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Effect of Chain Length on Thermal Conversion of Alkoxy-Substituted Copper Phthalocyanine Precursors

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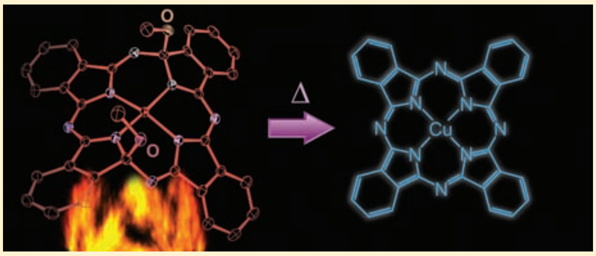
Supporting Information



ABSTRACT: A series of dialkoxy-substituted copper phthalocyanine (CuPc) precursors (**4a**−**4d**) have been prepared by treating phthalonitrile with the corresponding lithium alkoxide under mild conditions. The precursors exhibited high solubilities in common organic solvents, including acetone, toluene, tetrahydrofuran (THF), CH_2Cl_2, and $CHCl_3$. Elongation of the alkoxy chains improved the solubilities of the precursors effectively, and accordingly, the butoxy-substituted derivative (**4d**) showed the highest solubility among **4a**−**4d**. X-ray crystallography clarified that the conjugated skeletons of **4a**−**4d** are all isostructural, and have two alkoxy groups in a *syn*-conformation fashion, leading to highly bent structures. Thermal conversions of the precursors examined by thermogravimetry (TG) and differential thermal analysis (DTA) demonstrate that **4a** was converted into CuPc via two distinct exothermic processes in the 200−250 °C temperature range, while **4d** exhibits only one exothermic signal in the DTA. In the field emission scanning electron microscopy (FESEM) images of **4a**, the presence of two types of distinct crystal morphology (prismatic and plate-like crystals) can be recognized, implying that the two observed exothermic processes in the DTA can be attributed to the different crystal morphologies of the samples rather than the step-by-step elimination of the alkoxy groups. The thermal formation of CuPc from the precursors has been unambiguously confirmed by X-ray powder diffraction, UV−vis spectroscopy, and elemental analysis. The precursors were converted into CuPc at lower temperature with increasing chain length, presumably because of the increased void volume in the crystals. Thermal conversion performed in the solution phase results in a bright blue-colored solution with prominent absorption bands in the 650−700 nm region, strongly supporting the formation of CuPc.

■ INTRODUCTION

The first description of metallo phthalocyanine (Pc) appeared in the literature in 1907, in which Braun and Tcherniak observed the generation of unassignable blue materials by heating phthalimide in iron vessels.[1] Later, a series of studies performed by Linstead and co-workers revealed that Pcs consist of four angularly conjugated isoindole units connected via aza bridges.[2] The same group also introduced the name phthalocyanine after the Greek terms naphtha for mineral oil and cyanine for dark blue.[3] Not long after these pioneering studies, the exceptional thermal and light stabilities of Pcs attracted considerable attention as coloring materials through the growing petrochemical industry.[4] Among metalloPcs, CuPc has been established as one of the most chemically and physically stable Pc, and as a result, a large amount of CuPc derivatives has been industrially produced worldwide, primarily for the purpose of colorants for paints and plastics. On the other hand, Pcs also exhibit unique photophysical and electrochemical properties, based mainly on their π electron configurations. As a consequence, the applications of Pcs have been expanded recently from simple colorants to highly advanced functional materials, so that Pcs can play pivotal roles in high-tech products such as optical disks, photodynamic therapy, and organic semiconductors.[5] Of these, the formation of thin films of Pcs on a substrate is an essential process to fabricate Pc-based organic devices.

However, Pcs having neither peripheral nor axial substituents are barely soluble in common solvents such as water, alcohols, acetone, and hydrocarbons.[6] Therefore, the fabrication of thin films of Pcs generally requires either the introduction of appropriate substituents or the employment of the vacuum deposition technique to sublime the Pcs directly onto the substrate. However, substituted Pcs often lower the performance of the fabricated organic devices, while vacuum deposition is unsuitable for facile, large-scale production of the devices.

Recently, Ono and co-workers have proposed a new approach to overcome the low-solubility problem.[7] Their Pc derivatives have bulky substituents such as bicyclo[2.2.2]-octadiene (BCOD) or acetonide groups at the peripheral six-membered rings of the Pc skeleton, which deforms the planarity of the Pcs and consequently contributes to increase the

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Scheme 1. Synthesis of CuPc Precursors 4a−4d

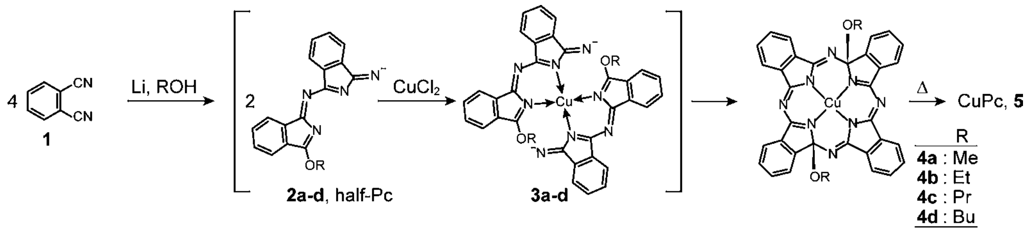

Table 1. Crystal Data and Structure Refinement Parameters

	4a	4b	4c	4d
empirical formula	$C_{35}H_{26}CuN_8O_3$	$C_{36}H_{26}CuN_8O_2$	$C_{38}H_{30}CuN_8O_2$	$C_{40}H_{34}CuN_8O_2$
formula weight	670.19	666.20	694.25	722.29
crystal color, habit	red, prism	red, prism	pale-red, platelet	red, prism
crystal dimensions [mm]	0.30 × 0.20 × 0.20	0.18 × 0.15 × 0.10	0.35 × 0.10 × 0.03	0.31 × 0.27 × 0.07
crystal system	monoclinic	triclinic	monoclinic	triclinic
a [Å]	14.038(4)	7.8987(2)	13.2549(7)	11.283(5)
b [Å]	13.225(4)	13.1465(3)	10.9039(7)	12.047(5)
c [Å]	17.039(6)	15.4334(3)	22.8570(2)	13.308(6)
α [deg]		108.554(8)		99.948(6)
β [deg]	112.242(3)	97.024(7)	107.793(2)	91.7156(15)
γ [deg]		96.510(7)		109.491(6)
V [Å^3]	2928.0(16)	1488.0(1)	3145.5(3)	1672.2(12)
space group	$P2_1/c$	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
Z	4	2	4	2
ρ_{calcd} [g cm^{-3}]	1.520	1.487	1.466	1.435
temperature [K]	173	200	296	173
residuals R/R_w	0.0446/0.1188	0.0351/0.0973	0.0515/0.0920	0.0387/0.1277
GOF	1.060	1.107	0.959	1.083
CCDC	818577	844879	844880	844881

solubility.[8] After the formation of the thin films using the soluble Pc derivative, the films can be converted into insoluble, unsubstituted Pcs by inducing quantitative thermal elimination of the substituents to generate peripherally fused benzo moieties of Pcs. Although the synthesis has been focused on the modification of the peripheral region of the Pcs, we have recently succeeded in developing another type of thermally convertible CuPc precursor by reacting phthalonitrile in the presence of lithium methoxide under moderate reaction conditions.[9] The reaction of phthalonitrile with lithium alkoxides such as $LiOC_5H_{11}$ and $LiOC_6H_{13}$ at high temperature (ca. 140−160 °C) generates so-called half-Pc intermediates, followed by the successive coupling of two half-Pc units and elimination of the alkoxy groups, leading to the formation of the aromatic Pc skeleton.[10] In contrast, we performed identical reactions at lower temperature by using methanol as the solvent, so that the reactions cannot proceed to the final elimination process. As a consequence, skeleton-modified Pc precursors, in which two methoxy groups are substituted at the diagonal pyrrole α-carbons in a *syn*-conformation fashion, **4a**, have been obtained (Scheme 1).[11,12] The sp^3-hybridized carbons at the methoxy substituted sites are responsible for the distortion of the molecular skeleton, while the presence of the methoxy groups contributes to increase the flexibility of the molecule. As a result, compound **4a** exhibits marked solubility in acetone, toluene, CH_2Cl_2, and so forth. By heating **4a**, the methoxy groups were removed and CuPc was generated quantitatively. Compared to the previous thermally convertible precursors, the one-pot facile reaction starting from commercially available inexpensive chemicals is of particular advantage in our method.

By extending the chain length of the substituted alkoxy groups, further improvement of the solubilities can be anticipated because of the enhanced structural flexibility of the precursors. However, the effects of these structural differences on the solubilities and thermal conversion processes have not yet been clarified. In the present paper, we have prepared a series of CuPc precursors **4a−4d** (Scheme 1) by the reaction of phthalonitrile and various primary alcohols, namely, methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), and 1-butanol (BuOH), in the presence of lithium, and performed a comparative study on the structural and thermal conversion properties.

■ EXPERIMENTAL SECTION

Synthesis. *CuPc(OMe)$_2$, **4a**.* This compound was reported in our previous paper.[9]

*CuPc(OEt)$_2$, **4b**.* Phthalonitrile (0.51 g, 4.0 mmol) was added to ethanol (20 mL) in which lithium metal (0.22 g, 25 mmol) was dissolved at room temperature under a nitrogen atmosphere. The mixture was heated at 70 °C with stirring for 13 min, followed by the addition of anhydrous copper(II) chloride (0.15 g, 1.1 mmol). The color of the mixture turned to dark green during the reaction. After 30 min, the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2, and filtered to remove insoluble CuPc. The filtrate was purified by alumina column chromatography using CH_2Cl_2 as the eluent. After the first red fraction was collected, the solution was concentrated in vacuo at below 40 °C. The resulting solution was added to hexane, to precipitate **4b** as a dark red powder in 2.0% yield (13 mg). Spectral data: UV−vis (1,2,4-trichlorobenzene, TCB): λ_{max}

nm, (log ε) 507 (2.59) 408 (3.84) 390 (3.91). MS (ESI): m/z = 666 $[M]^+$. Anal. Found: C, 63.18; H, 4.07; N, 16.11. Calcd for $C_{36}H_{26}N_8O_2Cu$: C, 64.71; H, 4.22; N, 16.77.

CuPc(OPr)$_2$, **4c**. Phthalonitrile (1.1 g, 8.2 mmol) was added to 1-propanol (40 mL) in which lithium metal (0.12 g, 15 mmol) was dissolved at room temperature under a nitrogen atmosphere. The mixture was heated at 75 °C with stirring for 12 min, followed by the addition of anhydrous copper(II) chloride (0.30 g, 2.2 mmol). The color of the mixture turned to dark green during the reaction. After 30 min, the solvent was evaporated in vacuo. The residue was dissolved in CH_2Cl_2, and filtered to remove insoluble CuPc. The filtrate was purified by alumina column chromatography using CH_2Cl_2 as the eluent. After the first red fraction was collected, the solution was concentrated in vacuo at below 40 °C. The resulting solution was added to hexane, to precipitate **4c** as a dark red powder in 3.1% yield (45 mg). Spectral data: UV–vis (TCB): λ_{max} nm, (log ε) 508 (2.43) 408 (3.74) 390 (3.80). MS (ESI): m/z = 694 $[M]^+$. Anal. Found: C, 65.68; H, 4.53; N, 15.83. Calcd for $C_{38}H_{30}N_8O_2Cu$: C, 65.74; H, 4.36; N, 16.14.

CuPc(OBu)$_2$, **4d**. Phthalonitrile (1.1 g, 8.4 mmol) was added to 1-butanol (40 mL) in which lithium metal (0.14 g, 18 mmol) was dissolved at 75 °C under a nitrogen atmosphere. The mixture was heated at 75 °C with stirring for 14 min, followed by the addition of anhydrous copper(II) chloride (0.32 g, 2.3 mmol). The color of the mixture turned to red brown during the reaction. After 30 min, the resulting solution was poured into water/methanol (2: 1 (v/v)). The suspension was filtered, and the residue was dissolved in CH_2Cl_2. After the solution was dried with Na_2SO_4, the solvent was removed in vacuo. The residue was purified further by alumina column chromatography using CH_2Cl_2 as the eluent. After the first red fraction was collected, the solution was concentrated in vacuo at below 40 °C. The resulting solution was added to hexane, to precipitate **4d** as a dark red powder in 1.6% yield (24 mg). Spectral data: UV–vis (TCB): λ_{max} nm, (log ε) 508 (2.73), 409 (3.73), 390 (3.78). MS (ESI): m/z = 722 $[M]^+$. Anal. Found: C, 66.82; H, 4.79; N, 15.53. Calcd for $C_{40}H_{34}N_8O_2Cu$: C, 66.51; H, 4.74; N, 15.51.

Measurements. Mass spectra were obtained by using an AB SCIEX QSTAR Elite Hybrid LC/MS/MS System mass spectrometer using acetonitrile as a solvent. Elemental analyses were carried out with a Yanaco MT-5 analyzer. Crystal structural analyses were performed at 200, 296, and 173 K for **4b**, **4c**, and **4d**, respectively, on a Rigaku R-AXIS VII diffractometer using filtered Mo–K_α radiation (**4b**), Rigaku R-AXIS RAPID (**4c**), and Rigaku Saturn 70-CCD (**4d**) diffractometers employing graphite monochromated Mo–K_α radiation. The structures were solved by a direct method and expanded using Fourier techniques. Hydrogen atoms were refined isotropically using a riding model, while those of other elements were refined anisotropically. Disorders on the substituted butoxy groups were recognized for **4d**. The crystal data and experimental details are summarized in Table 1. X-ray powder diffraction analyses were performed at room temperature using Cu–K_α radiation on a Rigaku Rint 2000 diffractometer. Thermogravimetry (TG) and differential thermal analysis (DTA) data were collected using a SHIMADZU DTG-60H analyzer. A scan rate of 5 K/min was employed. Field emission scanning electron microscopy (FESEM, JEOL JSM-7500F) was used to obtain surface images of the crystalline samples. Electronic absorption measurements were made with a Perkin ELMER Lambda 19 spectrophotometer.

■ RESULTS AND DISCUSSION

The general reaction protocols for **4a–4d** are shown in Scheme 1. To prepare the alkoxy-substituted CuPc precursors, phthalonitrile was first treated with a lithium alkoxide generated in situ in the corresponding primary alcohols at 70–75 °C for 10–14 min. The temperature and reaction time have been optimized for each derivative. The alkoxides attack at one of the cyano groups of the phthalonitrile during this process, followed by a coupling reaction between two phthalonitrile units to give the half-Pc intermediate (**2a–2d**), although these intermediates could be neither isolated nor characterized directly because of their unstable nature, presumably, at the imine sites. To the reaction mixture containing **2a–2d** was added anhydrous $Cu^{II}Cl_2$ to couple two half-Pcs by taking advantage of the template effect of Cu^{2+}. About a quarter equivalent of the copper salt with respect to the phthalonitrile gave the best results, while an excess amount of $Cu^{II}Cl_2$ resulted in reduced formation of the target compounds. Concentration of the reactants is crucial for achieving higher yields. It appears that oligomeric coupling of the phthalonitrile units is promoted in excessively concentrated reaction mixtures, while overdilution reduced the reaction probability between two phthalonitriles. After the addition of $Cu^{II}Cl_2$, the reaction was continued for an additional 30 min. Compounds **4a** and **4b** exhibit partial exchange reactions of the substituted alkoxy groups with ethoxy and methoxy groups when these are purified by column chromatography using $CHCl_3$ containing EtOH as a stabilizing agent, or using MeOH, respectively, which were detected by the electrospray ionization (ESI) mass (see Supporting Information, Figure S1). In contrast, compounds **4c** and **4d** showed no such exchange behaviors. The reaction yields ranged from 33 to 1.6%, depending on the alkoxy chain-length, and higher alcohols tend to depress the yield.

The X-ray quality single crystals of **4b–4d** were grown by slow concentration of methanol (**4c** and **4d**) and ethanol (**4b**) solutions at room temperature. The ORTEP representations of **4b** and **4d** are depicted in Figure 1. See ref 9 and Supporting Information, Figure S2 for the X-ray structures of **4a** and **4c**, respectively. As confirmed from the crystal structures, the π-structures of the precursors are almost identical to each other. In all cases, two alkoxy groups show *syn*-substitution at the diagonal pyrrole α-carbons. As a consequence, the Pc skeletons are forced to take on highly deformed, bent conformations. No *anti*-substituted isomers have been characterized at present,

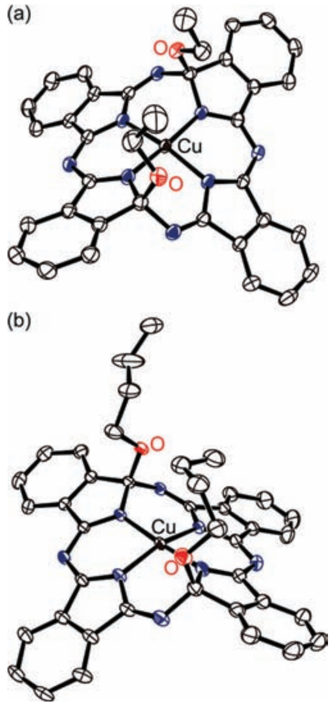

Figure 1. ORTEP representations of (a) **4b** and (b) **4d** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

although the mechanism of this selective formation is still unclear. All precursors exhibit high solubilities in acetone, toluene, tetrahydrofuran (THF), CH_2Cl_2, and $CHCl_3$, while **4d** even shows moderate solubility in hexane, as demonstrated in Figure 2 as a pale, red-colored solution.

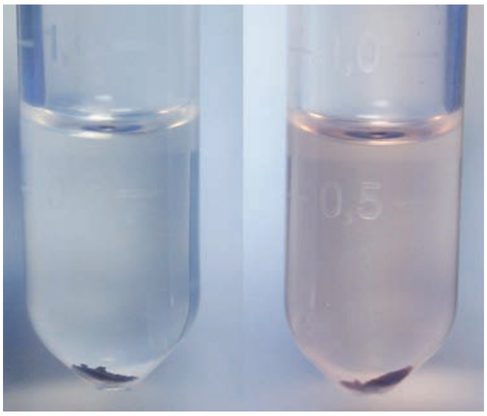

Figure 2. Photographs of centrifuged saturated solutions of **4a** (left) and **4d** (right) in hexane at room temperature.

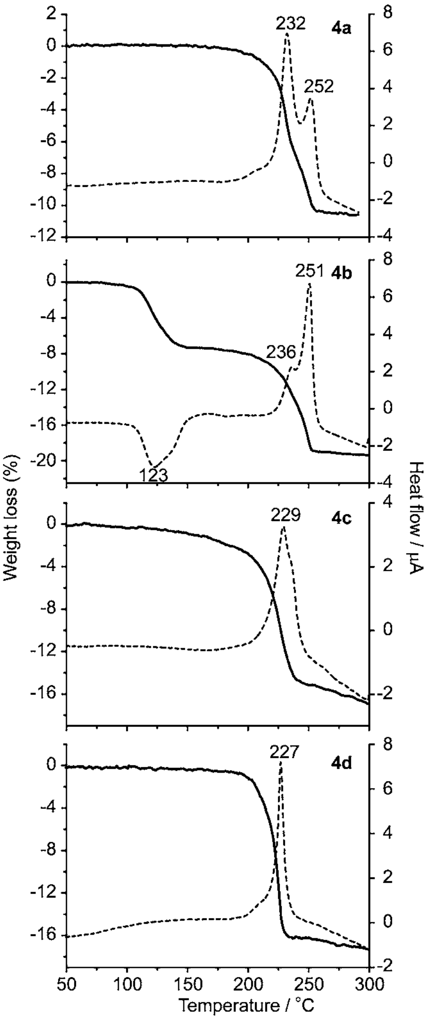

Figure 3. Weight loss (solid line) and DTA curves (dashed line) of **4a**–**4d** (from top to bottom) during the course of thermal elevation under nitrogen. Scan rate = 5.0 K min^{-1}.

The thermal conversion processes of **4a**–**4d** were investigated using TG-DTA analyses. For each measurement, microcrystalline samples were prepared by reprecipitation of the precursors from CH_2Cl_2/hexane, followed by vacuum desiccation at room temperature to remove as much of the solvated molecules as possible. The weight loss percentages of the precursors in the course of raising the temperature under a stream of nitrogen gas (solid line) and the corresponding DTA curves (dashed line) are displayed in Figure 3. In the DTA, the positive and negative signals indicate exothermic and endothermic processes, respectively. Monotonic weight loss with an inflection point at about 238 °C was observed for **4a** in the temperature range of about 200–250 °C, and the corresponding DTA curve having two clear positive peaks at 232 and 252 °C indicates that two exothermic processes take place in this temperature range, consistent with the stabilization of **4a** by the aromatization reaction. As already stated in ref 9, the total weight loss of about 10% is consistent with the quantitative conversion of **4a** into CuPc. The two positive peaks in the DTA curve suggest that two independent exothermic processes are involved in this region. However, two-step eliminations of the methoxy groups, in which the first step releases one of the two methoxy groups only to give a CuPc(OMe) intermediate, are unlikely because the inflection point is located outside the midpoint of the total weight loss. As discussed below, these two thermal processes can be attributed to the presence of two types of morphology in the microcrystalline samples. Compound **4b** exhibited two separate thermal processes. The first step at about 123 °C is endothermic, while the second step at temperature in the range of 230–260 °C is exothermic. The first endothermic step can be safely assigned to elimination of the remaining solvated molecules judging from the temperature. The observed weight loss for the second step (ca. 12%) is slightly lower than the theoretical value (14%). The aromatization temperature range is almost identical with that of **4a**, although the split of the DTA peaks is less distinct for **4b** compared to **4a**. Contrary to our intuitive expectation, the precursors are aromatized at lower temperatures for **4c** and **4d** (ca. 229 and 227 °C, respectively) than **4a** and **4b**. These observations can be rationalized by considering the increased void volume for **4c** and **4d** in the crystals, while tight crystal packing inhibits the dissociation of the carbon–oxygen bonds to some extent. This is evidenced by the fact that comparisons of **4a** and **4c** having $P2_1/c$ and $P2_1/a$ space groups, respectively (Supporting Information, Figure S3), and **4b** and **4d** having a $P\bar{1}$ space group (Supporting Information, Figure S4) clearly indicate that higher alkoxy groups increase the distances between the two main bodies of the precursors in the crystals. In other words, the conversion temperature is sensitive to the morphology of the precursors. For application purposes, we have already observed that the amorphous **4a** on an ITO electrode can be converted into CuPc at as low as 85 °C.[9] Results of the elemental analyses of the thermally generated products from **4a**–**4d** broadly support the formation of CuPc (Table 2), although the results are slightly outside the anticipated values for the product obtained from **4b**. We tentatively attribute these observations to the presence of unassignable impurities and/or partial decomposition of the precursor during the thermal process. Nevertheless, the formation of **4b** and CuPc generated therefrom can be unambiguously confirmed by the single crystal structures (Figure 1) and X-ray powder diffraction data (see below).

Table 2. Results of Elemental Analysis of Thermally Generated Materials

precursor	C(%)	H(%)	N(%)
4a	66.51	2.83	19.22
4b	64.33	2.85	18.37
4c	66.81	2.94	19.23
4d	66.38	2.92	18.82
calcd for CuPc	66.72	2.80	19.45

X-ray powder diffraction patterns of the precursors (left) and the CuPc thermally generated by the solid-to-solid conversions (right) are shown in Figure 4. Although the observed patterns differ from each other for the precursors, those of thermally generated samples are practically independent of the starting precursors, strongly suggesting the formation of the so-called α-phase CuPc irrespective of the alkoxy chain-length of the precursor.[13,14] The FESEM images of the crystalline sample of **4a** displayed in Figure 5 clearly show the presence of two distinct crystal morphologies. In Figure 5a, prismatic and plate-like crystals can be recognized in the upper left and lower right regions, respectively. The magnified images of these crystals (b and c) demonstrate that the columnar structures with smooth surfaces have approximately 8−14 μm length and 2−4 μm width, while the lamellarly structured unstriated plate crystals have less than 500 nm thickness. The presence of these two phases accounts for the two-step thermal eliminations observed for **4a**. The electronic absorption spectrum of **4d** in TCB exhibits practically no absorption bands above 500 nm because of interruption of the conjugation at the alkoxy-substituted sites (Figure 6, dashed line). Upon heating at 180 °C, prominent absorption bands appear in the 550−750 nm region, also indicating the formation of CuPc (Figure 6, solid line).[15]

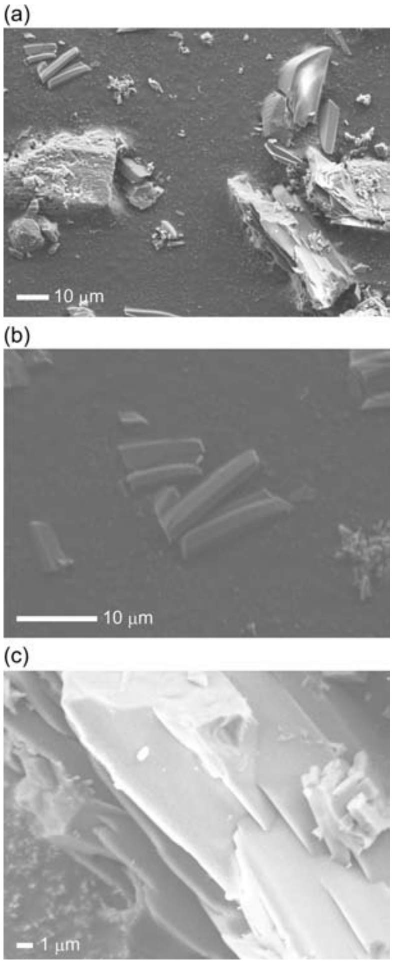

Figure 5. FESEM images of (a) **4a** prepared by reprecipitation from CH_2Cl_2/hexane followed by vacuum desiccation, and (b,c) two crystal morphologies appearing in (a).

■ CONCLUSIONS

In the present study, we have prepared a series of dialkoxy-substituted copper phthalocyanine (CuPc) precursors (**4a**−**4d**) by reacting phthalonitrile with lithium alkoxides such as LiOMe, LiOEt, LiOPr, and LiOBu under mild conditions. The precursors exhibited high solubilities in acetone, toluene, THF, CH_2Cl_2, and $CHCl_3$, while elongation of the alkoxy chains improved the solubility. As a consequence, we have even succeeded in dissolving the butoxy-substituted precursors in hexane to some degree. X-ray crystallography clarified that the conjugated skeletons of **4a**−**4d** are all isostructural. Thermal conversions of the precursors examined by a TG-DTA analyzer demonstrated that **4a** was converted into CuPc via two distinct exothermic processes, while **4d** exhibited only one exothermic signal in the DTA. FESEM images of **4a** clearly show the presence of two distinct morphologies, implying that the two observed exothermic processes in the DTA can be attributed to

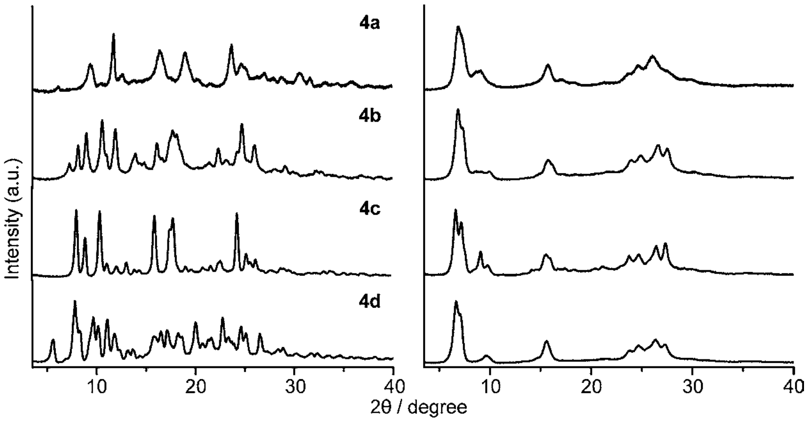

Figure 4. X-ray powder diffraction patterns of **4a**−**4d** (left, from top to bottom) and the corresponding thermally generated CuPc (right) by solid-to-solid conversion.

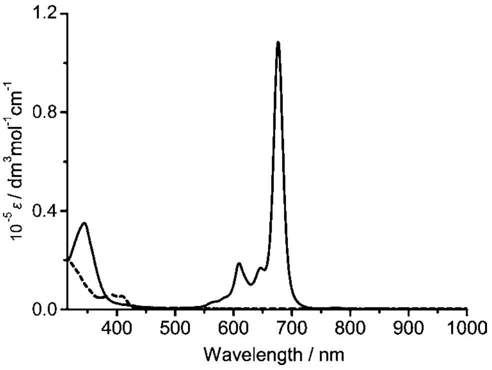

Figure 6. Electronic absorption spectrum of **4d** in TCB (dashed line) and of CuPc obtained by solution-phase thermal conversion (solid lines). Cell path length = 1 cm.

the different crystal morphologies of the samples rather than the step-by-step elimination of the alkoxy groups. The precursors were converted into CuPc at lower temperature with increasing chain length, presumably because of the increased void volume in the crystals. Thermal conversion performed in TCB resulted in a bright blue-colored solution with prominent absorption bands in the 650−700 nm region, also strongly supporting the formation of CuPc.

■ ASSOCIATED CONTENT

Supporting Information

ESI-mass of **4b**, ORTEP drawing of **4c**, crystal packing structures of **4a**−**4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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