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## Design and Characterization of 4,5-Bis(diarylamino)phthalic Acid Diesters as a New Class of Fluorophores Exhibiting Efficient Blue Emission in the Solid State

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Keywords: Materials science / Photochemistry / Charge transfer / Donor-acceptor systems / Fluorescence

We developed 4,5-bis(diarylamino)phthalic acid diesters as blue fluorophores exhibiting efficient photoluminescence in powder and in a thin film of pol(methyl methacrylate). Increasing the electron-donating nature of the substituents in the *para* positions of the diarylamino moieties in the dimethyl esters increased the redshift in the fluorescence spectrum. Replacing the methoxycarbonyl groups with aryloxylcarbonyl groups also induced a bathochromic shift in the

### fluorescence spectrum. Thus, the color of the emission was finely tuned by simple molecular modification. Single-crystal X-ray analysis revealed a twisted conformation with loose packing in the crystal. Density functional theory calculations suggested that the excitation process was governed by intramolecular charge transfer from the diarylamino moieties to the alkoxycarbonyl groups.

### Introduction

Organic light-emitting diodes (OLEDs) are currently attracting increased attention for applications in full-color flat displays and lighting devices.<sup>[1]</sup> OLED emission is derived from an organic emitter in a thin film or dispersed in a host matrix. Hence, advances in OLEDs are highly dependent on the development of organic chromophores that radiate visible light in the solid state with high luminescence efficiency.<sup>[2]</sup> Phosphorescent organometallic compounds such as iridium complexes can in principle attain 100% internal quantum efficiency in OLEDs owing to the heavymetal effect of transition metals.<sup>[1d]</sup> Therefore, they serve as very attractive emitters, especially for green and red OLEDs. However, the lifetime and color purity of blue phosphorescent OLEDs need improvement for practical applications as a result of the intrinsically wide band gap of blue materials. Therefore, for continued development of OLEDs, novel fluorophores are needed that efficiently emit blue light in the solid state.<sup>[3]</sup>

Fluorescence is one of the possible de-excitation processes of an excited molecule located at the lowest vibrational level of the singlet electronic state, that is, the  $S_1$ state.<sup>[4]</sup> The efficiency of fluorescence in solution depends on the inhibition of other intramolecular photophysical

 [a] Department of Biomolecular Engineering, Graduate School of Science and Technology, Kyoto Institute of Technology, 1 Hashikami-cho, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan E-mail: mshimizu@kit.ac.jp processes, such as internal conversion followed by vibrational relaxation and intersystem crossing. Fluorescence efficiency in the solid state is also strongly related to intramolecular nonradiative decay as well as intermolecular photophysical processes, such as the formation of excimers, exciplexes, or physical dimers and the transfer of energy or electrons, or both.<sup>[5]</sup> Accordingly, suppression of intermolecular interactions that result in luminescence quenching is key to the development of organic fluorophores that are efficiently emissive in the solid state.

We recently reported that dimethyl 2,5-bis(diorganoamino)terephthalates 1 exhibited green to yellow fluorescence with good to high quantum yields in crystals and in powder (Figure 1).<sup>[6]</sup> Terephthalates 1 are structurally characterized by the presence of two donors (i.e., amino groups) and two acceptors (i.e., methoxycarbonyl groups) and twofold ortho linkages of the donors and acceptors. The donoracceptor pairs induce intramolecular charge transfer that results in a large Stokes shift. The *ortho* linkages force the molecule to adopt a twisted conformation, which leads to inhibition of dense packing in the solid state. Thus, the structural characteristics of 1 minimize intermolecular energy migration from fluorophores in the excited state through Förster and Dexter mechanisms.<sup>[7]</sup> On the basis of these results, we envisioned the development of novel blue fluorophores by changing the substitution patterns of the two amino groups and the two alkoxycarbonyl groups, while retaining the two sets of ortho linkages. We report herein the structure, photophysical properties, and molecular orbital calculations of 4,5-bis(diarylamino)phthalic acid diesters 2 as a new class of blue emitters exhibiting good fluorescence efficiency in the solid state (Figure 1).

http://www.cis.kit.ac.jp/~orgsynth/en/index.html

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Figure 1. Molecular structures of diaminoterephthalates 1 and diaminophthalates 2.

#### **Results and Discussion**

Diaminophthalates 2 were easily synthesized from commercially available 4,5-dichlorophthalic acid through three (for 2a-c) or five (for 2d-f) steps (see the Supporting Information for details). The decomposition temperature  $(T_d)$ , defined as the temperature at which 5% of the mass is lost, ranged from 279 to 360 °C for all derivatives of 2, which was indicative of their good thermal stability. Dimethyl phthalate 2b crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane solution in the monoclinic space group  $P2_1/n$ .<sup>[8]</sup> The molecular and crystal structures of **2b** are shown in Figure 2. Both phenyl groups of the amino moieties and methoxycarbonyl groups largely or significantly deviated from the central benzene plane, as expected (Figure 2, a). The dihedral angles of C(2)-C(1)-N(1)-C(5), C(6)-N(2)-C(2)-C(1), C(3)-C(4)-C(8)-O(2), and C(4)-C(3)-C(7)-O(1) were found to be 55.57, 59.85, 62.25, and 28.47°, respectively. The corresponding dihedral angles of C-C-N-C and C-C-C-O for 1a (R = Ph) were 44.62 and 48.47°, respectively (see Figure S1, Supporting Information). Thus, the contortions of the Ph<sub>2</sub>N moieties of **2b** were both larger than those of **1a**, whereas one CO<sub>2</sub>Me moiety was more twisted and the other was less twisted relative to those of 1a. There was no  $\pi - \pi$ stacking in the crystal lattice, which minimized luminescence quenching, likely as a result of the twisted molecular conformation (Figure 2, b).

The absorption spectra of 2 in toluene are shown in Figure 3a as is the spectrum of 1a (R = Ph). The spectra of all derivatives of 2 were significantly blueshifted relative to the spectrum of 1a and all had small shoulders between 360 and 380 nm, which were assigned to charge-transfer bands. The absorption edges of all derivatives of 2 ranged from around 400 to 440 nm, much shorter than that of 1a (493 nm), which indicated that the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) energy gaps of 2 were larger than that of 1a. Considering the molecular conformation disclosed by X-ray analysis, the blueshift may be attributed to the larger distortion of the diarylamino moieties from the central benzene ring. These results clearly demonstrate that the molecular design of 2 resulted in shorter effective conjugation lengths than in 1. Indeed, 2 exhibited blue to bluish-green fluorescence in solution and in the solid state with good quantum yields. The fluorescence data and spectra of 2 in toluene, in powder, and in a thin film of poly(methyl methacrylate)



Figure 2. (a) Molecular structure of **2b**. Selected dihedral angles [°]: C(2)–C(1)–N(1)–C(5) 55.57, C(6)–N(2)–C(2)–C(1) 59.85, C(3)–C(4)–C(8)–O(2) 62.25, C(4)–C(3)–C(7)–O(1) 28.47. (b) Crystal structure of **2b** (viewed from the *b* axis). Space group:  $P_{2_1}/n$ . Unit cell dimensions: a = 14.1377(8) Å, b = 9.1624(5) Å, c = 22.2157(12) Å,  $\beta = 104.6720(10)^{\circ}$ .

(PMMA) are shown in Table 1 and Figure 3 (b-d). Comparison of each absorption spectrum of 2 in toluene with its respective fluorescence spectrum in toluene showed that the spectral overlap was very small; this suggested that deactivation of 2 from the excited state to the ground state through Förster-type energy migration was minimal (overlaid absorption and fluorescence spectra of **2b** in toluene are shown as an example in the Supporting Information). The presence of electron-withdrawing  $(CF_3)$  or electrondonating (tBu) groups in the 4-positions of each phenyl group of the amino moieties induced a blue- or redshift in the spectrum, respectively, relative to the spectrum of 2b, irrespective of the state of 2. Replacing the methoxycarbonyl groups with aryloxycarbonyl groups also resulted in a bathochromic shift in the spectrum (compare that of 2b with those of 2d-f), presumably because the methoxy group is more electron-donating than aryloxy groups. Among 2df, a greater number of methyl groups on the aryloxy moieties shortened the emission maximum, except for 2e dispersed in a PMMA film. Thus, the emission color could be finely tuned by simple molecular modification. The substituent effects on the photophysical properties described above were in good agreement with the anticipated intramolecular charge transfer from the diarylamino moieties to the alkoxycarbonyl groups. Fluorescence quantum yields of 2 in powder and doped PMMA film were generally good and ranged from 0.39-0.58, except for 2a likely because of its twisted molecular conformation, which results in loose packing, and because of its electronic structure, which exhibits a large Stokes shift. In some cases, the quantum yields in the solid states were higher than those in solution. The lower efficiency in solution is presumably ascribed to





Figure 3. (a) Absorption spectra of 1a and 2 in toluene. Fluorescence spectra of 2 in (b) toluene, (c) powder, and (d) PMMA film.

Density functional theory (DFT) calculations were performed at the B3LYP/cc-pVDZ/B3LYP/cc-pVDZ level by using the Gaussian 09 package.<sup>[9]</sup> The HOMO and LUMO diagrams of **2b** and **2d** are illustrated in Figure 4, and the calculated energies and the energy gaps between the HOMOs and LUMOs of **1a** and **2** are depicted in Figure 5. For both **2b** and **2d**, the HOMO developed over the central benzene ring and the two Ph<sub>2</sub>N moieties, whereas the

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Table 1.	Fluorescent	properties	of 2

	In toluene <sup>[</sup> $\lambda_{\max}$ (nm)	$\Phi^{[c]}$	Powder <sup>[a]</sup> $\lambda_{max}$ (nm)	$\Phi^{[c]}$	In PMMA $\lambda_{max}$ (nm)	${\displaystyle                                    $
2a	432	0.34	428	0.33	420	0.20
2b	463	0.43	458	0.58	451	0.49
2c	495	0.42	476	0.39	472	0.45
2d	488	0.34	496	0.50	468	0.47
2e	482	0.47	495	0.44	474	0.49
2f	480	0.49	461	0.46	460	0.41

[a] Excitation was effected by UV light at 320 nm. [b] Prepared by spin coating. [c] Absolute quantum yield was determined by a calibrated integrating sphere system.

LUMO was mainly delocalized across the central benzene ring and the two C(=O)O units. Time-dependent DFT calculations assigned the lowest energy transition mainly to the HOMO–LUMO transition. Hence, the small shoulders between 360 and 380 nm in the absorption spectra of **2** originated from intramolecular charge transfer from the amino moieties to the alkoxycarbonyl groups. The chargeseparated nature of the excited state was supported by the redshift in the fluorescence spectra in more polar solvents (see Figure S3, Supporting Information). The calculated HOMO–LUMO energy gaps of **2** were much larger than



Figure 4. (a) HOMO and (b) LUMO drawings of **2b**. (c) HOMO and (d) LUMO drawings of **2d**.



Figure 5. Calculated HOMO and LUMO energies of **1a** and **2**; values between the HOMO and LUMO levels are the energy gaps between the HOMOs and LUMOs.

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that of **1a**, which is consistent with the trend in the absorption edges shown in Figure 3 (a) and the blueshifted fluorescence spectra of **2**. The observed electronic effects of substituents in the *para* positions of each phenyl group of the diarylamino moieties on the energy differences in the HOMOs and LUMOs were consistent with the DFT calculations.

## Conclusions

In conclusion, the molecular design of 4,5-bis(diarylamino)phthalates, which involved construction of 1,2bis(donor)-4,5-bis(acceptor)-substituted benzenes, was effective for the development of blue fluorophores exhibiting good luminescence efficiency in the solid state. The designed blue emitters were easy to synthesize and were thermally stable, which are attractive features for practical applications. The emission color could be finely tuned by modifying the substituents in the para positions of each phenyl group of the diarylamino groups as well as the carbonaceous moieties of the alkoxycarbonyl groups. The good luminescence efficiency in powder and in the poly-(methyl methacrylate) host matrix indicates the strong potential of these phthalates for use as blue-emissive host materials and dopants in organic light-emitting diodes. Further extension of this novel molecular design principle to the development of non-blue-emissive materials and application of the blue-emissive phthalates to organic lightemitting diodes are in progress.

**Supporting Information** (see footnote on the first page of this article): General experimental methods, representative procedures for synthesis, characterization data, NMR spectra of **2**, summary of X-ray crystallographic analysis of **2d**, overlaid absorption and fluorescence spectra of **2d** in toluene, and procedures for measurement and PMMA film preparation.

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#### Fluorophores

Diorgano 4,5-bis(diarylamino)phthalates exhibited blue fluorescence in solution and in the solid state with good efficiency. The emission spectra were finely shifted by changing the substituents in the *para* positions of each phenyl group of the diarylamino moieties as well as the carbonaceous moieties of the alkoxycarbonyl groups.

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