

(Poly)terephthalates with Efficient Blue Emission in the Solid State

Masaki Shimizu,*^[a] Ryosuke Shigitani,^[a] Takumi Kinoshita,^[a] and Hiroshi Sakaguchi^[b]

Abstract: We prepared dimethyl and diaryl 2,5-dialkoxyterephthalates from dimethyl 2,5-dihydroxyterephthalate in good-to-high yields via alkylation or a sequence of alkylation, hydrolysis, chlorination, and condensation. The absorption spectra of the dialkoxyterephthalates contain a small band at 332–355 nm, which could be assigned to intramolecular charge-transfer transition from the alkoxy to alkoxycarbonyl groups on the basis of theoretical calculations using density functional theory. The dialkoxyterephthalates exhibited blue fluorescence with moderate-to-excellent quantum yields not only in solution but also in the solid state, such as a poly(methyl methacrylate) (PMMA) film and

Introduction

The creation of organic small molecules that efficiently fluoresce in the solid state is an important research subject in the field of functional molecular materials.^[1] This is because the creation of such novel fluorophores would lead to advances in organic solid-state light-emitting devices, such as organic lightemitting diodes (OLEDs),^[2] organic light-emitting field effect transistors,^[3] and semiconducting lasers.^[4] In the fields of not only OLEDs but also bio- and molecular sensing, conjugated polymers that exhibit efficient fluorescence in film have also attracted much attention.^[5] Therefore, the design of fluorescent small molecules that can be developed into luminescent polymer films is considered of significant value.

Blue fluorescent materials with high efficiency in the solid state are particularly desired in the field of OLEDs.⁽⁶⁾ Because the internal quantum efficiency of phosphorescent OLEDs is 100%, extensive research has been carried out on the development of phosphorescent organometallic complexes containing precious metals, such as iridium and platinum.⁽⁷⁾ However, the lifetimes of OLEDs using such blue-emissive complexes are not

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[a]	Prof. M. Shimizu, R. Shigitani, T. Kinoshita
	Faculty of Molecular Chemistry and Engineering
	1 Hashikami-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585 (Japan) E-mail: mshimizu@kit.ac.jp
[b]	Prof. H. Sakaguchi Institute of Advanced Energy
	Kyoto University Cokasha Ulii Kyoto 611 0011 (Janan)
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a powder. The solid-state quantum yields of the diisopropoxy-substituted terephthalates were similar or considerably higher than those of the dimethoxy-substituted counterparts. Copolymerization of 2,5-diisopropoxyterephthaloyl chloride and 1,4-butanediol with or without terephthaloyl chloride gave brilliantly blue fluorescent polymers, whose quantum yields were 0.72 and 0.71 in toluene and 0.46 and 0.40 in the neat film, respectively. Furthermore, white emission was achieved when a fluorescent yellow 2,5-diaminoterephthalate was doped into the thin film of the blue fluorescent polymer at 0.4 wt%.

sufficient for commercial use. In addition, precious metal complexes generally experience concentration quenching, which limits their use as blue dopants. Considering that blue-emissive materials can serve as not only blue emitters but also host materials for dopants that emit in the longer wavelength region than blue light, the development of blue fluorescent materials that overcome aggregation-caused quenching (ACQ) is crucial.^[8]

We have previously demonstrated that 2,5-diaminoterephthalic acid diesters **1a** and dithioesters **1b** exhibit efficient green-to-yellow and orange-to-red fluorescence in the solid state, respectively (Scheme 1).^[9] The key to the efficient solidstate emissions is the *ortho*-arrangement of the donors (amino groups) and acceptors (carbonyl moieties), as well as the intramolecular charge-transfer (ICT) from the donors to the accept-



Scheme 1. Molecular structures of fluorescent (poly)terephthalates 1-3.

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ors. The ortho-arrangement-induced twisted molecular conformation results in the suppression of dense packing in the solid state, thereby inhibiting intermolecular electronic communication via the Dexter mechanism. The ICT results in a large Stokes shift, which reduces the loss of the excited energy via the Förster mechanism. In cases of organic luminophores whose excitation processes involve ICTs, the emission maximum can be hypochromically or bathochromically shifted by weakening or strengthening the degree of ICT character by the appropriate combination of donor and acceptor.^[10] Thus, we designed 2,5-dialkoxyterephthalates 2 in which the amino groups in 1a are replaced by less electron-donating alkoxy groups for use as ACQ-free blue emitters.^[11] We further expected that the development of blue fluorescent terephthalates would lead to the development of blue luminescent polyterephthalates. Indeed, we confirmed the validity of the molecular design. Here, we report the preparation, photophysical properties, structures, and theoretical study of blue-emissive 2 and 2-based blue fluorescent polyesters 3, which may serve as coating emitting layers for OLEDs.

Results and Discussion

Synthesis of 2,5-dialkoxyterephthalates 2

Dialkoxyterephthalates **2** were prepared from dimethyl 2,5-dihydroxyterephthalate (Scheme 2).^[12] Alkylation of the dihydroxyterephthalate with methyl iodide or isopropyl iodide gave dimethyl esters **2aa** and **2ba** in 92% and 95% yields, respectively. Diaryl terephthalates **2ab-2ae** and **2bb-2be** were synthesized from **2aa** and **2ba**, respectively, in good-to-excellent yields through hydrolysis with LiOH, chlorination with SOCl₂, and esterification with phenol derivatives. We chose the substituents R² listed in Scheme 2 in view of the salient differences of electronic and steric effects, and the readily availability of



²ab–2ae, 2bb–2be

2	R ¹	R ²	Yield (%)	2	R ¹	R ²	Yield (%)
2aa	Ме	Me	92	2ba	<i>i</i> Pr	Me	95
2ab	Me	C ₆ H₅	96	2bb	<i>i</i> Pr	C ₆ H₅	97
2ac	Me	4–CF ₃ C ₆ H ₄	68	2bc	<i>i</i> Pr	4–CF ₃ C ₆ H ₄	77
2ad	Me	2,5–Me ₂ C ₆ H ₃	89	2bd	<i>i</i> Pr	2,5–Me ₂ C ₆ H ₃	66
2ae	Me	3,5–(CF ₃) ₂ C ₆ H ₃	96	2be	<i>i</i> Pr	$3,5-(CF_3)_2C_6H_3$	71

Scheme 2. Synthesis of 2,5-dialkoxyterephthalates 2.

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the corresponding phenol derivatives. Although the decomposition temperatures (T_d), which is defined as the temperature at which 5% mass is lost, of **2aa** and **2ba** were less than 170°C, diaryl esters **2ab-2ae** and **2bb-2be** were thermally stable, and their T_d values ranged from 225 to 273°C (as shown in the Experimental Section).

Photophysical properties

UV absorption data of **2** in toluene are listed in Table 1, and selected spectra are shown in Figure 1 (for spectra of **2 ba–2 be**, refer Figure S1). The absorption maxima (λ_{abs}) appeared at 332–355 nm with small molar absorption coefficients (ε), ranging from 4000 to 7100 M^{-1} cm⁻¹, which can be assigned to ICTs

Table 1. Absorption maxima and molar absorption coefficients of 2 in toluene. $^{\left[a\right] }$					
2	λ_{abs} [nm]	$\varepsilon \ [\mathrm{M}^{-1}\mathrm{cm}^{-1}]$	2	λ_{abs} [nm]	$\varepsilon \ [m^{-1} cm^{-1}]$
2 aa	337	4600	2 ba	332	4000
2 ab	345	5500	2 bb	342	4700
2 ac	345	6200	2 bc	347	4800
2 ad	343	7100	2 bd	341	4800
2ae	355	5600	2 be	353	4900
[a] 1.0×10 ⁻⁴ м.					



Figure 1. Absorption spectra of 2 in toluene.

from the alkoxy to alkoxycarbonyl groups (refer Theoretical calculations). The differences in the absorption maxima between each methoxy-substituted derivative **2a** and the corresponding isopropoxy-substituted derivative **2b** are less than 6 nm (for example, compare **2aa** and **2ba**). Meanwhile, with respect to **2aa** or **2ba**, the absorption maxima of **2ab-2ae** or **2bb-2be** were red-shifted by 6–18 or 9–21 nm, respectively. In other words, the highest occupied molecular orbital (HOMO)lowest unoccupied molecular orbital (LUMO) energy gaps of the diaryl esters are narrower than those of the dialkyl esters. These results indicate that the effect of the alkyl or alkoxy substituent at the central benzene ring on the energy gap of the HOMO and LUMO is small, and the ICT characters of the diaryl esters **2ab-2ae** and **2bb-2be** are stronger than those of the dimethyl esters **2aa** and **2ba**. Because the absorption maxima

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of **1** appeared at much longer wavelengths (for example, λ_{abs} = 415 nm for dimethyl 2,5-bis(diphenylamino)terephthalate),^[9a] the ICT character of **2** is, as expected, weaker than that of **1**.

All molecules of type **2** in toluene exhibited blue fluorescence with emission maxima in the range of 402–434 nm in moderate-to-excellent quantum yields ($\Phi = 0.31-0.95$), except for **2ad** ($\Phi = 0.08$) (Table 2). The fluorescence spectra of **2aa-2ae** and **2ba** are shown in Figure 2 (for spectra of **2ba-2be**,

Table 2. Fluorescence data of 2. ^[a]				
2	$\lambda_{_{ m em}}$ [nm] (${m \Phi})^{^{[m b]}}$ In toluene $^{^{[m c]}}$	In PMMA film	In powder ^[d]	
2 aa	402 (0.57)	402 (0.33)	413 (0.36)	
2 ab	418 (0.54)	418 (0.30)	437 (0.22)	
2 ac	422 (0.76)	418 (0.38)	426 (0.65)	
2 ad	415 (0.08)	410 (0.19)	420 (0.18)	
2 ae	428 (0.95)	422 (0.57)	426 (0.81)	
2 ba	410 (0.69)	409 (0.57)	413 (0.63)	
2 bb	425 (0.70)	422 (0.56)	420 (0.58)	
2 bc	429 (0.87)	428 (0.64)	425 (0.64)	
2 bd	423 (0.31)	422 (0.42)	416 (0.51)	
2 be	434 (0.88)	431 (0.59)	431 (0.75)	

[a] Excited at 320 nm. [b] Φ : Absolute quantum yield determined using the calibrated integrating sphere system. [c] 1.0×10^{-4} M. [d] Semicrystalline powder.



Figure 2. Fluorescence spectra of 2aa-2ae, 2ba, and 2be in toluene.

refer Figure S2). The relatively large Stokes shifts (65-83 nm)^[13] of 2 in toluene imply that the structural difference between the ground and lowest singlet excited states is significant because of the ICT, and the spectral overlap between absorption and fluorescence is small, which is beneficial for diminishing the probability of Förster-type energy transfer from the lowest singlet excited state. As observed in the absorption maxima, the emission maxima of the diaryl esters were red-shifted compared to those of dimethyl esters. In the series of diaryl esters, substitution of electron-withdrawing or -donating groups, that is, CF₃ or CH₃, into the phenyl rings as R² resulted in bathochromic or hypochromic shift of the spectra, respectively, compared with that of unsubstituted 2ab or 2bb. Changing methyl groups as R¹ to isopropyl groups induced red-shift (for example, compare 2aa and 2ba). Similar fluorescence spectra (Figures S3 and S4) were observed when 2 was dispersed in a



thin film of poly(methyl methacrylate) (PMMA), having quan-

tum yields of 0.19-0.64 (Table 2). The powder of 2 also exhibit-

ed blue fluorescence with moderate-to-excellent quantum yields (Table 2 and Figure 3, and for spectra of **2 ba-2 be**, refer

Figure 3. Fluorescence spectra of 2aa-2ae, 2ba, and 2be in powders.

Figure S5).^[14] Because the quantum yields of diisopropoxy derivatives 2ba-2be were similar or much higher than those of dimethoxy derivatives 2aa-2ae, the choice of a bulkier alkyl group as substituent R¹ in 2 is beneficial for attaining the solid-state fluorescence of 2 with high efficiency. The differences in the emission peak wavelengths between the samples in toluene and those in powder form were generally small, suggesting that the intermolecular electronic communications between each molecule of 2 in the solid state were weak, which is another reason for the efficient solid-state blue emission. Full-widths at half maxima (fwhm) of fluorescence spectra of 2 in powder were smaller than those in toluene, which was rare phenomenon. Considering the weak intermolecular electronic interactions of 2 in powder, the narrower emission bands of the powders are presumably ascribed to the smaller conformational variations in powder than those in solution. The guantum yields of the 2,5-dimethylphenyl esters 2ad and 2bd were the lowest compared with those of the others in any state. The electron-rich nature of 2,5-dimethylphenyl group, the steric effect of a methyl group at 2-position of the benzene ring, which force to make the benzene ring orthogonal to the carbonyl plane (as confirmed by X-ray crystallography of 2bd), or both may destabilize the excited states of 2 ad and 2 bd.

X-ray crystallography

Single crystals of **2ac** and **2bd** suitable for X-ray diffraction analysis were obtained by recrystallization from a solution of CH_2Cl_2 /hexane.^[15] The molecular and crystal structures of **2ac** and **2bd** are shown in Figures 4 and 5, respectively. Each molecule of **2ac** and **2bd** is centrosymmetric with an inversion center at the centroid of the central benzene ring. As shown in Figure 4a, the methyl carbons of **2ac** are located in the same plane as the central benzene ring (C1-O1-C2-C3=4.16°). The dihedral angle between the carbonyl group of **2ac** and the central benzene ring (C2-C4-C5-O2) is 11.39°. Thus, the carbon-

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Figure 4. Molecular (a) and crystal (b) structures of 2 ac (hydrogen atoms are omitted for clarity). Each molecule in (b) is color-coded based on symmetry operations.

yl groups are not significantly twisted with respect to the central benzene ring, irrespective of the *ortho*-arrangement of carbonyl and methoxy groups. In turn, the CF₃-substituted phenyl groups are oriented almost perpendicular to the carbonyl planes (C5-O3-C6-C7 = 87.31°). Probably because of the twisted molecular structure, there is no π - π stacking between the fluorescent cores in the crystal of **2ac** (Figure 4b), which is advantageous for preventing the loss of the excited energy via the Dexter mechanism and for the highly efficient solid-state fluorescence of **2ac** (Φ = 0.65).

In the case of **2bd**, the dihedral angles between the central benzene ring, and the methine carbon of the isopropyl group and a carbonyl group are 27.79° (C1-O1-C2-C3) and 42.34° (C5-C4-C6-O2), respectively (Figure 5a). Thus, the two isopropyl and two carbonyl groups are significantly distorted from the plane of the central benzene ring as expected. The 2,5-dimethylphenyl groups are almost orthogonal to the carbonyl plane (C6-O3-C7-C8=86.12°). As shown in Figure 5 b, **2 bd**, which has a fully twisted molecular framework, forms a loosely packed crystal with no π - π stacking, resulting in the efficient solid-state emission of **2 bd** (Φ =0.51).

Theoretical calculations

To confirm the ICT in the excitation process of **2**, frontier orbital calculations of **2ac** and **2bd** were carried out using the density functional theory (DFT) at the B3LYP/cc-pVDZ level of theory using the Gaussian 09 package.^[16] The structural optimizations were performed with the initial geometries determined by X-ray diffraction analysis. The HOMOs, LUMOs, and their en-



Figure 5. Molecular (a) and crystal (b) structures of 2 bd (hydrogen atoms are omitted for clarity). Each molecule in (b) is color-coded based on symmetry operations.



Figure 6. Frontier molecular orbitals and their energies of 2 ac and 2 bd.

ergies are illustrated in Figure 6. The HOMOs are delocalized over the central benzene ring and the ethereal oxygen atoms, while the LUMOs are concentrated on the central benzene ring and carbonyl groups. Time-dependent DFT (TD-DFT) calculations of **2ac** and **2bd** showed that the lowest energy transitions correspond to the HOMO-LUMO transitions with coefficients of 0.699 and 0.697, and oscillator strengths of 0.1323 and 0.1529, respectively. Hence, the weak absorption peaks of **2** at 332–355 nm can be assigned to the ICT from the alkoxy to alkoxycarbonyl groups.

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Blue-fluorescent polymers

Polyesters made from terephthalic acid and aliphatic diols such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) constitute a class of versatile engineering plastics.^[17] Because we have succeeded the development of terephthalates showing efficient solid-state blue fluorescence, we envisioned that polyesters consisting of dialkyl 2,5-dialkoxyterephthalate framework could be efficient blue fluorescent polymers in the neat films.^[18] Because we observed that the guantum yields of 2ba were higher than those of 2aa (Table 2), we chose an isopropoxy group as the alkoxy group. Then, 2,5-diisopropoxyterephthaloyl chloride (4) was polymerized with 1,4butanediol in the absence or presence of terephthaloyl chloride (5) in CH_2Cl_2 using pyridine as a base to produce **3a** or **3b** in 59% or 56% yield, respectively (Scheme 3). The glass transition temperatures of polymer **3a** and **3b** were 71 and 15°C, respectively. Hence, the incorporation of 5 as the second monomer into 3a resulted in the lowering of the glass transition temperature.



Scheme 3. Synthesis of poly(2,5-dialkoxyterephthalate)s 3.

The photophysical properties of **3a** and **3b** are summarized in Table 3. Their absorption spectra are completely overlapped at 300–400 nm and almost identical with that of **2ba** (Figure S6). Toluene solutions of **3a** and **3b** exhibited efficient blue fluorescence at the emission maxima of 413 and 414 nm with quantum yields of 0.71 and 0.72, respectively (Figure 7). Neat thin films of **3a** and **3b** were prepared by spin-coating

Table 3. Photophysical properties of 3.					
3	Absorption λ _{max} [nm] In toluene	Fluorescence ^(a) $\lambda_{ m em}$ [nm] $(arPhi)^{ m (b)}$ In toluene	In neat film ^[c]		
3a 3b	334 335	413 (0.71) 414 (0.72)	418 (0.40) 420 (0.46)		
[a] Excitation was effected at 320 nm. [b] Φ : Absolute quantum yield determined using the calibrated integrating sphere system. [c] Prepared by spin-coating.					

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Figure 7. Fluorescence spectra of **3a** and **3b** in toluene and neat film, and their fluorescent images upon irradiation using a UV lamp (365 nm).

and fluoresced with slightly red-shifted spectra with respect to those in toluene.^[19] Although the fluorescence quantum yields in neat films of **3a** and **3b** were slightly lower than that of **2ba** in PMMA, it is valuable that polymers **3a** and **3b** in film was demonstrated to exhibit blue fluorescence with good quantum yields in view that a new molecular design principle for blue-luminescent polymers is provided. Very recently, Zhang, Yuan, and co-workers reported that poly(ethylene terephthalate) exhibit aggregation-induced emission in solids.^[20] The emission mechanism involves the formation of terephthalate clusters leading to excimer emission, which is completely different from the mechanism of **2**.^[21]

Furthermore, to demonstrate the potential of **3b** as a host blue-emitting polymer for white emissions,^[22] we prepared spin-coated films of 3b doped with the yellow fluorescent dimethyl 2,5-bis[bis(4-tert-butylphenyl)amino]terephthalate (6).^[9a] The reason that we chose 6 as the dopant was that the CIE coordinates of **6** in the PMMA film are (x = 0.43, y = 0.55); thus, they are approximately located on the line penetrating the CIE coordinates of blue-emissive film **3b** (x=0.16, y=0.05) and ideal white emission (x = 0.33, y = 0.33) (Figure S7). The molecular weight ratios of 3b and 6 were varied from 500:1 to 250:1, and the photoluminescent properties of the 6-doped films of **3b** are summarized in Table S2, and the spectra are shown in Figure S8. The film consisting of **3b** and **6** in a ratio of 250:1 exhibited almost ideal white emission (CIE coordinate: x=0.32, y=0.34) with a quantum yield of 0.43. The spectrum and luminescence image of the white-emissive film are shown in Figure 8 along with the spectra of 3b in film and 6 in PMMA film.

Conclusions

We developed 2,5-dialkoxyterephthalates, which are readily prepared from commercially available chemicals via facile

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Figure 8. Fluorescence spectra of **3 b** in film, **6** in PMMA film, and **6**-doped **3 b** in film, and the fluorescent image of the doped film of **3 b**.

chemical transformations, as blue luminophores that efficiently fluoresce in the solid state, such as polymer films and powders. In addition, we confirmed that poly(2,5-diisopropoxyterephthalate)s consisting of the developed blue-emissive luminogen exhibited efficient blue fluorescence as a neat film, and the blueemissive film effectively serves as a host polymer for white emission that is useful for lighting applications. Considering that polyterephthalates are valuable thermoplastic elastomers with superior properties, such as high solvent-resistance, high mechanical strength, and high insulating performance, the present findings could contribute to the creation of polymeric materials that unite luminescence with the merits of polyterephthalates. Furthermore, considering that 2,5-diaminoterephthalic acid di(thio)esters serve as efficient solid-state emitters, the present results clearly implied that 2,5-bis(donor)-substituted terephthalate frameworks are promising platforms for the development of highly luminescent organic solids, which may serve as coating emitting layers for OLEDs.

Experimental Section

General

Melting and decomposition points were determined with a Seiko Instrument Inc. TG/DTA6200. ¹H NMR spectra were measured with a Varian Mercury 400 (400 MHz) spectrometer. The chemical shifts of 'H NMR signals are expressed in parts per million downfield relative to the internal tetramethylsilane standard ($\delta = 0$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; sept, septet; or m, multiplet. ¹³C NMR spectra were measured with a Varian Mercury 400 (100 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). ¹⁹F NMR spectra were measured with a Bruker Avance II 300 (282 MHz) spectrometer with hexafluorobenzene as an internal standard ($\delta = -163.7$ ppm). Chemical shift values are given in parts per million downfield relative to the internal standards. Infrared spectra (IR) of 2 were recorded on a Shimadzu FTIR-8400 spectrometer. IR attenuated total reflectance (IRATR) spectra of 3 were recorded by using a Shimadzu FTIR-8400 spectrometer equipped with a Specac Quest ATR diamond accessory. Fast atom bombardment, high-resolution mass spectrometry (FAB-HRMS) analyses were performed with a JEOL JMS-700 spectrometer. TLC analyses were performed using Merck Kieselgel 60 F254 silica plates. Silica gel column chromatography was carried out using Merck's Kieselgel 60 (230–400 mesh). Reagent-grade CH_2CI_2 and THF were passed through two packed columns of neutral alumina and copper oxide under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere.

Measurement of absorption and photoluminescence spectra

The spectroscopic-grade toluene for photoluminescence measurements was purchased from Kanto Chemical Co., Inc. and degassed with argon before use. UV-visible absorption spectra were measured with a Shimadzu UV-2550 spectrometer. Luminescence spectra and absolute quantum yields were recorded with a Hamamatsu Photonics C9920-02 Absolute PL Quantum Yield Measurement System.

Preparation of 2-doped PMMA film

In a glass tube, **2** (1.0 mg) was placed and dissolved in a toluene solution of PMMA (99 mg in 1 mL). The resulting solution was dropped onto a quartz plate (10 mm \times 10 mm) and spin-coated at 300 rpm for 40 s and then at 1000 rpm for 60 s. The **2**-doped PMMA film was dried under vacuum at room temperature for 3 h.

Preparation of neat film of 3

In a glass tube, **3** (10 mg) was placed and dissolved in CH_2CI_2 (0.1 mL). The resulting solution was dropped onto a quartz plate (10 mm x 10 mm) and spin-coated at 300 rpm for 40 s and then at 1000 rpm for 60 s. The neat film was dried under vacuum at room temperature for 3 h.

Preparation of white-emissive 6-doped thin film of 3 b

In a glass tube, **3b** (2.0 mg) was placed and dissolved in a CH_2CI_2 solution of **6** (0.16 g L⁻¹, 50 μ L). The resulting solution was dropped onto a quartz plate (10 mm *x* 10 mm) and spin-coated at 300 rpm for 40 s and then at 1000 rpm for 60 s. The **6**-doped thin film was dried under vacuum at room temperature for 3 h.

Synthesis of 2

6

Preparation of 2aa: A 200 mL round-bottomed flask was charged with dimethyl 2,5-dihydroxyterephthalate (2.3 g, 10.0 mmol), K₂CO₃ (4.1 g, 30 mmol), iodomethane (1.9 mL, 30 mmol), and acetone (50 mL). The solution was refluxed for 48 h. The precipitate was removed by filtration and washed with acetone. The filtrate was concentrated by using a rotary evaporator, and the residue was dissolved in CH₂Cl₂ (50 mL). The organic layer was washed with water three times (50 mL), dried over anhydrous MgSO₄, and concentrated in vacuo. The crude product was purified by recrystallization from a CH₂Cl₂/hexane solution to give 2 aa (2.3 g, 9.2 mmol, 92%) as colorless solid. **2aa**: $R_f = 0.11$ (hexane/EtOAc 5:1); mp 140 °C; T_d : $162^{\circ}C$; ¹H NMR (CDCl₃, 400 MHz): $\delta = 3.90$ (s, 6H), 3.92 (s, 6H), 7.40 ppm (s, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 52.5, 56.7, 115.4, 123.9, 152.3, 165.9 ppm; IR (KBr): $\tilde{\nu} = 3017$, 2907, 1715, 1682, 1634, 1505, 1427, 1308, 1238, 1105, 943, 827, 779, 698 cm⁻¹; HRMS (FAB): *m*/*z* calcd for C₁₂H₁₄O₆: 254.0790 [*M*⁺]; found: 254.0797.

Compound **2ba** was prepared in 95% yield as colorless solid in the same procedure as for **2aa** except for use of 2-iodopropane (2.5 mL, 25 mmol) and Cs₂CO₃ (8.1 g, 25 mmol) in place of iodome-thane and K₂CO₃, respectively. **2ba**: $R_{\rm f}$ =0.32 (hexane/EtOAc 5:1); mp 85°C; $T_{\rm d}$ 165°C; ¹H NMR (CDCl₃, 400 MHz): δ =1.34 (d, J= 6.0 Hz, 12H), 3.90 (s, 6H), 4.50 (sep, J=6.0 Hz, 2H), 7.36 ppm (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ =22.1, 52.2, 73.2, 119.5, 126.0,

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150.8, 166.3 ppm; IR (KBr): $\tilde{\nu}$ = 2980, 1722, 1680, 1472, 1333, 1142, 966, 829, 783, 667 cm⁻¹; HRMS (FAB): *m/z* calcd for C₁₆H₂₂O₆: 310.1416 [*M*⁺]; found: 310.1425.

Typical procedure for preparation of 2ab-2ae and 2bb-2be: To a 200 mL round-bottomed flask charged with 2aa (1.8 g, 7.0 mmol) and THF (20 mL) was added aqueous solution prepared from LiOH·H₂O (1.2 g, 28.0 mmol) and water (7 mL) at room temperature. The resulting solution was refluxed for 4 h. The precipitate was removed by filtration, and HCl aq. (6 M) was added to the filtrate until the solution became acidic. The generated precipitate was collected by suction filtration and dried at $80\,^\circ\text{C}$ under vacuum for 10 h, giving rise to 2,5-dimethoxyterephthalic acid as colorless solid quantitatively, which was used for the next step without further purification. To a 20 mL Schlenk flask was added 2,5-dimethoxyterephthalic acid (0.25 g, 1.0 mmol). The flask was evacuated and filled with argon. This evacuation-purge operation was repeated twice before adding CH2Cl2 (3 mL) and DMF (one drop). To the solution was slowly added SOCl₂ (0.22 mL, 3.0 mmol) at 0°C. The resulting mixture was heated at reflux for 2 h. Organic solvent was removed by evaporation under vacuum to give 2,5-dimethoxyphthaloyl chloride as yellow solid, which was used for the next step without further purification. To the flask was added PhOH (0.23 g, 2.5 mmol), catalytic amount of DMAP, and CH_2Cl_2 (5 mL) at room temperature. After cooling at 0°C, pyridine (0.40 mL, 5.0 mmol) was slowly added to the mixture. The solution was heated at reflux for 12 h before quenching with ice-cooled HCl aq. (1 m, 5 mL). The reaction mixture was washed with water (30 mL \times 3), and the combined aqueous layer was extracted with CH₂Cl₂ (50 mL). The organic solvent was dried over anhydrous MgSO₄ and removed by vacuum evaporation. The crude product was purified by silica gel column chromatography to give 2ab (0.36 g, 0.96 mmol, 96%) as colorless solid. **2 ab**: $R_f = 0.39$ (hexane/ EtOAc 2:1); mp 166 °C; $\mathit{T}_{\rm d}$ 250 °C; $^1{\rm H}$ NMR (CDCl_3, 400 MHz): $\mathit{\delta}\,{=}\,$ 3.97 (s, 6H), 7.24-7.30 (m, 4H), 7.45 (t, J=8.0 Hz, 4H), 7.64 ppm (s, 2 H); ¹³C NMR (CDCl₃, 100 MHz): $\delta = 56.9$, 115.9, 121.7, 123.8, 126.1, 129.5, 150.7, 153.0, 163.8 ppm; IR (KBr): $\tilde{\nu} = 3015$, 1703, 1493, 1302, 1229, 1161, 1065, 920, 862, 779, 689 cm⁻¹; HRMS (FAB): *m/z* calcd for C₂₂H₁₉O₆: 379.1182 [*M*⁺ + H]; found: 379.1183.

2 ac: $R_{\rm f}$ =0.66 (hexane/EtOAc 2:1); mp 207 °C; $T_{\rm d}$ 258 °C; ¹H NMR (CDCl₃, 400 MHz): δ =3.99 (s, 6H), 7.39 (d, J=8.4 Hz, 4H), 7.64 (s, 2H), 7.72 ppm (d, J=8.4 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ = 56.9, 115.9 (q, ³J_{CF}=3.8 Hz), 122.3, 123.4, 123.8 (q, ¹J_{CF}=270.6 Hz), 126.9, 128.4 (q, ²J_{CF}=32.8 Hz), 153.1, 153.2, 163.2 ppm; ¹⁹F NMR (CDCl₃, 282 MHz): δ =-64.2 ppm; IR (KBr): $\tilde{\nu}$ =3078, 2943, 1742, 1611, 1505, 1414, 1385, 1236, 1072, 959, 841, 723, 667 cm⁻¹; HRMS (FAB): m/z calcd for C₂₄H₁₇F₆O₆: 515.0929 [M^+ +H]; found: 515.0927.

2 ad: $R_{\rm f}$ =0.43 (hexane/EtOAc 4:1); mp 147 °C; $T_{\rm d}$ 266 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 2.24 (s, 6H), 2.35 (s, 6H), 3.97 (s, 6H), 7.00 (s, 2H), 7.01 (d, J=7.6 Hz, 2H), 7.17 (d, J=7.6 Hz, 2H), 7.64 ppm (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ =15.9, 20.9, 56.8, 115.8, 122.4, 123.9, 126.9, 130.9, 137.0, 149.2, 152.9, 163.9 ppm; IR (KBr): $\tilde{\nu}$ = 2953, 2849, 1707, 1674, 1479, 1383, 1238, 1094, 1061, 945, 854, 719, 608 cm⁻¹; HRMS (FAB): m/z calcd for C₂₆H₂₇O₆: 435.1808 [M^+ + H]; found: 435.1798.

2ae: $R_{\rm f}$ =0.28 (hexane/EtOAc 10:1); mp 163 °C; $T_{\rm d}$ 230 °C; ¹H NMR (CDCl₃, 400 MHz): δ =4.01 (s, 6H), 7.66 (s, 2H), 7.76 (d, J=0.4 Hz, 4H), 7.83 (d, J=0.4 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ =56.8, 115.9 (q, ³ $J_{\rm CF}$ =3.8 Hz), 120.0, 122.8, 122.8 (q, ¹ $J_{\rm CF}$ =271.4 Hz), 122.9, 133.1 (q, ² $J_{\rm CF}$ =34.3 Hz), 151.1, 153.2, 162.7 ppm; ¹⁹F NMR (CDCl₃, 282 MHz): δ =-64.9 ppm; IR (KBr): $\tilde{\nu}$ =3084, 1748, 1607, 1505, 1462, 1306, 1236, 1109, 1003, 920, 841, 731, 613 cm⁻¹; HRMS (FAB): m/z calcd for C₂₆H₁₅F₁₂O₆: 651.0677 [M^+ + H]; found: 651.0673.

2 bb: $R_{\rm f}$ =0.30 (CHCl₃), mp 127 °C; $T_{\rm d}$ 249 °C; ¹H NMR (CDCl₃, 400 MHz): δ =1.40 (d, J=6.0 Hz, 12 H), 4.64 (sep, J=6.0 Hz, 2 H), 7.24–7.31 (m, 4 H), 7.45 (t, J=8.0 Hz, 4 H), 7.58 ppm (s, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ =22.1, 73.0, 119.3, 121.7, 125.7, 126.0, 129.5, 150.8, 151.2, 164.4 ppm; IR (KBr): $\tilde{\nu}$ =2974, 1724, 1591, 1483, 1329, 1209, 1134, 1005, 918, 814, 787, 615 cm⁻¹; HRMS (FAB): *m/z* calcd for C₂₆H₂₇O₆: 435.1808 [*M*⁺ + H]; found: 435.1798.

2 bc: $R_{\rm f}$ =0.60 (CHCl₃); mp 174°C; $T_{\rm d}$ 251°C; ¹H NMR (CDCl₃, 400 MHz): δ =1.40 (d, J=6.0 Hz, 12 H), 4.65 (sep, J=6.0 Hz, 2 H), 7.38 (d, J=8.4 Hz, 4 H), 7.58 (s, 2 H), 7.73 ppm (d, J=8.4 Hz, 4 H); ¹³C NMR (CDCl₃, 100 MHz): δ =22.1, 73.0, 119.1 (q, ³ $J_{\rm C-F}$ =3.8 Hz), 122.2, 123.8 (q, ¹ $J_{\rm C-F}$ =269.9 Hz), 125.2, 126.9, 128.3 (q, ² $J_{\rm C-F}$ =32.8 Hz), 151.2, 153.3, 163.7 ppm; ¹⁹F NMR (CDCl₃, 282 MHz): δ = -64.2 ppm; IR (KBr): $\tilde{\nu}$ =2992, 1713, 1601, 1414, 1377, 1227, 1067, 964, 835, 725, 677 cm⁻¹; HRMS (FAB): m/z calcd for C₂₈H₂₅F₆O₆: 571.1555 [M^+ + H]; found: 571.1546.

2 bd: $R_{\rm f}$ =0.44 (hexane/EtOAc 5:1); mp 132 °C; $T_{\rm d}$ 273 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 1.39 (d, J=6.0 Hz, 12H), 2.24 (s, 6H), 2.36 (s, 6H), 4.65 (sep, J=6.0 Hz, 2H), 6.98 (s, 2H), 7.01 (d, J=8.0 Hz, 2H), 7.17 (d, J=8.0 Hz, 2H), 7.58 ppm (s, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ = 16.0, 21.0, 22.1, 72.7, 119.0, 122.4, 125.6, 127.0, 130.9, 137.0, 149.3, 151.0, 164.3 ppm; IR (KBr): $\tilde{\nu}$ = 2920, 1728, 1694, 1506, 1451, 1356, 1292, 1140, 993, 843, 719, 667 cm⁻¹; HRMS (FAB): m/z calcd for C₃₀H₃₅O₆: 491.2434 [M^+ + H]; found: 491.2439.

2 be: $R_{\rm f}$ =0.41 (hexane/EtOAc 10:1); mp 131 °C; $T_{\rm d}$ 225 °C; ¹H NMR (CDCl₃, 400 MHz): δ =1.42 (d, J=6.0 Hz, 12 H), 4.68 (sep, J=6.0 Hz, 2 H), 7.60 (s, 2 H), 7.75 (s, 4 H), 7.83 ppm (s, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ =22.1, 72.9, 118.8 (q, ³J_{C-F}=3.8 Hz), 119.9, 122.7, 122.8 (q, ¹J_{C-F}=271.4 Hz), 124.5, 133.1 (q, ²J_{C-F}=34.3 Hz), 151.3, 151.4, 163.2 ppm; ¹⁹F NMR (CDCl₃, 282 MHz): δ =-64.9 ppm; IR (KBr): $\tilde{\nu}$ = 2993, 1753, 1223, 1186, 1001, 937, 826, 754, 667 cm⁻¹; HRMS (FAB): m/z calcd for C₃₀H₂₂F₁₂O₆: 706.1225 [M^+]; found: 706.1226.

Synthesis of 3

3a: To an 80 mL Schlenk flask was charged with 2,5-diisopropoxyterephthaloyl chloride (4, 0.19 g, 0.6 mmol) prepared from 2 ba. The flask was evacuated and filled with argon. This evacuationpurge operation was repeated twice before adding CH₂Cl₂ (6 mL) and 1,4-butandiol (53 µL, 0.6 mmol). To this solution was slowly added pyridine (0.19 mL, 2.4 mmol) at 0°C, and the resulting solution was stirred for 3 h at room temperature before quenching with HCl aq. (1 μ). The reaction mixture was diluted with CH₂Cl₂ (50 mL), and the organic layer was washed with HCl aq. (1м, 20 mL), sat. NaHCO3 aq. (20 mL), and sat. NaCl aq. (20 mL), and dried over anhydrous MgSO₄. The organic solvent was removed by vacuum evaporation to give the crude product, which was dried under vacuum and purified by GPC (eluent: CHCl₃) and reprecipitation from CH₂Cl₂ and MeOH, giving rise to **3a** (0.12 g, 59%) as colorless solid. **3a**: M_n 3850; M_w 5250; PDI 1.36 (polystyrene standard); Mp 120 °C; T_d 333 °C; T_q 71 °C; ¹H NMR (CDCl₃, 400 MHz): $\delta = 1.31$ (d, J=6.0 Hz, 12 H), 1.93 (brs, 4 H), 4.37 (brs, 4 H), 4.51 (sep, J= 6.0 Hz, 2H), 7.33 ppm (s, 2H); 13 C NMR (CDCl₃, 100 MHz): $\delta = 22.1$, 25.4, 64.6, 72.5, 118.7, 126.0, 150.5, 166.2 ppm; IR (neat): $\tilde{\nu} = 2976$, 2938, 2895, 1719, 1688, 1483, 1414, 1385, 1371, 1300, 1207, 1177, 1140, 1105, 1053, 980, 955, 899, 789, 766, 746 cm⁻¹.

3 b: To an 80 mL Schlenk flask were charged with **4** (96 mg, 0.3 mmol) and terephthaloyl chloride (**5**, 61 mg, 0.3 mmol). The flask was evacuated and filled with argon. This evacuation-purge operation was repeated twice before adding CH_2CI_2 (6 mL) and 1,4-butandiol (53 μ L, 0.6 mmol). To this solution was slowly added pyridine (0.19 mL, 2.4 mmol) at 0°C, and the resulting solution was stirred for 3 h at room temperature before quenching with HCl aq.

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(1 м). The reaction mixture was diluted with CH₂Cl₂ (50 mL), and the organic layer was washed with HCl aq. (1 м, 20 mL), sat. NaHCO₃ aq. (20 mL), and sat. NaCl aq. (20 mL), and dried over anhydrous MgSO₄. The organic solvent was removed by vacuum evaporation to give the crude product, which was dried under vacuum and purified by GPC (eluent: CHCl₃) and reprecipitation from CH₂Cl₂ and MeOH, giving rise to **3 b** (95 mg, 56%) as colorless solid. **3 b**: M_n 5160; M_w 9190; PDI 1.78 (polystyrene standard); Mp (dec) 332 °C; T_g 15 °C; ¹H NMR (CDCl₃, 400 MHz): δ = 1.31 (d, J = 6.0 Hz, 12H), 1.93–1.97 (m, 8H), 4.37–4.43 (m, 8H), 4.52 (sep, J = 6.0 Hz, 2H), 7.33 (s, 2H), 8.39 ppm (s, 4H); ¹³C NMR (CDCl₃, 100 MHz): δ = 22.1, 25.4, 64.6, 64.8, 72.5, 118.7, 125.9, 129.5, 134.0, 150.4, 165.7, 166.2 ppm; IR (neat): $\hat{\nu}$ = 2976, 2897, 1717, 1692, 1491, 1410, 1385, 1267, 1250, 1225, 1200, 1099, 1017, 957, 874, 789, 727 cm⁻¹.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arenes · conjugation · donor-acceptor systems · fluorescence · materials science

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FULL PAPER

Masaki Shimizu,* Ryosuke Shigitani, Takumi Kinoshita, Hiroshi Sakaguchi



(Poly)terephthalates with Efficient Blue Emission in the Solid State



To di for: The disubstitution of isopro-

poxy groups at 2- and 5-positions of

terephthalic acid diesters leads to the

ganic solids. The copolymerization of

2,5-diisopropoxyterephthaloyl chloride

creation of efficient blue fluorescent or-

with butane-1,4-diol produces an efficient blue fluorescent polyester film, and the doping of a yellow-fluorescent terephthalate into the polyester film allows us to achieve efficient white emission.