with a $P2_1/c$ space group with two pairs of enantiomeric molecules in an unit cell. Attempts to resolve the two enantiomers of phthalocyanines **1**−**3** by HPLC using a silica gel column coated with cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate) were

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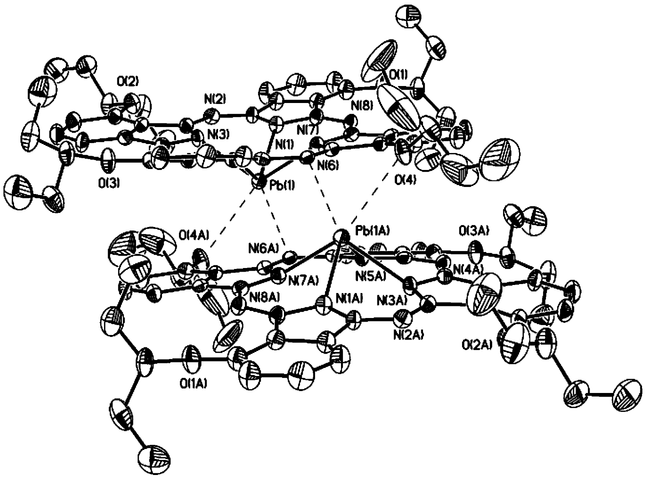

Figure 3. Pseudo-double-decker supramolecular structure in crystal of Pb[Pc(α-OC_5H_{11})$_4$] (**1**) in side view showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

not successful due to the very small difference in properties between the two enantiomers.

As shown in Figure 3, the two enantiomeric molecules of **1** are bound to each other via an unusual Pb−η^2-Pc(α-OC_5H_{11})$_4$ coordination. The lead atom of one molecule binds to an aza nitrogen atom and a neighboring oxygen atom from an alkoxy group of another molecule, forming a pseudo-double-decker structure. The intermolecular Pb(1)−N(6A) distance (3.177 Å) and the Pb(1)−O(4A) bond length (3.142 Å) are significantly longer than the average intramolecular Pb−N distance (2.376 Å) but shorter than that found for the intermolecular Ni−N distance (3.38 Å), which is also the ring-to-ring separation, in NiPc crystals.[21] The ring-to-ring separation of these two virtually parallel N(isoindole)$_4$ mean planes of Pc(α-OC_5H_{11})$_4$ is 2.726 Å. This value is comparable with that found in the sandwich bis(phthalocyaninato) complexes of the heavy lanthanides such as [Ho(Pc)$_2$][NBu]$_4$·H_2O, 2.76 Å, and Lu(Pc)$_2$, 2.68 Å,[22] revealing intense $\pi\angle\pi$ interaction between the two phthalocyanine rings in the pseudo-double-decker supramolecular structure. It is noteworthy that a similar pseudo-double-decker structure seems also to exist in the lead phthalocyanine substituted with eight hexylthio groups at the nonperipheral positions, formed through the coordination of lead with one aza nitrogen atom and two neighboring sulfur atoms from hexylthio groups of another phthalocyanine ring.[16]

In each monomeric unit in the dimeric supramolecular structure, the lead ion is coordinated with four isoindole nitrogen atoms of the phthalocyanine ligand, Pc(α-OC_5H_{11})$_4$, in addition to coordinating with one aza nitrogen atom and one adjacent 3-pentyloxy oxygen atom of the other phthalocyanine ligand. The coordination polyhedron of the lead is thus essentially a slightly distorted trigonal prism. However, due to the larger ionic size, the divalent lead ion cannot situate in the central hole of Pc(α-OC_5H_{11})$_4$ but sits atop 1.305 Å above the N(isoindole)$_4$ plane. As a result, the substituted Pc(α-OC_5H_{11})$_4$ ring adopts conformation that is domed toward the lead cation (ϕ = 7.9°).

Table 1. Half-Wave Redox Potentials of **1**−**3** (V vs SCE) in CH_2Cl_2 Containing 0.1 M TBAP

compd	oxd$_2$	oxd$_1$	red$_1$	red$_2$	red$_3$	red$_4$	red$_5$	$\Delta E°_{1/2}$[a]
1	+1.01	+0.58	−0.85	−1.22	−1.57	−1.75	−2.09	1.43
2	+0.93	+0.51	−0.91	−1.31	−1.65	−1.81		1.42
3	+1.09	+0.71	−0.74	−1.10	−1.43	−1.88		1.45

[a] $\Delta E°_{1/2}$ is the potential difference between the first oxidation and first reduction processes, i.e., the HOMO−LUMO gap of Pb[Pc(α-OR)$_4$]: $\Delta E°_{1/2}$ = oxd$_1$ − red$_1$.

Electrochemical Properties. Study of the electrochemistry of lead phthalocyanines is very rare and is limited to the unsubstituted species in DMF or DMSO.[23] The redox behavior of the newly synthesized lead phthalocyanines **1**−**3** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. Our observations of the electrochemistry of these (substituted phthalocyaninato)-lead complexes in CH_2Cl_2 differ from those previously reported for unsubstituted analogue PbPc. For instance, in the most complete study reported, two oxidations and at most three reductions were observed for PbPc in DMF.[23] However, under our experimental conditions, the compounds of lead Pb[Pc(α-OR)$_4$] (**1**−**3**) have been revealed to undergo two one-electron oxidations and up to five one-electron reductions according to the CV and more clearly the DPV results. All these redox processes can be attributed to the successive removal of electrons from and addition of electrons to the ligand-based orbitals, respectively, as the divalent lead cannot be oxidized or reduced under the present conditions. As shown in Table 1, replacement of the four electron-donating 3-pentyloxy groups with 2,4-dimethyl-3-pentyloxy groups induces a slight cathodic shift of all redox processes, probably due to the increased deformation in **2** as a result of the bulkier 2,4-dimethyl-3-pentyloxy groups at the nonperipheral positions. Compound **3** contains electron-withdrawing 2-naphthyloxy groups;[24] the half-wave potentials of all the redox processes for **3** are thus shifted to the opposite direction. The potential difference between oxd$_1$ and red$_1$, which reflects the HOMO−LUMO gap, for the three complexes **1**−**3** ($\Delta E°_{1/2}$ = 1.42−1.45 V), however, remains essentially the same.

Conclusion

In summary, we have prepared three novel nonperipherally (tetrasubstituted phthalocyaninato)lead(II) complexes as racemic mixtures. The compounds have been fully characterized with various spectroscopic and electrochemical methods. The crystal structure of Pb[Pc(α-OC_5H_{11})$_4$] shows an unusual aza coordination of phthalocyanine in a pseudo-double-decker supramolecular structure.

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Experimental Section

General Methods. *n*-Pentanol was distilled from sodium. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70−230 mesh). All other reagents and solvents were used as received. 3-(2-Naphthyloxy)-phthalonitrile[25] and corresponding metal-free phthalocyanines $H_2Pc(\alpha\text{-}OC_{10}H_7)_4$ (**6**)[26] were prepared according to the literature procedures. 3-(3-Pentyloxy)phthalonitrile, 3-(2,4-dimethyl-3-pentyloxy)phthalonitrile, and $H_2Pc(\alpha\text{-}OR)_4$ ($R = C_5H_{11}$, C_7H_{15}) (**4**, **5**) were reported in earlier work.[11,27]

^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$. Spectra were referenced internally using the residual solvent resonances (δ 7.26) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded as KBr pellets using a BIORAD FTS-165 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences.

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}(Fe^+/Fe) = 501$ mV vs SCE]. Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.

3-(2-Naphthyloxy)phthalonitrile. To a solution of 3-nitrophthalonitrile (3.46 g, 20 mmol) in dry DMSO (30 mL) were added 2-naphthol (5.80 g, 40 mmol) and dry fine-powdered K_2CO_3 (25 g, 160 mmol). The resulting mixture was stirred at room temperature for 48 h and then poured into 300 mL of cold water and stirred for 0.5 h. The precipitate obtained by filtration was further purified by silica gel column chromatography using CH_2Cl_2 as eluant, giving pure product (4.65 g, 86%). MS (GCT-MS): an isotopic cluster peaking at *m*/*z* 270 (calcd for M^+, *m*/*z* 270.3). Anal. Calcd for $C_{18}H_{10}N_2O$: C, 79.98; H, 3.73; N, 10.37. Found: C, 79.08; H, 3.79; N, 10.05.

$H_2Pc(\alpha\text{-}OC_{10}H_7)_4$ (6). A mixture of 3-(2-naphthyloxy)phthalonitrile (540 mg, 2 mmol) and lithium (28 mg, 4 mmol) in *n*-pentanol (6 mL) was heated at a temperature lower than 120 °C under nitrogen for 2 h. After being cooled to room temperature, the resulting green solution was poured into methanol (100 mL) containing 2 mL of concentrated HCl. The precipitate was collected by filtration and chromatographed on a silica gel column using $CHCl_3$ as eluent. A green band was developed. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure $H_2Pc(\alpha\text{-}OC_{10}H_7)_4$ as green powder (108 mg, 20%). UV−vis ($CHCl_3$) [λ_{max}/nm (log ϵ)]: 330 (4.91), 408 (4.41), 623 (4.62), 657 (4.76), 688 (5.25), 721 (5.31). MS (MALDI-TOF): an isotopic cluster peaking at *m*/*z* 1082.9 (calcd for M^+, *m*/*z* 1083.1). Anal. Calcd for $C_{72}H_{42}N_8O_4$ (**6**): C, 79.83; H, 3.91; N, 10.35. Found: C, 78.68; H, 4.09; N, 9.90.

Table 2. Crystallographic Data for **1**·$CHCl_3$

molecular formula	$C_{53}H_{57}Cl_3N_8O_4Pb$
M	1183.61
cryst system	monoclinic
space group	$P2_1/c$
a/Å	16.708(19)
b/Å	23.30(3)
c/Å	14.576(16)
β/deg	113.867(17)
V/Å^3	5189(10)
Z	4
D_c/Mg m^{-3}	1.515
μ/mm^{-1}	3.459
data collcn range/deg	1.59−25.03
reflcns measd	27 028
indpndnt reflcns	9163 ($R_{int} = 0.1046$)
params	622
R1 [$I > 2\sigma(I)$]	0.0466
wR2 [$I > 2\sigma(I)$]	0.0960
goodness of fit	0.926

$Pb[Pc(\alpha\text{-}OR)_4]$ ($R = C_5H_{11}$, C_7H_{15}, $C_{10}H_7$) (1−3). In a typical procedure, a mixture of $Pb(Ac)_2$·$3H_2O$ (76 mg, ca. 0.20 mmol) and 1,8,15,22-tetrakis(alkoxy)phthalocyanine (0.10 mmol) in *n*-pentanol (4 cm^3) was heated at 140 °C under nitrogen for ca. 8 h. The solvent was then removed in vacuo, and the residue was subjected to chromatography on a silica gel column using $CHCl_3$ as eluent. The crude product was purified by recrystallization from $CHCl_3$/MeOH, giving dark green needles.

$Pb[Pc(\alpha\text{-}OC_5H_{11})_4]$ (**1**) (97 mg, 91%): ^1H NMR ($CDCl_3$) δ 9.02 (d, *J* = 7.5, 4 H, H_a), 8.08 (t, *J* = 7.5, 4 H, H_b), 7.64 (d, *J* = 8.1, 4 H, H_c), 4.88−4.93 (m, 4 H, OCH), 2.33−2.50 (m, 4 H, CH_2), 2.19−2.31 (m, 12 H, CH_2), 1.44 (t, *J* = 7.2, 12 H, CH_3), 1.24 (t, *J* = 7.2, 12 H, CH_3); UV−vis ($CHCl_3$) [λ_{max}/nm (log ϵ)] 333 (4.75), 432 (4.42), 673 (4.62), 751 (5.39); MS (MALDI-TOF) an isotopic cluster peaking at *m*/*z* 1064.2 (calcd for M^+, *m*/*z* 1064.4). Anal. Calcd for $C_{52}H_{56}N_8O_4Pb$: C, 58.68; H, 5.30; N, 10.53. Found: C, 58.60; H, 5.33; N, 10.51.

$Pb[Pc(\alpha\text{-}OC_7H_{15})_4]$ (**2**) (94 mg, 80%): ^1H NMR ($CDCl_3$) δ 9.08 (d, *J* = 7.4, 4 H, H_a), 8.05 (t, *J* = 7.8, 4 H, H_b), 7.72 (d, *J* = 8.2, 4 H, H_c), 4.67 (t, *J* = 5.7, 4 H, OCH), 2.57−2.67 (m, 8 H, CH), 1.67 (d, *J* = 6.7, 12 H, CH_3), 1.36 (d, *J* = 6.8, 12 H, CH_3), 1.29 (d, *J* = 6.6, 12 H, CH_3), 1.11 (d, *J* = 6.8, 12 H, CH_3); UV−vis ($CHCl_3$) [λ_{max}/nm (log ϵ)] 333 (4.70), 437 (4.39), 676 (4.57), 755 (5.33); MS (MALDI-TOF) an isotopic cluster peaking at *m*/*z* 1176.1 (calcd for M^+, *m*/*z* 1176.5). Anal. Calcd for $C_{61.25}H_{73.25}N_8O_4Cl_{3.75}Pb$ (**2**·1.25$CHCl_3$): C, 55.49; H, 5.57; N, 8.45. Found: C, 55.99; H, 5.66; N, 8.35.

$Pb[Pc(\alpha\text{-}OC_{10}H_7)_4]$ (**3**) (89 mg, 69%): UV−vis ($CHCl_3$) [λ_{max}/nm (log ϵ)] 340 (4.83)), 431 (4.36), 666 (4.62), 741 (5.38); MS (MALDI-TOF) an isotopic cluster peaking at *m*/*z* 1289.3 (calcd for MH^+, *m*/*z* 1289.3). Anal. Calcd for $C_{72.75}H_{40.75}N_8O_4Cl_{2.25}Pb$ (**3**·0.75$CHCl_3$): C, 63.41; H, 2.98; N, 8.13. Found: C, 63.37; H, 3.14; N, 8.14.

X-ray Crystallography. Crystal data and details of data collection and structure refinement are given in Table 2. Data were collected on a Bruker SMART CCD diffractometer with a Mo Kα sealed tube ($\lambda = 0.710\,73$ Å) at 293 K, using a ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for col-

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lecting frames of data, indexing reflections, and determination of lattice constants, SAINT-PLUS for integration of intensity of reflections and scaling,[28] SADABS for absorption correction,[29] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[30] All the H atoms in these compounds were obtained geometrically. These H atoms were included in the subsequent least-squares refinement as fixed contributors. The final refinement with anisotropic temperature factors for non-H atoms led to an *R* value of 0.0466 for this compound. The CCDC reference number is 244420.

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