Preparation of solid solution and crystal-glass composite consisting of stable phenoxyl radical and its phenol analogue

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Abstract

Evaporation of mixed solution of 2,4,6-tris(4-*tert*-butylphenyl)phenoxyl 1_M and its phenol analogue 1_{OH} yielded a solid solution (**III**), where $1_{OH} : 1_M = 0.70 : 0.30$, which was isomorphic to crystal of 1_{OH} (**II**). In contrast, slow evaporation of 1_M concomitant with gradual decomposition giving 1_{OH} yielded crystal-glass composite (**IV**) consisting of $1_{OH} : 1_M$ with a molar ratio of $0.40 : 0.60$. The outer crystal region of **IV** was attributed to solid solution of 1_{OH} and 1_M, while the inner glassy region to amorphous consisting of 1_M and its dimer 1_D (**I**).
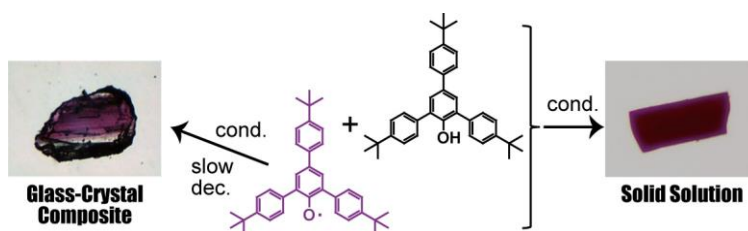
Keywords: Solid solution, crystal-glass composite, stable phenoxyl radical, amorphous

Introduction

The most common molecular solids are single-component crystals, but there are many other types of molecular solids, which include non-crystalline solids (amorphous or glass, liquid crystals, and plastic crystals) and multi-component solids (cocrystals, eutectic mixtures, and solid solutions). Owing to their unique structure and properties, these molecular solids have attracted much attentions.[1,2] Above all, solid solutions are particularly important because the design of solid-state properties is facile. Generally, prediction of structure and properties of molecular solids is difficult. This is because properties of molecular solids are determined by both intrinsic character of the molecule and packing structure. While the former can be predicted rather precisely by theoretical calculations, the latter is essentially unpredictable because it alters readily by responding sharply to the change in molecular size, shape, and participating intermolecular interactions. This is a big issue to design the molecular solids possessing desired structure and/or properties.

On the other hand, the aforementioned principle determining packing structure also indicates that, when the molecules have virtually identical size, shape, and intermolecular interactions, they should give isostructural crystals and/or solid solutions. Indeed, it is well known that molecules bearing chloro group and their methyl analogue often give isostructural crystals. This relationship is referred to as "chloro-methyl rule".[3,4] Pairs of benzene and pyrazine, benzene and thiophene, and thiophene and selenophene moieties are also known to be interchangeable.[5] It may be noted that, although they have similar size and shape, C–H and C–F groups are less likely interchangeable due to the presence of C–H⋯F–C interaction or F/π repulsion.[6] Pairs of compounds giving isostructural crystals are likely to afford solid solutions, which are isostructural to crystals of the individual components mostly. At this point, properties of the solid solution can be reasonably predicted based on the crystal structure of individual components and difference in their properties, thus solid solution can be a powerful tool to design the molecular solids possessing desired structure and/or properties.

Although phenoxyl radicals have rather similar size and shape to its phenol analogue, they do not necessarily give solid solutions. This should be because these compounds have different solubility, the difference of O· of phonoxyl and OH group of phenol in size and shape is small but significant, and O· and OH groups participate in different intermolecular interactions (for example, OH group can behave as a hydrogen bond donor, while O· cannot). In contrast, since different behavior of O· and OH groups become ignorable by the presence of the substituent, phenoxyl radicals that are sterically stabilized are prone to form solid solutions with their phenol analogue. For example, galvinoxyl and hydrogalvinoxyl can yield a solid solution with a molar ratio of 4 : 96.[7] This solid solution showed remarkable magnetic property, in which intermolecular exchange interaction was ferromagnetic in contrast to antiferromagnetic character of the pure galvinoxyl crystal.[7] Stabilized phenoxyl radicals are widely used to develop functional magnetic materials[8–11] and redox materials including battery,[12,13] and in these fields solid solutions may play an important role to control the magnetic properties.
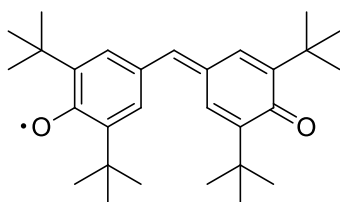
galvinoxyl

hydrogalvinoxyl

(R = Et and Pr)
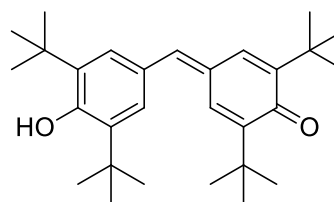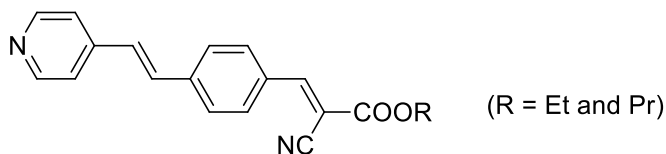
ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates
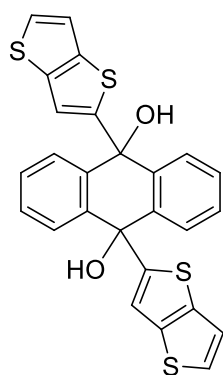
trans-9,10-dihydroxy-9,10-bis(thieno[3,2-b]thienyl)-9,10-dihydroanthracene
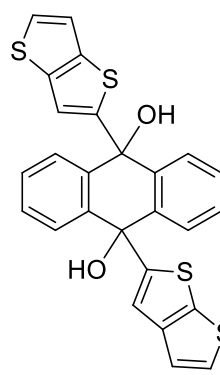
trans-9,10-dihydroxy-9-(thieno[2,3-b]thienyl)-10-(thieno[3,2-b]thienyl)-9,10-dihydroanthracene

Although most solid solutions are isostructural with crystals of their individual components, there are a small number of exceptions, where both crystal structures of individual components and solid solutions are not identical. For example, although packing structures of ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates were virtually identical, that of their solid solution was different.[14] Crystal structures of *trans*-9,10-dihydroxy-9,10-bis(thieno[3,2-*b*]thienyl)-9,10-dihydroanthracene, and its solid solution with *trans*-9,10-dihydroxy-9-(thieno[2,3-*b*]thienyl)-10-(thieno[3,2-*b*]thienyl)-9,10-dihydroanthracene were isomorphic, crystal structure of the latter itself was different.[15] Furthermore, crystal structures of benzoic acid, 4-fluorobenzoic acid, and their solid solution were all different.[16] These facts indicate that relationship between crystal structure of individual components and their solid solution should be more complicated than generally considered.

In the present paper, we have the attention to a stabilized phenoxyl radical, 2,4,6-tris(4-*tert*-butylphenyl)phenoxyl 1_M. 1_M owns a unique characteristic that it can yield both amorphous solid (**I**) consisting of 1_M and its equilibrium dimer 1_D (where $1_M : 1_D = 0.09 : 0.91$) and crystal consisting solely of 1_D depending on solidification solvents.[17] Since there was no report on solidification behaviour of combination of such unique phenoxyl radicals and their phenol analogues, solidification behaviour of 1_M and its phenolic analogue (1_{OH}) has been examined herein.

1_M: R = O•
1_{OH}: R = OH

1_M: R = O•
1_{OH}: R = OH

1_D
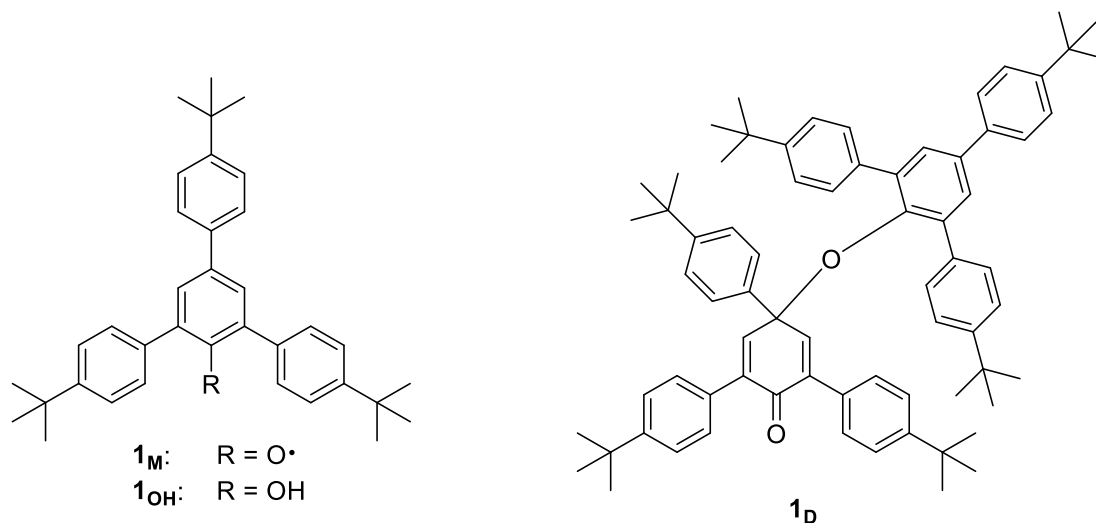
Results and Discussion

First, crystal structure of 1_{OH} itself (**II**) was determined. **II** was obtained by recrystallization from ethyl acetate-hexane solution as colorless prism. When 1 : 1 mixture of 1_{OH} and 1_M in acetone were evaporated, homogeneously purple crystal (**III**) was yielded (See Graphical Abstract). The 1_{OH} : 1_M ratio in **III** was determined by the titration experiment using hydroquinone to be 0.70 : 0.30. A preliminary experiment showed that 1_M was degraded in acetone by 3% in 1 h likely due to the abstraction of α-hydrogen atom of acetone. This indicates that the stoichiometric ratio of 1_{OH} and 1_M should have been no longer 1 : 1 when **III** was precipitated. The higher 1_{OH} content ratio than that in the initial solution should be due to the reaction of 1_M with the solvent. Also, the lower solubility of 1_{OH} should be responsible, by which 1_{OH} precipitated prior to 1_M. Similar purple crystal was yielded from solutions where 1_{OH} contained more than 1_M; on the contrary, even when solutions where 1_{OH} contained much less than 1_M were evaporated, no purple crystal containing 1_M more than 1_{OH} but a mixture of **I** and **II** was yielded.

In contrast, on very slow evaporation of ethereal solution of 1_M over one week, apparently crystalline solid (**IV**) was obtained. **IV** consisted of a purple inner region and an apparently colourless outside region (See Graphical Abstract). When **IV** was dissolved in benzene and oxidized by using $K_3[Fe(CN)_6]$ under basic condition, the resultant solution consisted solely of 1_M and 1_D, as similar to benzene solution of **I**. When **IV** was reduced by using hydroquinone in benzene, 1_{OH} was obtained as a single product. These results indicate that the purple and colorless component in **IV** was attributed to 1_M and 1_{OH}, respectively. Titration experiment revealed that **IV** contained 1_{OH} less than 1_M, a stoichiometric ratio of which was 0.40 : 0.60. 1_{OH} should have arisen by reaction of 1_M with solvent likely due to the abstraction of α-hydrogen atom of ether. Indeed, when ethereal solution of 1_M in a sealed flask was left for two months, 1_M was thoroughly deteriorated into 1_{OH}.

X-ray structure of **II** is depicted in Figures 1a. **II** consists of one independent 1_{OH} molecule, whose OH group was disordered. The occupancy factors of O1, O2, and O3 were 29%, 54%, and 17%, respectively. There are two possible reasons for the presence of the disorder. First, the molecular structure of 1_{OH} has pseudo 3-fold symmetry, which would give the packing energy to be rather close whichever disorder site the OH group occupies. Second, OH group cannot form intermolecular hydrogen bond at any disorder site due to the vicinal aryl substituents. This is confirmed by the following facts. In the X-ray structure, any pair of 1_{OH} molecules has

no shorter intermolecular O···O contact than sum of van der Waals radii. Also, in the infrared spectrum of **II**, O–H vibration was observed at 3542 cm^{-1} as a sharp peak (Figure S2).

       X-ray analysis of **III** revealed that it was isomorphic to **II** (Figure 1b). The O· group was also disordered, and the occupancy factors of O1, O2, and O3 were 33%, 48%, 19% respectively, which were similar to those of **II**. Although two oxygen atoms which were of OH and O· groups, respectively, were not observed separately, **III** can be regarded to as a solid solution, because all C–O bonds were essentially shorter in the X-ray structure than the corresponding ones in **II**. Indeed, C–O bond lengths in **III** were 1.385(8) Å for C11–O1, 1.366(6) Å for C13–O2, and 1.400(12) Å for C15–O3, while they were 1.433(11) Å, 1.398(6) Å, and 1.404(13) Å in **II**, respectively. It is known that C–O bond length in phenoxyl radical (1.25 Å for PhO· as a calculated value)[18] is by more than 0.1 Å shorter than standard length of phenolic C–O bond (1.37 Å),[19,20] because of delocalization of unpaired electron on the oxygen atom to the benzene ring, which gives rise to increase a higher double-bond character of the C–O bond. Given the fact, it is reasonably considered that the observed shorter C–O bonds are attributed to an averaged structure of **1$_{OH}$** and **1$_M$**, and **III** was a solid solution consisting of **1$_{OH}$** and **1$_M$**.

Table 1. Crystallographic parameters of **II–IV**

	II	**III**	**IV**
	(1$_{OH}$)	**(1$_{OH}$: 1$_M$ = 70 : 30)**	**(1$_{OH}$: 1$_M$ = 40 : 60)**
Molecular Formula	C$_{36}$H$_{42}$O	C$_{36}$H$_{42}$O	C$_{36}$H$_{41}$O
Molecular Weight	490.69	490.69	490.69
Crystal System	orthorhombic	orthorhombic	orthorhombic
Space Group	*Pbca* (no. 61)	*Pbca* (no. 61)	*Pbca* (no. 61)
a / Å	23.785(14)	23.71(2)	23.849(14)
b / Å	24.885(19)	24.866(13)	24.993(6)
c / Å	9.82(2)	9.699(6)	9.798(4)
α / °	90	90	90
β / °	90	90	90
γ / °	90	90	90
V / Å^3	5810(13)	5720(7)	5840(4)
Z	8	8	8
T / K	200(2)	200(2)	200(2)
D$_c$ / g cm^{-3}	1.122	1.140	1.114
R1 (*I* > 2 σ(*I*))	0.0851	0.0698	0.0806
wR2 (all data)	0.2317	0.2061	0.2292
CCDC number	1895027	1895028	1895078

       X-ray structure of **IV** was also isomorphic to those of **II** and **III** (Figure 1c). Crystal parameters of **II–IV** are shown in Table 1 for comparison. Oxygen atoms were again disordered with occupancy factors of 34%, 50%, and 16% for O1, O2, and O3, respectively. **IV** had seemed to be a composite crystal[21–23] consisting of **1$_{OH}$** and **1$_M$** in the outer and inner regions, respectively. This hypothesis was, however, denied by the fact that C11–O1 (1.413(9) Å) and C13-O2 (1.396(7) Å) bonds of **IV** were much longer than the corresponding ones in **III** and comparable or slightly shorter than those in **II**, although **1$_M$**/**1$_{OH}$** ratio in **IV** is larger than that in **III** (C15-O3 bond lengths of **II–IV** cannot be compared meaningfully because they have large errors). Considering that solid solution character of **III** is responsible for their shorter C–O bond, **1$_M$** may contribute the X-ray structure of **IV**

slightly. Consequently, it is reasonably considered that most of **1$_M$** should be present in the inner region of **IV** as an amorphous solid, although the outer region may contains only slight part.
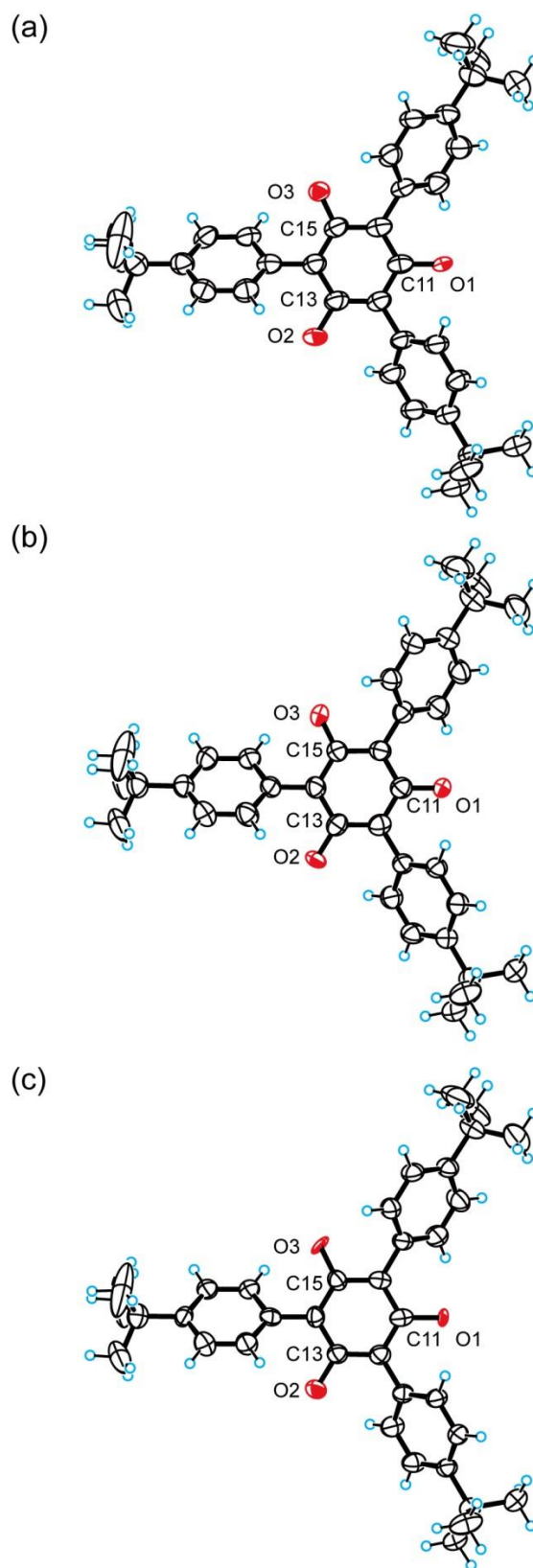

Figure 1. X-ray structures of **II** (a), **III** (b) and **IV** (c). Some oxygen and carbon atoms are labelled.

Structure of **III** and **IV** was supported by means of differential scanning calorimetry (DSC) analysis (Figure 2). First, **I** was found to give an exotherm at T_{peak} 143 °C (T_{onset} 124 °C) on heating. The products of the thermolysis were **1$_{OH}$** (44%), **2** (55%), and a small amount (3%) of benzofuran derivative **3** (Figure 3). It was previously reported that **1$_{OH}$** and **2** were obtained in thermolysis of an equilibrium solution of **1$_M$** and **1$_D$** in tetrachloroethylene at 124 °C.[24] Although **3** was not referred to in ref. 24, we found that **3** was obtained in the pyrolysis at the higher temperature (~ 180 °C) in tetrachloroethylene. When it was heated, **II** simply melted at T_{melt} 268 °C without decomposition.

On heating of **III**, an endotherm was found not around 140 °C but at T_{peak} 257 °C (T_{onset} 246 °C). By NMR analysis, the product was mostly **1$_{OH}$** (95%) concomitant with a small amount of **2** (2%) and **3** (3%). Since **III** is a solid solution, intermolecular hydrogen abstraction of **1$_M$** yielding the principal product (**1$_{OH}$**) should be difficult to occur therein. Thus, it is most likely that **III** melted around T_{peak} (which was by 11 °C lower than the melting point of **II**, 268 °C), and consequently (or simultaneously) the thermolysis occurred. In contrast, on heating of **IV**, an exotherm was observed at T_{peak} 136 °C (T_{onset} 117 °C). The products contained **1$_{OH}$** (73%) and **2** (27%), and no **3** was yielded. It is noteworthy that the yields of **2** in the thermolyses of **IV** and **I** were even higher than that in **III**. In conjunction with similar T_{onset} in the thermolyses of **I** and **IV**, the thermolysis of **IV** appeared to proceed in the inner region initially. Since the inner region of **IV** is attributable to amorphous **I** and the outer region to crystal **II**, **IV** should be regarded as a crystal-glass composite. The fact that **IV** consisted of **I** was further supported by comparison of diffuse reflectance spectra of **I**, **III**, and **IV** (Figure 4). Diffuse reflectance spectra of **I** and **IV** appeared to be virtually identical, in which the longest wavelength absorption maxima (λ_{max}) were observed commonly at 564 nm, while λ_{max} was by 9nm shifted hypsochromically in that of **III**.
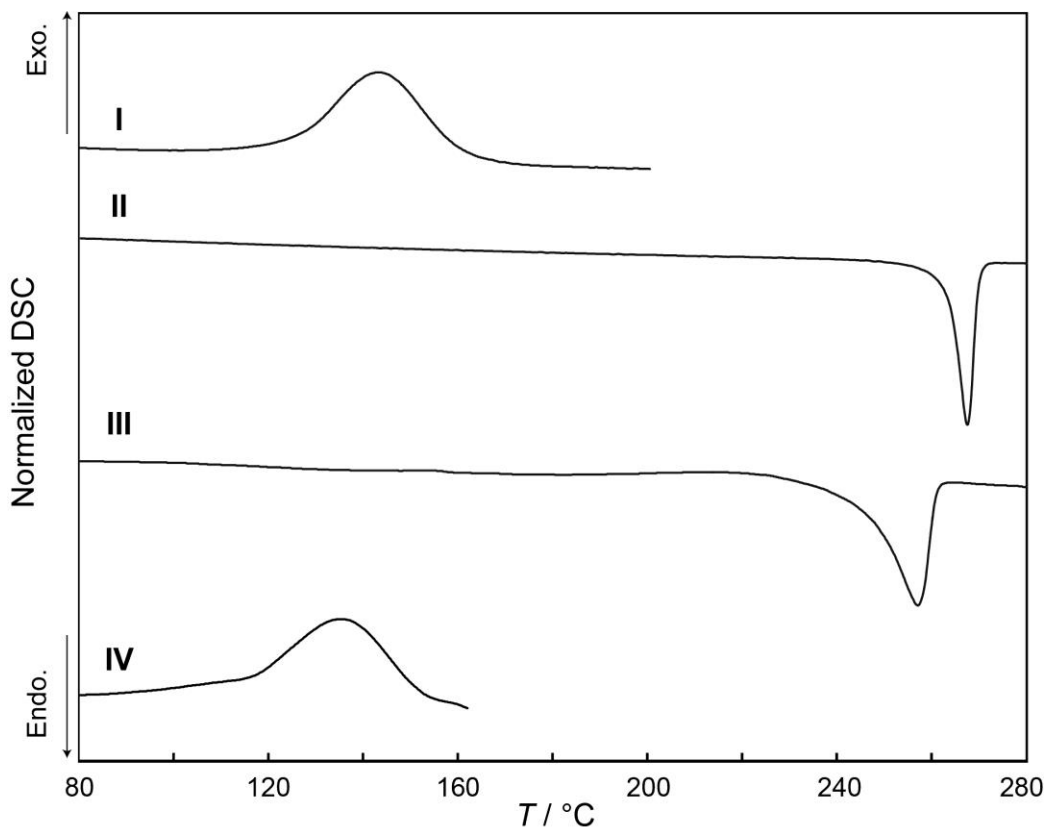

Figure 2. DSC curves of **I–IV**. Samples (~3 mg) were heated at 5 °C min^{-1}.
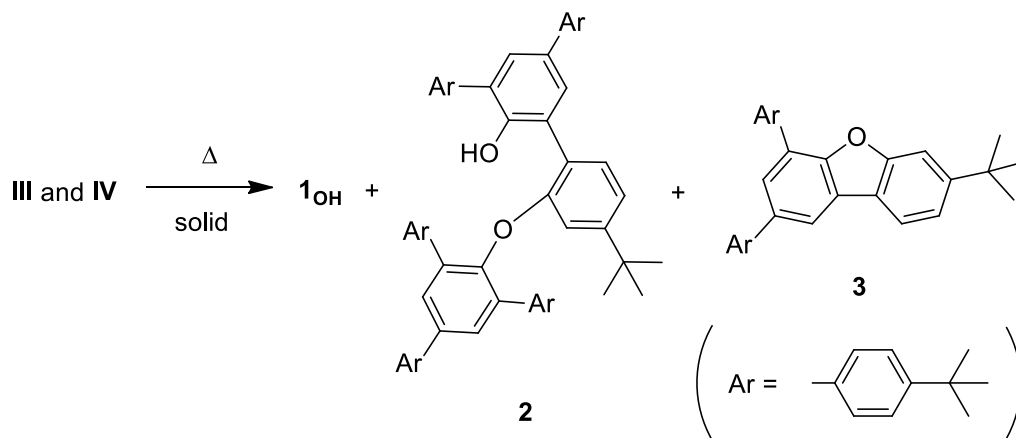
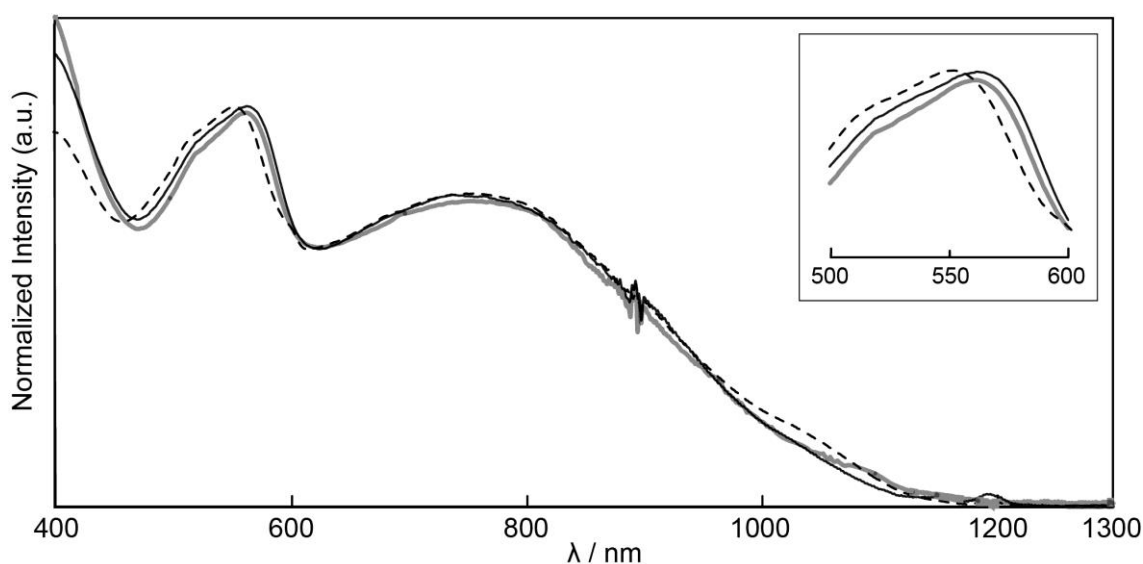**Figure 3.** Products of thermal decomposition of **III** and **IV**.

Figure 4. Diffuse reflectance spectra of **I** (black solid), **III** (black dotted), and **IV** (gray bold). (inset) An expansion of the range of 500 to 600 nm.

Conclusions

While evaporation of acetone solutions of phenoxyl radical 1_M and phenol 1_{OH} yield amorphous (**I**) and crystal (**II**), respectively, evaporation of mixed acetone solution of 1_M and 1_{OH} yielded solid solution **III**, which is isomorphic to **II**. When 1_M was contained more than 1_{OH}, acetone solution gave a mixture of **I** and **II**, while ethereal solution yielded crystal-glass composite **IV** bearing purple inner region and apparently colorless outer region. Phenoxyl C–O bonds were observed to be slightly shorter in X-ray structure of **IV** as compared to the corresponding bonds in that of **II**, indicating that the colorless region may be a solid solution containing a small amount of 1_M. A crystal-glass composite character of **IV** was confirmed by analyzing thermal decomposition products and the diffuse reflectance spectra of **I–IV**. The inorganic crystal-glass composites have been extensively studied recently because they have high potential for luminescent and photo-functional materials,[25–27] although studies on organic crystal-glass composites were scarce. In this regard, the present study may be a path-breaking work to develop noble organic luminescent materials. Studies on effect of

solvent in the generation of **IV** by microscopic analysis on the surfaces and interfaces and examination of distribution of **1$_M$** are currently underway.

Experimental Section

General. Ethyl acetate and hexane was used as purchased. Acetone was dried over Drierite$^{(R)}$, then distilled under an inert argon atmosphere. Diethyl ether was dried over CaCl$_2$, then distilled over Na wire under an inert argon atmosphere. DSC measurements were performed on a SHIMADZU DSC-60. Diffuse reflectance spectra were measured on a JASCO V-570 spectrometer. ^{1}H (600 MHz) and ^{13}C (151 MHz) NMR spectra were measured on a JEOL JNM-ECP600. Mass spectral analysis was conducted on a JEOL JMS-700V using the FAB ionization method. IR spectra were measured on a JASCO FT/IR-6100 spectrometer.

1$_{OH}$ and **1$_M$** were synthesized according to the literature procedure.[17,28] The purity of **1$_M$** was confirmed as follows. Since **1$_M$** was prepared from **1$_{OH}$**, possible impurities were (unreacted) **1$_{OH}$** and by-products. Absence of **1$_{OH}$** was confirmed by IR spectrum of **I**, where no O–H vibration was observed at 3542 cm^{-1} unlike **II**. Absence of the by-products was confirmed by ^{1}H NMR spectrum of the product from the reaction of **I** with hydroquinone, in which no signal attributed to **1$_{OH}$** and quinone was observed (see below).

Preparation of I–IV. Preparation of **I–IV** was conducted at an ambient temperature. Amorphous solids **I** was prepared as reported previously.[17] Crystal **II** suitable for single-crystal X-ray analysis was obtained by slow evaporation of 5 mg of **1$_{OH}$** in a mixture of ethyl acetate and hexane (15 mL) for a few days. Solid solutions **III** were given when 2 mg of **1$_{OH}$** and 2 mg of **1$_M$** (as **I**) was dissolved in distilled acetone (10 mL), the mixed solution was evaporated for 12 h, then the precipitated deep purple needles were filtered from mother solution. Crystal-glass composites **IV** were given when an Erlenmeyer flask containing a solution of 10 mg of **1$_M$** (as **I**) in distilled diethyl ether (5 mL) was plugged with a cork stopper then left standing over one week to dryness. After washing carefully, **IV** was obtained as a platelet or prism.

X-ray analysis of II, III, and IV. Cell dimensions were obtained by a least-squares fit to the settings for 20 carefully centered reflections. The data collected on a RIGAKU AFC-7S diffractometer ($\lambda_{Mo, K\alpha}$ = 0.71069 Å) to 2θ = 55° gave 6635, 6570, and 6708 independent reflections for **II**, **III**, and **IV**, respectively, and all reflections were used in refinement. Diffraction intensity was not corrected by standard reflections. The data were corrected for Lorentz and polarization factors but no absorption correction was made. The crystal structure was solved by direct methods and Fourier technique (SHELXL-97[29] on PC-Linux). All non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms except those of OH groups were placed geometrically with fixed individual displacement parameters [U(H) = 1.5(C_{methyl}) or 1.2(C_{phenyl})] using a riding model. Hydrogen atoms of OH groups were not included during refinemt. The site-occupancy factors of O1, O2 and O3 (occ(O1), occ(O2) and occ(O3), respectively) were refined under conditions that occ(O1) + occ(O2) + occ(O3) = 1, occ(H1) = 1 – occ(O1), occ(H2) = 1 – occ(O2) and occ(H3) = 1 – occ(O3).

II. C$_{36}$H$_{42}$O, *MW* 490.69, orthorhombic, *Pbca* (no. 61), a = 23.785(14), b = 24.885(19), c = 9.82(2) Å, α = 90°, β = 90°, γ = 90°, V = 5810(13) Å^3, Z = 8, T = 200(2) K, D_c = 1.122 g cm^{-3}, $R1$ = 0.0851 (I > 2 σ(I)), $wR2$ = 0.2317 (all data). CCDC 1895027.

III. C$_{36}$H$_{42}$O, *MW* = 490.69, orthorhombic, *Pbca* (no. 61), a = 23.71(2), b = 24.866(13), c = 9.699(6) Å, α = 90°, β = 90°, γ = 90°, V = 5720(7) Å^3, Z = 8, T = 200(2) K, D_c = 1.140 g cm^{-3}, $R1$ = 0.0698 (I > 2 σ(I)), $wR2$ = 0.2061 (all data). CCDC 1895028.

IV. $C_{36}H_{41}O$, *MW* = 489.69, orthorhombic, *Pbca* (no. 61), *a* = 23.849(14), *b* = 24.993(6), *c* = 9.798(4) Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 5840(4) Å^3, *Z* = 8, *T* = 200(2) K, D_c = 1.114 g cm^{-3}, *R1* = 0.0806 (*I* > 2 σ(*I*)), *wR2* = 0.2292 (all data). CCDC 1895078.

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Thermal deterioration of I, III, and IV. Typical procedure. **I** (50 mg) in round-bottom flask was heated at 143 °C (= T_{peak} in the DSC analysis) in an oil bath under nitrogen for 2 h. After cooling, the reaction mixture was subjected to NMR analysis to determine the product ratio. Afterwards, the reaction mixture was separated by the column chromatography (SiO$_2$, hexane : CHCl$_3$ 10 : 1) to yield **1$_{OH}$**, **2**, and **3**.

4,6-Bis(4-*tert*-butylphenyl)-2-{4-*tert*-butyl-2-[2,4,6-tris(4-*tert*-butylphenyl)phenoxy]phenyl}phenol (**2**). ^{1}H NMR (CDCl$_3$): δ 7.65 (s, 2H, Ar), 7.63 (d, *J* 8.4 Hz, 2H, Ar), 7.59 (d, *J* 1.8 Hz, 1H, Ar), 7.58 (d, *J* 8.8 Hz, 2H, Ar), 7.55 (d, *J* 8.4 Hz, 2H, Ar), 7.48-7.44 (m, 6H, Ar), 7.34 (d, *J* 8.4 Hz, 4H, Ar), 7.29 (d, *J* 2.6 Hz, 1H, Ar), 7.22 (d, *J* 8.4 Hz, 4H, Ar), 7.04 (d, *J* 8.1 Hz, 1H, Ar), 6.82 (dd, J_a 7.7, 1.8 Hz, 1H, Ar), 6.51 (d, *J* 1.8 Hz, 1H, Ar), 1.39 (s, 9H, *tert*-Bu), 1.38 (s, 9H, *tert*-Bu), 1.36 (s, 9H, *tert*-Bu), 1.20 (s, 18H, *tert*-Bu), 1.11 (s, 9H, *tert*-Bu). FT-IR (cm^{-1}): 3542 (v_{OH}). MS: *m/z* 978 (M$^+$).

2,4-Bis(4-*tert*-butylphenyl)-7-*tert*-butyldibenzofuran (**3**). ^{1}H NMR (CDCl$_3$): δ 8.06 (d, *J* 1.8 Hz, 1H, Ar), 7.92 (d, *J* 8.1 Hz, 1H, Ar), 7.90 (d, *J* 1.1 Hz, 2H, Ar), 7.79 (d, *J* 1.8 Hz, 1H, Ar), 7.66 (d, *J* 8.4 Hz, 2H, Ar), 7.65 (d, *J* 1.1 Hz, 1H, Ar), 7.58 (d, *J* 8.4 Hz, 2H, Ar), 7.52 (d, *J* 8.4 Hz, 2H, Ar), 7.43 (dd, *J* 7.6, 1.8 Hz, 1H, Ar), 1.42 (s, 9H, *tert*-Bu), 1.41 (s, 9H, *tert*-Bu), 1.39 (s, 9H, *tert*-Bu). ^{13}C NMR (CDCl$_3$): δ 157.1, 153.1, 151.5, 150.8, 150.1, 138.6, 136.6, 133.7, 128.5, 127.1, 125.8, 125.7, 125.4, 121.7, 120.4, 120.0, 117.5, 117.5, 108.8, 108.8, 35.3, 34.7, 34.6, 31.6, 31.4, 29.7. MS: *m/z* 488 (M$^+$). HRMS (*m/z*): 488.3083 (M$^+$, calcd. 488.3079 for C$_{36}$H$_{40}$O).

Supplementary Material

The Supplementary Material file can be found in the online version. It contains experimental details of titration experiment of **III** and **IV** and solvolysis of 1M in acetone, the IR spectrum of **II** and ^{1}H and ^{13}C NMR spectra of **2** and **3**.

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