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Molecular Properties of 2-Pyrone-4,6-dicarboxylic Acid (PDC) as a Stable Metabolic Intermediate of Lignin Isolated by Fractional Precipitation with Na^+ Ion

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A chemically stable metabolic intermediate of lignin, 2-pyrone-4,6-dicarboxylic acid (PDC), was isolated, and the molecular properties were comprehensively investigated by using thermal analysis, optical spectroscopy, potentiometric titration, and X-ray crystallography. UV absorption spectra of PDC did not show any solvent effects, whereas the fluorescence spectra displayed distinct solvatochromism. Despite the fairly good planarity of the PDC geometry, dual fluorescence was observed in some small donor number solvents. The emission behaviors are thought to be due to the significant twist between the pyrone ring and carboxylate substituents, found in the X-ray crystal structures of the Na^+ complex. The crystal structure also showed the intermolecular, centrosymmetric short hydrogen bonding of the carboxylate moieties with an O···H···O distance of 0.2452 nm, which made it possible to assign the pK_a values to the molecular structure. PDC was thermally stable and could be sublimed even at atmospheric pressure, offering the preparation possibility of ultra-thin films by vapor-deposition techniques. The fact that the chemically and thermally stable compound possessing many attractive functions, such as unique emission, facile sublimation, and strong acidity, resulting in exceptionally short intermolecular contacts, can be obtained from biomass on a large quantity will lead to establishment of carbon neutral system in future industry.

Utilization of biomass in valuable fuels and industrial products has attracted much attention, because society requires a change from nonrenewable carbon resources to renewable bioresources.[1] Lignin is one of the most abundant natural carbon resources, existing in trees at 15–36% by weight. However, an advanced system of utilizing it as biomass has not been established, because the highly networked three-dimensional structures make it difficult to transform into well-defined versatile substances by conventional synthetic methods. Accordingly, the metabolic conversion of lignin into stable and functional intermediates has become the focus in this research field,[2,3] and we have recently succeeded in producing pure 2-pyrone-4,6-dicarboxylic acid (PDC) on a large scale from lignin via protocatechuate by using transformed bacterium.[4] PDC is chemically stable and expected to be a versatile functional substance, because the pyrone ring has some useful functions, such as an acceptor property in donor–acceptor type chromophores[5,6] as well as the biodegradability induced by PDC hydrolase.[7] Additionally, two carboxylic acids attached to the pseudo-aromatic ring can be chemically modified when larger molecular systems are constructed. A typical example is the use as a bifunctional monomer for polycondensation with another bi- or tri-functional monomer, furnishing linear and networked polymers, respectively. Furthermore, PDC cannot be synthesized using petrochemistry, only from plant components at the moment in spite of much effort to synthesize naturally occurring compounds.[3,4,8] This fact would lead to completely novel functional materials. Thus, PDC is highly promising as a renewable biosource for establishing carbon neutral system in industrial materials science, and to this end, a comprehensive understanding of PDC properties is needed.

Many reports on PDC, including the first attempt of the isolation and tentative characterization by Maruyama,[9] suggest that it is difficult to purify, probably due to the inherent sensitivity of the 2-pyrone ring towards bases.[10] Therefore, there has been no systematic study on the detailed properties of PDC. In the course of development of the preparation protocol on a large scale, we have found that PDC can be selectively

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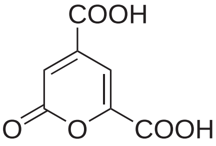

Chart 1. Chemical structure of 2-pyrone-4,6-dicarboxylic acid (PDC).

recovered as the Na^+ salt when NaCl is added to the centrifuged aqueous solution. Subsequent acidification of the Na^+ salt-dispersed solution, followed by the solvent extraction, readily gives the pure PDC. Here, we report detailed properties of PDC, determined by using thermal analysis, optical spectroscopy, potentiometric titration, and X-ray crystallography. The $PDC \cdot Na^+$ complex was also investigated by using X-ray crystallography, by which a remarkable, centrosymmetric short hydrogen bonding as a result of partial deprotonation of the carboxylic acids was observed (Chart 1).

Results and Discussion

Characterization of PDC. Crude PDC produced by the metabolic pathway was isolated by addition of NaCl, followed by the acidification of the solution. Since purification difficulty generally arises in many biomass production processes owing to the co-existence of bacteria bodies and metabolic wastes, such simple recovery of the product is remarkable. Pure PDC was unambiguously characterized by using ^{1}H and ^{13}C NMR, FT-IR, and MALDI-TOF mass spectrometry. The compound was very soluble in polar solvents, such as water, acetone, methanol, THF, and acetonitrile, but hardly soluble in apolar solvents, such as benzene, hexane, and heptane. Complexation with Na^+ ion decreased the solubility even in polar solvents. For example, the solubility in water decreased from 182 mM (PDC) to 9.5 mM ($1\,M = 1\,mol\,dm^{-3}$) ($PDC \cdot Na^+$ complex) upon complexation. Although PDC tends to interact strongly with Na^+ ion, the complexed cationic peak could not be detected by the MALDI-TOF-MS measurements in the positive ionization mode, but the molecular ion peak was observed in the negative ionization mode. This result is consistent with the fact that the pyrone ring has electron-accepting features especially when electron-withdrawing substituents are attached.[5,6]

The thermal stability of PDC was investigated by using thermogravimetric analysis (TGA). When measurements were performed at a heating rate of $10\,°C\,min^{-1}$ under N_2, no weight loss was observed up to at least ca. 200 °C, and the decomposition temperature was determined to be 253 °C (see Supporting Information). However, the melting point measurement indicated that slow sublimation occurs at ca. 190 °C. For example, leaving PDC at 190 °C for 1 day provided very thin white films deposited on a glass plate, of which the purity was confirmed by using NMR measurements. This result offers the possibility of preparing functional ultra-thin films, which possesses attractive optical properties of PDC (vide infra), by using vapor-deposition techniques.[11]

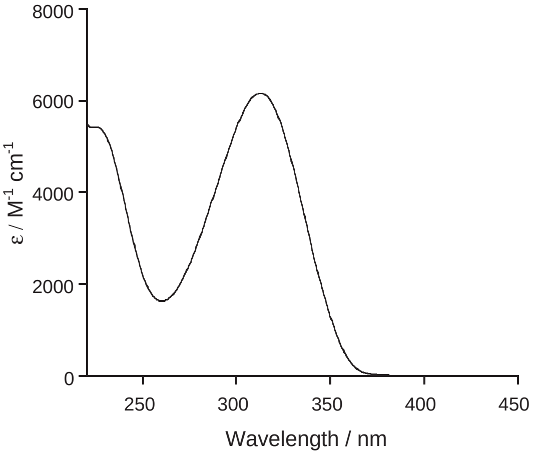

Fig. 1. UV absorption spectrum of PDC in water at 20 °C.

Table 1. Donor Number of the Employed Solvents and Optical Absorption and Fluorescent Spectral Data for PDC in Various Solvents

Solvent	Donor number[a)]	λ_{max} /nm	$\lambda_{em,\,max}$ /nm	Stokes shift /cm^{-1}
Acetic anhydride	10.5	316	451, 468	10278
Acetonitrile	14.1	316	428	8254
1,4-Dioxane	14.8	320	432	8102
Acetone	17.0	327	414	6426
Water	18.0	313	406[b)]	7318
Methanol	19.0	316	428	8281
Ethanol	19.2	317	416	7507
Diethyl ether	19.2	319	433	8227
Dimethylformamide	26.6	319	379	4977

a) Taken from the Ref. 12a. b) The quantum yield measured in water at 20 °C against 2-aminopyridine is 7.9%.

UV Absorption and Fluorescence Spectroscopy. It is reported that 2-pyrone ring possesses efficient electron-accepting properties as well as strong fluorescence when conjugation is extended.[5,6] Since biomass-based functional materials must find utility in the vast and fascinating fields of industry, it is significant to investigate the detailed optical properties of PDC. PDC showed a longest-wavelength absorption peak (λ_{max}) at 313 nm with a molar extinction coefficient (ε) of $6200\,M^{-1}\,cm^{-1}$ in water at 20 °C (Fig. 1). The λ_{max} value was hypsochromically shifted, and the ε value is much smaller as compared to the reported 2-pyrone compounds with extended π-conjugations. This result is also explained by the electronic effects of the substituents. Introduction of donor groups at the 4- and 6-positions of 2-pyrone ring is reported to induce intramolecular donor–acceptor interactions, leading to bathochromic shift of λ_{max}. In this case, carboxylic acid groups at the 4,6-positions of PDC did not generate such interactions in the π-conjugated chromophore. UV absorption spectra, measured in different solvents with various polarities or other interactions, such as hydrogen bonding, did not show significant solvent effects except for shifted λ_{max} value in acetone (Table 1). However, considerable solvatochromism was observed in the fluorescence spectra. Emission maxima ($\lambda_{em,max}$) of PDC range from 379 nm in *N*,*N*-dimethylformamide to 468 nm in acetic anhydride (Table 1 and Fig. 2a). The fluorescence spectra did not display any relationship with solvent polarities, whereas a linear trend was seen in relation to the hydrogen-bonding ability of the solvents. In this case, we used solvent donor number (quantitative measurement of

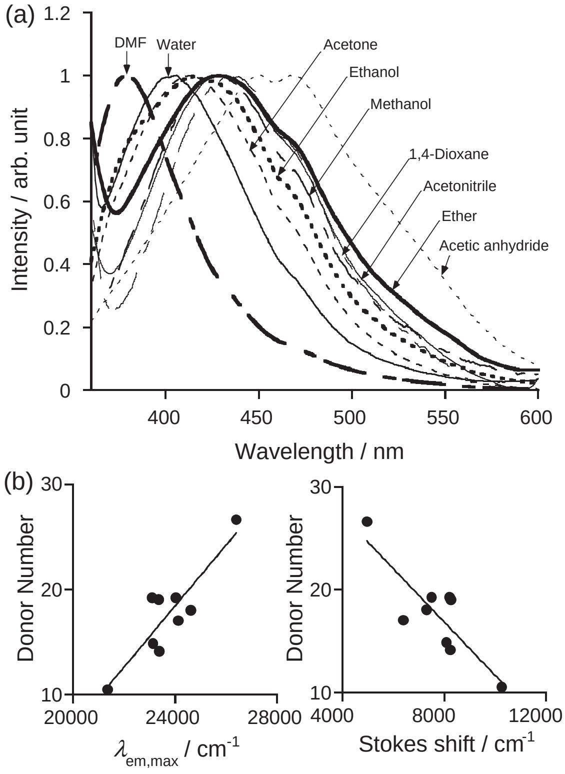

Fig. 2. (a) Fluorescence spectra of PDC in various solvents at 20 °C. (b) Plots of donor number of the employed solvents versus emission peak maxima or Stokes shift values for PDC.

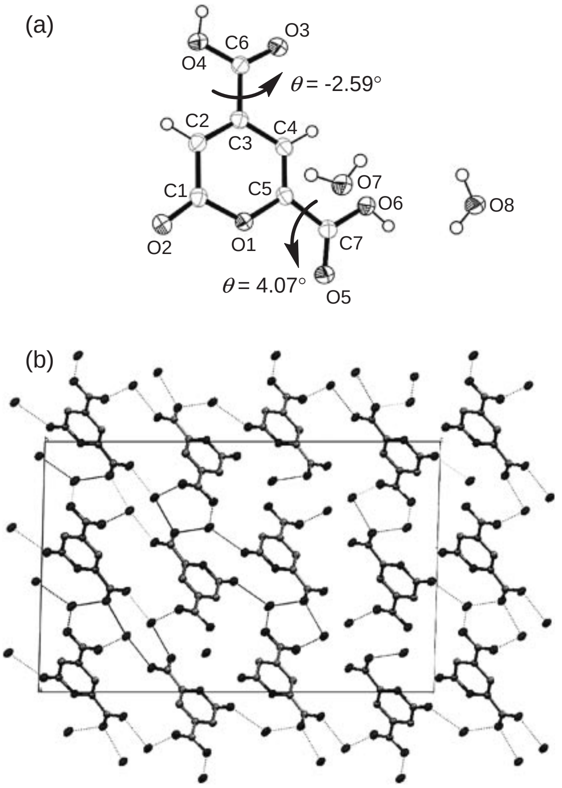

Fig. 3. (a) ORTEP drawing of PDC•$2H_2O$ with vibrational ellipsoids shown at the 50% probability level and (b) arrangement of neighboring molecules via hydrogen bonding with water molecules in the crystal packing of PDC•$2H_2O$.

Lewis basicity) as a measure of hydrogen-bonding strength with a solute.[12] Plots of the $\lambda_{\mathrm{em,max}}$ values against the donor numbers showed a linear correlation ($R = 0.88$) between the two quantities (Fig. 2b). Since the absorption λ_{max} values do not vary remarkably in the employed solvents, the fluorescence can also be characterized by a linear increase in the Stokes shift with decreasing solvent donor number ($R = 0.85$) (Fig. 2b). It should be noted here that no clear relationship between the absorption λ_{max} values and solvent features, including polarity and hydrogen bonding, was found for PDC. These results suggest that the emitting excited state is more strongly associated with solute–solvent hydrogen-bonding interactions than the ground state.

For some small donor number solvents, two emission peaks or one emission peak with an additional shoulder were observed. The most noticeable example is the emission in acetic anhydride, in which two peaks were observed at 451 and 468 nm (Fig. 2a). This dual fluorescence behavior has previously been reported for organic donor–acceptor type compounds as a result of a twisted intramolecular charge-transfer state (TICT).[13] If this is also true for PDC, the emission might originate from both the initial excited state and a lower-energy TICT state, in which the carboxylic acid groups take an orthogonal orientation with respect to the planar 2-pyrone ring.

X-ray Crystal Structures. To obtain information on the molecular geometry, the crystal structures of PDC•$2H_2O$ and the Na^+ complex were determined. Single crystals of PDC•$2H_2O$ and the Na^+ complex suitable for X-ray crystallographic analysis were grown in water at 5 °C. PDC•$2H_2O$ and the Na^+ complex crystallize in the monoclinic space group $C2/c$ ($Z = 8$) and $P2_1/c$ ($Z = 4$), respectively. ORTEP drawings of the asymmetric unit are depicted in Figs. 3a and 5a, respectively, and selected bond lengths and angles are listed in Table 2. In the crystals of PDC•$2H_2O$, the 2-pyrone ring and the two carboxylic acid moieties are in a relatively planar orientation. The interplanar angles between the least-square plane of the 2-pyrone ring and the plane of the carboxylic acids at the 4- and 6-positions are 2.59 and 4.07°, respectively. Each PDC molecule is further linked to the neighboring molecules via hydrogen bonding with a water molecule in a planar fashion, leading to a two-dimensional sheet-like structure (Fig. 3b). The interplanar distance between the sheets is 0.301 nm. This unusual short packing is probably caused by the strong antiparallel dipolar interactions of the carbonyl moieties of the pyrone ring as well as of the carboxylic acids (Fig. 4).[14]

The highly polarizable electronic state within the small molecular size of PDC results in facile release of protons. Previously, the pK_a values of two carboxylic acids of PDC have been estimated to be <2.1, but the presumably low purity has prevented the complete determination of the values.[9] Since we obtained the pure compound, the pK_a values were carefully determined by potentiometric titration in an aqueous solution of PDC at 30 °C. Addition of aq NaOH solution to the PDC solution showed a distinct pH jump exactly at a [NaOH]/[COOH] ratio of 1 (see Supporting Information). The pK_{a_1}

Table 2. Summary of Selected Bond Lengths and Angles of the Crystals of PDC•$2H_2O$ and PDC•Na^+ Complex

PDC•$2H_2O$		PDC•Na^+ complex	
Bond length/nm			
O(1)–C(1)	0.13759(16)	O(1)–C(1)	0.13786(13)
C(1)–C(2)	0.14484(16)	C(1)–C(2)	0.14534(16)
C(2)–C(3)	0.13481(18)	C(2)–C(3)	0.13464(14)
C(3)–C(4)	0.14339(19)	C(3)–C(5)	0.14365(15)
C(3)–C(6)	0.15006(16)	C(3)–C(4)	0.15128(16)
C(4)–C(5)	0.13345(16)	C(5)–C(6)	0.13495(16)
O(1)–C(5)	0.13650(15)	O(1)–C(6)	0.13660(13)
C(5)–C(7)	0.14902(19)	C(6)–C(7)	0.15064(15)
O(2)–C(1)	0.12115(15)	O(2)–C(1)	0.12138(13)
O(3)–C(6)	0.12137(16)	O(3)–C(4)	0.12077(13)
O(4)–C(6)	0.13091(16)	O(4)–C(4)	0.13170(13)
O(5)–C(7)	0.12212(15)	O(5)–C(7)	0.12213(13)
O(6)–C(7)	0.12997(16)	O(6)–C(7)	0.12914(11)
Bond angle/°			
C(1)–O(1)–C(5)	121.40(9)	C(1)–O(1)–C(6)	122.38(8)
O(1)–C(1)–C(2)	117.05(11)	O(1)–C(1)–C(2)	116.58(8)
C(1)–C(2)–C(3)	120.41(12)	C(1)–C(2)–C(3)	120.17(10)
C(2)–C(3)–C(4)	119.99(11)	C(2)–C(3)–C(5)	120.93(10)
C(3)–C(4)–C(5)	118.71(11)	C(3)–C(5)–C(6)	118.11(9)
O(1)–C(5)–C(4)	122.44(12)	O(1)–C(6)–C(5)	121.78(9)

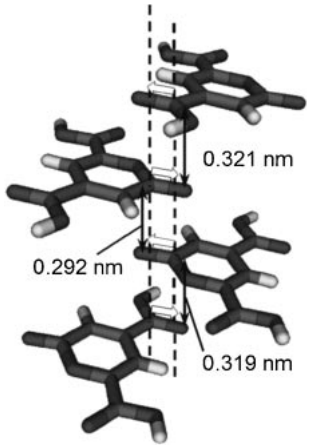

Fig. 4. Crystal packing of PDC•$2H_2O$, showing the anti-parallel stacking of carbonyl moieties with an unusual short distance of 0.29–0.32 nm.

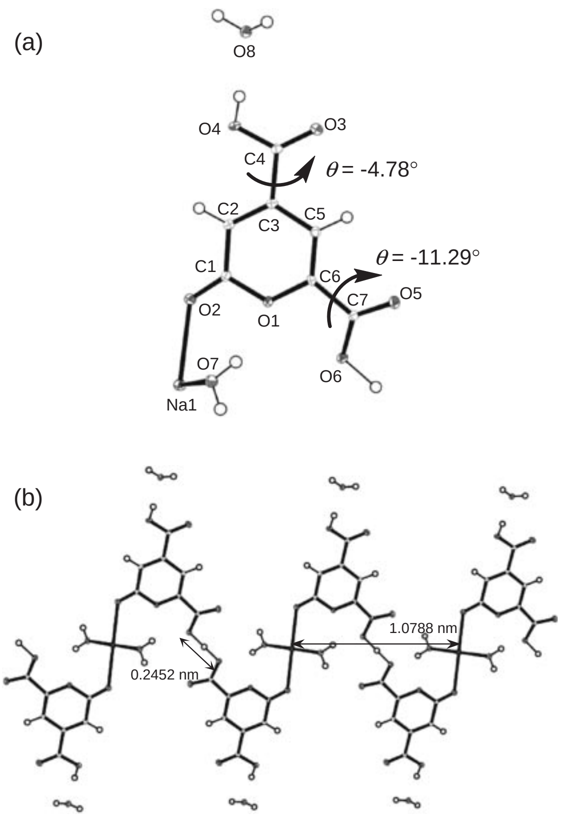

Fig. 5. ORTEP drawings of (a) the repeat unit and (b) zig-zag chain structure of the PDC•Na^+ complex with vibrational ellipsoids at the 50% probability level. The O···H···O distance of the short hydrogen bonding and the intrachain Na···Na distance through the PDC moiety are 0.2452 and 1.0788 nm, respectively.

and pK_{a_2} values, calculated from the dibasic acid model, in which the dissociation of two protons is under equilibrium, were 1.13 and 2.52 ($R \geqq 0.99$), respectively. This strong acidic nature of PDC is supported by the finding during the development of the purification procedure that addition of NaCl to an aqueous PDC solution afforded a white precipitate in an almost quantitative yield. The crystal structure of the PDC•Na^+ complex showed that the carbonyl group of the 2-pyrone ring, instead of the carboxylate moieties at the 4,6-positions, coordinates to the Na^+ ion (Fig. 5a). Remarkably, short centrosymmetric intermolecular hydrogen bonding occurs between the 6-carboxylic acids of the 2-pyrone rings as a result of partial deprotonation of the carboxylic acids (Fig. 5b). This type of short hydrogen bonding between carboxylic acids has sometimes been seen for the complexes of electron deficient carboxylic acids and alkali or alkaline earth metals.[15] Some neutron diffraction studies have shown that the hydrogen atom shared between two carboxylate groups in a manner of COO–H···$^-$OOC ↔ COO$^-$···H–OOC is located exactly on a center to symmetry between the two oxygen atoms, which also coincides with the inversion center of the crystals.[16] A database search of Cambridge Structural Database indicated the average O···H···O distance of such a short hydrogen bonding in the 76 examples found in the database is 0.2443 nm, which is quite short as compared to the usual dimers of carboxylic acids (ca. 0.27 nm).[17] The observed O···H···O distance for the PDC•Na^+ complex is 0.2452 nm, which is fairly in good agreement with the average value of the previously reported examples. This remarkable short hydrogen bonding as well as the Na^+···O=C coordination, as a result, cause the formation of an alternated zigzag chain structure (Fig. 5b).[18] The intrachain Na···Na distance through the PDC moiety is 1.0788 nm. This one-dimensional coordination chain further interacted with each other via hydrogen bonding and coordination with water molecules to provide the two- and three-dimensional networked structures, respectively (see Supporting Information). The interchain distance along the *a* axis is 0.358 nm, which is greater than that for the PDC•$2H_2O$ crystals.

Comparison of the crystal structures between PDC$\cdot$2H_2O and the Na^+ complex gave some more information on the molecular properties of PDC. As shown by the X-ray crystal structure of the Na^+ complex (Fig. 5a), each of two pK_a values could be assigned to the molecular structure. The pK_{a_1} corresponds to the carboxylic acid at the 6-position of the pyrone ring, associated with the short hydrogen bonding based on a proton release. Accordingly, pK_{a_2} originates from the other carboxylic acid at the 4-position. The bond lengths and angles of the PDC framework are almost the same between the two crystals, except for the torsion angles of the carboxylate moieties at the 4- and 6-positions (Table 2). In comparison to the PDC$\cdot$2H_2O crystals, in the Na^+ complex, the carboxylate moieties were distorted farther from the pyrone ring plane. For example, the interplanar angles between the least-square plane of the 2-pyrone ring and the plane of the carboxylate groups at the 4- and 6-positions are 4.78 and 11.29°, respectively (Fig. 5a). The latter significant deviation from the coplanarity might represent the possible molecular geometry of PDC in the excited state responsible for the observed dual fluorescence in small donor number solvents. Small donor number solvents can less efficiently interact with PDC molecules than large donor number solvents. Thus, the intermolecular short and strong hydrogen bonding of the two carboxylic acids should predominantly occur in these kinds of solvents, leading to the deviation of the substituents from the pyrone ring planarity and, consequently, a dual fluorescence.

IR Spectra. There was also a significant difference in the IR spectra of the crystals of PDC$\cdot$2H_2O and the Na^+ complex. The frequency of the OH stretching vibrations is a good guide to the hydrogen-bonding strength. The ν_{OH} of the PDC$\cdot$2H_2O crystals appeared at a very low frequency (3102 cm^{-1}) as a single broad peak, which completely overlapped the sharp ν_{CH} peak of the pyrone ring (Fig. 6a). This low frequency indicates very strong hydrogen bonding between water and PDC molecules, resulting in the two-dimensional sheet structure (vide supra). The spectrum also included multiple C=O stretching vibrations ascribed to the carboxylic acids and Fermi resonance of the 2-pyrone ring in the region of 1757–1726 cm^{-1}. On the other hand, the ν_{OH} of the PDC$\cdot Na^+$ complex was shifted to a higher frequency relative to that of the PDC$\cdot$2H_2O crystals. Two broad peaks appeared at 3488 and 3338 cm^{-1}, indicating that hydrogen bonding, especially associated with water molecules, is much weaker (Fig. 6b). Consequently, a one-dimensional chain structure composed of the Na^+ coordination and short hydrogen bonding of the carboxylic acids is suggested for this complex (vide supra). Upon complexation with Na^+ ion, Fermi resonance of the pyrone ring disappeared, and a strong single peak ascribed to the coordinated C=O vibration appeared at 1719 cm^{-1}. Furthermore, a noticeable peak was assigned to the vibration derived from the intermolecular short hydrogen bonding of the carboxylate moieties.[19] A broad, but relatively strong, peak was observed at 772 cm^{-1} for the PDC$\cdot Na^+$ complex, which does not exist in the spectrum of the PDC$\cdot$2H_2O crystals. Judging from previous reports, this peak could be ascribed to the asymmetric stretching vibration of the O···H···O bond in the short hydrogen bonding. Thus, the IR spectra of both crystals reasonably explain the X-ray crystallographic analysis, which is also helpful in understanding the PDC properties.

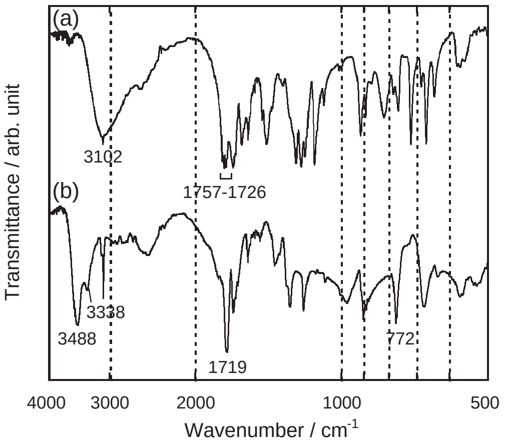

Fig. 6. IR spectra of the crystals of (a) PDC$\cdot$2H_2O and (b) PDC$\cdot Na^+$ complex in KBr at 20 °C.

Conclusion

The molecular properties of 2-pyrone-4,6-dicarboxylic acid (PDC), a lignin-derived stable metabolic intermediate, were comprehensively investigated by using thermal analysis, optical spectroscopy, potentiometric titration, and X-ray crystallography. It was revealed that PDC shows solvent-dependent fluorescence and, in particular, dual fluorescence in small donor number solvents. The unique optical properties suggest that the emitting excited state is strongly associated with solute–solvent hydrogen-bonding interactions. Further detailed investigations are expected to determine its opto-electronic applications. The fluorescence behavior was also elucidated by using potentiometric titration as well as the X-ray crystal structures of PDC$\cdot$2H_2O and the Na^+ complex. A more pronounced deviation of the carboxylic acid groups from the pyrone ring plane was found in the crystal of the Na^+ complex, which forms a one-dimensional polymeric structure via Na^+ ion coordination to the carbonyl moiety of the pyrone ring and short intermolecular hydrogen bonding of the carboxylate moieties with an O···H···O distance of 0.2452 nm. This rare, very short hydrogen bonding has sometimes been seen in the crystal structures of electron-deficient carboxylic acids,[20] but to the best of our knowledge, this is the first report for biomass-derived products.

For material applications of PDC, we mainly envision two approaches. One is the preparation of ultra-thin films by vapor-deposition techniques, which are often employed for device fabrications of functional small molecules. The other is the chemical conversion into covalently linked polymeric structures by the use of PDC as a bifunctional monomer for polycondensation with another bi- or tri-functional monomer. As an advantage, a wide variety of monomers with desired functionalities can be employed as a co-monomer, thus leading to biomass-derived functional polymers. Furthermore, polymeric materials can be readily applied for device fabrications by using simple and low-cost methods, such as spin-coating. The recent trend to substitute petrochemicals with biomass-based products will enhance the future development of PDC-containing functional materials and devices.

Experimental

General Apparatus. Thermogravimetric analysis (TGA) was carried out on a Rigaku Thermo plus TG8120 under nitrogen flow, at a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$ from 20 to 450 °C. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL AL400 MHz spectrometer at 20 °C. Chemical shifts are reported in ppm downfield from $SiMe_4$, using the solvent's residual signal as an internal reference. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. UV/Vis spectra were recorded on a JASCO V-550 spectrophotometer. Fluorescence spectra were measured on a JASCO FP6500 spectrophotometer. The spectra were measured for the dehydrated PDC in a quartz cuvette of 1 cm. The quantum yield was determined against 2-aminopyridine in 0.1 M H_2SO_4 ($\Phi_F = 0.60$).[21] MALDI-TOF-MS spectrum was measured on an Applied Biosystems model Voyager-DE STR instrument with 2-(4-hydroxyphenylazo)benzoic acid as a matrix. The hydrogen ion activities were determined with a Mettler Toledo Portable Ion Analyzer MA130. Sodium nitrate (0.1 M) was added as the supporting electrolyte. The initial PDC concentration was 5 mM. Chemicals were purchased from Kanto, Wako, and Tokyo Kasei, and used as received.

Preparation. 2-Pyrone-4,6-dicarboxylic acid (PDC) was prepared from protocatechuate via the metabolic pathway of *Sphingomonas paucimobilis* SYK-6.[4] After the removal of bacteria by centrifugation, the crude PDC was first precipitated as a brown solid by addition of NaCl. This salt (24 g) was dissolved in hot water (1500 mL), and acetone (1500 mL) and concn. HCl aqueous solution (45 mL) were added. Activated carbon (20 g) was added to this solution, and the mixture stirred for 15 min. After filtration, the filtrate was evaporated to ≈1500 mL, which was again acidified with concn. HCl aqueous solution (18 mL). The solution was extracted with ethyl acetate (500 mL × 5), and the organic phase was dried over $MgSO_4$. After filtration, the solvent was evaporated to afford PDC as a white solid (11 g). ^{1}H NMR (400 MHz, DMSO-d_6, 20 °C): δ 6.93 (d, $J = 3$ Hz, 1H), 7.24 (d, $J = 3$ Hz, 1H), 13.13 (brs, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 20 °C): δ 108.77, 121.93, 145.10, 150.62, 160.78, 160.88, 164.59 ppm; IR (KBr): ν 3102, 1757, 1743, 1726, 1669, 1603, 1559, 1456, 1425, 1239, 1211, 1186, 1135, 1086, 912, 891, 818, 782, 765, 719, 685, 669, 645, 571, 460 cm^{-1}; MALDI-TOF-MS (negative mode, matrix: 2-(4-hydroxyphenylazo)benzoic acid): m/z: calcd for $C_7H_4O_6{}^-$: 184.00; found: 184.44 $[M]^-$; elemental analysis calcd (%) for $C_7H_4O_6$ (184.10): C, 45.67; H, 2.19%. Found: C, 45.48; H, 2.06%.

X-ray Structure Analysis. Single crystals of PDC•2H$_2$O and PDC•Na$^+$ complex were prepared for X-ray crystallographic analysis. PDC (2.03 g, 11.0 mmol) was dissolved in water (5.5 mL) at 50 °C. After cooling to 20 °C, aq HCl was added to this solution to make the pH value of 1.5, and then the crystals were grown in a refrigerator at 5 °C. A platelet colorless crystal of PDC•2H$_2$O (linear dimensions ca. $0.16 \times 0.10 \times 0.08\,\mathrm{mm^3}$) was obtained and subjected to X-ray crystallographic analysis. For single crystals of PDC•Na$^+$ complex, aq NaCl (1.07 g, 18.3 mmol) solution (3.0 mL) was added to the aq PDC (2.03 g, 11.0 mmol) solution (5.5 mL), giving a white precipitate. Addition of water (90 mL) and stirring at 70 °C were continued until the white solid was completely dissolved. After cooling to 20 °C, the crystals were grown in a refrigerator at 5 °C. A colorless crystal of PDC•Na$^+$ complex (linear dimensions ca. $0.12 \times 0.10 \times 0.08\,\mathrm{mm^3}$) was obtained and subjected to X-ray crystallographic analysis.

X-ray Crystal Structure of PDC•2H$_2$O: Crystal data at 93.1 K for $(C_7H_4O_6)\cdot 2(H_2O)$ [$M_r = 220.14$] monoclinic, space group $C2/c$, $D_{calcd} = 1.589\,\mathrm{g\,cm^{-3}}$, $Z = 8$, $a = 1.50912(6)$, $b = 0.512354(17)$, $c = 2.38057(9)$ nm, $\beta = 91.481(3)^\circ$, $V = 1.84005(12)\,\mathrm{nm^3}$. Rigaku RAXIS-RAPID, Cu Kα radiation ($\lambda = 0.154187$ nm), $\mu = 1.3386\,\mathrm{mm^{-1}}$. Numbers of measured and unique reflections are 9720 and 1678, respectively ($R_{int} = 0.031$). Final $R(F) = 0.0309$, $wR(F^2) = 0.0869$ for 151 parameters and 1402 reflections with $I > 2\sigma(I)$ and $3.7^\circ < \theta < 68.2^\circ$.

X-ray Crystal Structure of PDC•Na$^+$ Complex: Crystal data at 103.1 K for $(C_7H_{3.5}O_6)\cdot 2(H_2O)\cdot Na_{0.5}$ [$M_r = 231.13$] monoclinic, space group $P2_1/c$, $D_{calcd} = 1.749\,\mathrm{g\,cm^{-3}}$, $Z = 4$, $a = 0.35841(12)$, $b = 1.0175(5)$, $c = 2.4081(9)$ nm, $\beta = 91.329(14)^\circ$, $V = 0.8779(6)\,\mathrm{nm^3}$. Rigaku RAXIS-RAPID, Mo Kα radiation ($\lambda = 0.071075$ nm), $\mu = 0.1832\,\mathrm{mm^{-1}}$. Numbers of measured and unique reflections are 8679 and 2000, respectively ($R_{int} = 0.019$). Final $R(F) = 0.0280$, $wR(F^2) = 0.0770$ for 150 parameters and 1640 reflections with $I > 2\sigma(I)$ and $3.2^\circ < \theta < 27.4^\circ$.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-654109 and CCDC-654110 for PDC•2H$_2$O and PDC•Na$^+$ complex, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

Thermogravimetric analysis and potentiometric titration of PDC and the crystal packing of PDC•Na$^+$ complex. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

References

1 a) B. Kamm, R. R. Gruber, M. Kamm, *Biorefineries: Industrial Processes and Products*, Wiley-VCH, Weinheim, **2006**. b) A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, Jr., J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484. c) Y. Nishio, *Adv. Polym. Sci.* **2006**, *205*, 97. d) Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982. e) B. Kamm, *Angew. Chem., Int. Ed.* **2007**, *46*, 5056.

2 a) R. Vicuna, B. Gonzalez, D. Seelenfreund, C. Ruttimann, L. Salas, *J. Biotechnol.* **1993**, *30*, 9. b) A. Brune, E. Miambi, J. A. Breznak, *Appl. Environ. Microbiol.* **1995**, *61*, 2688. c) M. S. Barber, V. S. McConnell, B. S. DeCaux, *Phytochemistry* **2000**, *54*, 53. d) L. Hoffmann, S. Maury, F. Martz, P. Geoffroy, M. Legrand, *J. Biol. Chem.* **2003**, *278*, 95.

3 a) E. Masai, S. Shinohara, H. Hara, S. Nishikawa, Y. Katayama, M. Fukuda, *J. Bacteriol.* **1999**, *181*, 55. b) E. Masai, K. Momose, H. Hara, S. Nishikawa, Y. Katayama, M. Fukuda,

J. Bacteriol. **2000**, *182*, 6651. c) H. Hara, E. Masai, Y. Katayama, M. Fukuda, *J. Bacteriol.* **2000**, *182*, 6950. d) H. Hara, E. Masai, K. Miyauchi, Y. Katayama, M. Fukuda, *J. Bacteriol.* **2003**, *185*, 41. e) D. Kasai, E. Masai, K. Miyauchi, Y. Katayama, M. Fukuda, *J. Bacteriol.* **2004**, *186*, 4951. f) M. Sasoh, E. Masai, S. Ishibashi, H. Hara, N. Kamimura, K. Miyauchi, M. Fukuda, *Appl. Environ. Microbiol.* **2006**, *72*, 1825. g) E. Masai, Y. Katayama, M. Fukuda, *Biosci. Biotechnol. Biochem.* **2007**, *71*, 1.

4 Y. Otsuka, M. Nakamura, K. Shigehara, K. Sugimura, E. Masai, S. Ohara, Y. Katayama, *Appl. Microbiol. Biotechnol.* **2006**, *71*, 608.

5 a) K. Hirano, S. Minakata, M. Komatsu, *Chem. Lett.* **2001**, 8. b) K. Hirano, S. Minakata, M. Komatsu, J. Mizoguchi, *J. Phys. Chem. A* **2002**, *106*, 4868.

6 J. C. Collings, A. C. Parsons, L. Porrès, A. Beeby, A. S. Batsanov, J. A. K. Howard, D. P. Lydon, P. J. Low, I. J. S. Fairlamb, T. B. Marder, *Chem. Commun.* **2005**, 2666.

7 P. J. Kersten, S. Dagley, J. W. Whittaker, D. M. Arcicro, J. D. Lipscomb, *J. Bacteriol.* **1982**, *152*, 1154.

8 a) R. W. Eaton, D. W. Ribbons, *J. Bacteriol.* **1982**, *151*, 48. b) R. W. Eaton, D. W. Ribbons, *J. Bacteriol.* **1982**, *151*, 465. c) P. J. Kersten, S. Dagley, J. W. Whittaker, D. M. Arciero, J. D. Lipscomb, *J. Bacteriol.* **1982**, *152*, 1154. d) K. Maruyama, *J. Biochem.* **1983**, *93*, 557. e) P. Martin, E. Steiner, J. Streith, T. Winkler, D. Bulluš, *Tetrahedron* **1985**, *41*, 4057. f) S. Wilkes, H. Glasl, *Phytochemistry* **2001**, *58*, 441. g) R. W. Eaton, *J. Bacteriol.* **2001**, *183*, 3689. h) E. Shimoni, T. Baasov, U. Ravid, Y. Shoham, *J. Biotechnol.* **2003**, *105*, 61. i) K. Maruyama, T. Shibayama, A. Ichikawa, Y. Sakou, S. Yamada, H. Sugisaki, *Biosci. Biotechnol. Biochem.* **2004**, *68*, 1434.

9 K. Maruyama, *J. Biochem.* **1979**, *86*, 1671.

10 I. J. S. Fairlamb, A. F. Lee, F. E. M. Loe-Mie, E. H. Niemelä, C. T. O'Brien, A. C. Whitwood, *Tetrahedron* **2005**, *61*, 9827.

11 For recent examples of ultra-thin film preparation of functional organic molecules by vapor-deposition techniques, see: a) H. Wu, Y. Song, S. Du, H. Liu, H. Gao, L. Jiang, D. Zhu, *Adv. Mater.* **2003**, *15*, 1925. b) G. Jiang, T. Michinobu, W. Yuan, M. Feng, Y. Wen, S. Du, H. Gao, L. Jiang, Y. Song, F. Diederich, D. Zhu, *Adv. Mater.* **2005**, *17*, 2170. c) T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2005**, 737. d) N. N. P. Moonen, W. C. Pomerantz, R. Gist, C. Boudon, J.-P. Gisselbrecht, T. Kawai, A. Kishioka, M. Gross, M. Irie, F. Diederich, *Chem. Eur. J.* **2005**, *11*, 3325. e) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889.

12 a) V. Gutmann, *Coord. Chem. Rev.* **1976**, *18*, 225. b) J. P. Hill, A. L. Schumacher, F. D'Souza, J. Labuta, C. Redshaw, M. R. J. Elsegood, M. Aoyagi, T. Nakanishi, K. Ariga, *Inorg. Chem.* **2006**, *45*, 8288.

13 a) E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boos, H. Prigge, I. Seibold-Blankenstein, *Angew. Chem.* **1961**, *73*, 695. b) J. Herbich, B. Brutschy, in *Electron Transfer in Chemistry*, ed. by V. Balzani, Wiley-VCH, Weinheim, **2001**, Vol. 4, pp. 697–741.

14 F. H. Allen, C. A. Baalham, J. P. M. Lommerse, P. R. Raithby, *Acta Crystallogr., Sect. B* **1998**, *54*, 320.

15 a) J. C. Speakman, *Nature* **1948**, *162*, 695. b) J. C. Speakman, *J. Chem. Soc.* **1949**, 3357. c) S. Grimvall, R. F. Wengelin, *J. Chem. Soc. A* **1967**, 968. d) L. Manojlović, J. C. Speakman, *J. Chem. Soc. A* **1967**, 971. e) L. Manojlović, *Acta Crystallogr., Sect. B* **1968**, *24*, 326. f) A. Sequeira, C. A. Berkebile, W. C. Hamilton, *J. Mol. Struct.* **1968**, *1*, 283. g) J. Kroon, J. A. Kanters, *Acta Crystallogr., Sect. B* **1972**, *28*, 714. h) L. Golič, P. Lazarini, *Cryst. Struct. Commun.* **1974**, *3*, 411. i) E. A. Green, W. L. Duax, G. M. Smith, F. Wudl, *J. Am. Chem. Soc.* **1975**, *97*, 6689. j) P. B. Moore, J. J. Pluth, J. A. Molin-Norris, D. A. Weinstein, E. L. Compere, Jr., *Acta Crystallogr., Sect. B* **1980**, *36*, 47. k) D. L. Kepert, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1980**, *33*, 1847. l) P. S. Jaulmes, G. Cassanas, P. Laruelle, *Acta Crystallogr., Sect. B* **1982**, *38*, 279. m) J. Longo, M. F. Richardson, *Acta Crystallogr., Sect. B* **1982**, *38*, 2482. n) J. Kroon, J. A. Kanters, *Croat. Chem. Acta* **1982**, *55*, 99. o) Z.-H. Zhou, S.-Y. Hou, H.-L. Wan, *Dalton Trans.* **2004**, 1393. p) J.-L. Ma, L. Yang, B. Chen, Y. Zou, F.-J. Meng, H.-L. Zhu, *Z. Kristallogr.* **2004**, *219*, 161. q) Z.-B. Zhu, S. Gao, L.-H. Hua, S. W. Ng, *Acta Crystallogr., Sect. E* **2005**, *61*, m192. r) G. S. Nichol, W. Clegg, *Polyhedron* **2006**, *25*, 1043.

16 a) A. McAdam, M. Currie, J. C. Speakman, *J. Chem. Soc. A* **1971**, 1994. b) M. J. Barrow, M. Currie, K. W. Muir, J. C. Speakman, D. N. J. White, *J. Chem. Soc., Perkin Trans. 2* **1975**, 15. c) M. Currie, J. C. Speakman, J. A. Kanters, J. Kroon, *J. Chem. Soc., Perkin Trans. 2* **1975**, 1549. d) G. E. Bacon, C. R. Walker, J. C. Speakman, *J. Chem. Soc., Perkin Trans. 2* **1977**, 979.

17 N. Albert, R. M. Badger, *J. Chem. Phys.* **1958**, *29*, 1193.

18 For some examples of one-dimensional infinite crystal structures of functional organic molecules via hydrogen bonding, see: a) H. Nagashima, H. Inoue, N. Yoshioka, *J. Phys. Chem. B* **2004**, *108*, 6144. b) K. Uemura, K. Saito, S. Kitagawa, H. Kita, *J. Am. Chem. Soc.* **2006**, *128*, 16122. c) H. Maeda, M. Hasegawa, A. Ueda, *Chem. Commun.* **2007**, 2726.

19 a) A. L. Macdonald, J. C. Speakman, D. Hadži, *J. Chem. Soc., Perkin Trans. 2* **1972**, 825. b) I. Leban, A. Kolbe, A. Kolbe, D. Hadži, *J. Chem. Crystallogr.* **1982**, *12*, 343.

20 For very recently reported, similar short hydrogen bonding by two amide oxygens of an artificial macrocyclic compound, which is postulated to exist within protein interiors, see: V. W. Day, Md. A. Hossain, S. O. Kang, D. Powell, G. Lushington, K. Bowman-James, *J. Am. Chem. Soc.* **2007**, *129*, 8692.

21 R. Rusakowicz, A. C. Testa, *J. Phys. Chem.* **1968**, *72*, 2680.