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Single Benzene-Based Fluorophore and Optical Waveguiding in Its Crystal

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Abstract: A single benzene-based, blue-emissive diethyl 2,5dihydroxyterephthalate (DDT) was prepared by Fischer esterification of 2,5-dihydroxyterephthalic acid (DHT) and ethanol. The strong fluorescence in both the solution and the solid state from such a simple structure stemmed from the push-pull structure of the electron-donating hydroxyl groups and the accepting carbonyl groups, as well as structural planarity from intramolecular hydrogen bonds. The strong intermolecular hydrogen bonds enabled DDT to crystallize easily. The color CCD imaging technique showed efficient 1D optical waveguiding with a large optical loss coefficient of 0.15 dB/ μ m, which has a potential application in optical sensor, photonic device, and optoelectronic communication, because of its highly ordered structure and light-emitting ability.

Introduction

Organic fluorescent molecules have attracted much interest because of their potential applications in various fields such as optoelectronic devices, bioimaging, and chemical sensors.^[1-7] Benzene is one of the effective units that form a π -conjugated system in an organic fluorophore, and more than one benzene ring is required to extend the π -conjugation length for visible light emission. However, organic fluorophores with such a large π -conjugation usually have limited solubility in common organic solvents.^[8] As such, emissive small molecules based on a single benzene have the advantage of high solubility and easy synthesis because of their simple chemical structures.

Benzene is a simple structure so that its fluorescence emission can be tuned depending on the substituents attached to the single benzene.^[9,10] For example, the presence of electrondonating and -withdrawing groups in the benzene ring provided a strong fluorescence by extending the π -conjugation induced by the push-pull structure.^[11] In addition, intra- and intermolecular interactions including hydrogen bonding and the π - π interaction are

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considered to be important in designing highly fluorescent molecules. The strong intramolecular interaction allows the molecules to have a planar structure and to generate an extended π -conjugated system in the molecule, leading to high fluorescence.[12-14] In addition, strong intermolecular interactions play an important role in fluorescence via charge transfer.^[15] Substituents in benzene that could induce intramolecular hydrogen bonding often result in an effective emission via an excited-state intramolecular proton transfer (ESIPT).^[12,16,17] In addition, it has been reported that fluorescence depends on the packing structure of the fluorescent molecules. In general, most πconjugated molecules have limited fluorescence in their solid state because the strong π - π interaction causes unexpected quenching, known as aggregation-caused quenching (ACQ).[18-20] To supress ACQ, it was reported that the intramolecular hydrogen bond was introduced to lessen the ACQ to some degree, exhibiting desirable fluorescence.^[14,21] Therefore, the high fluorescence would be maintained in the solid state, as long as the intramolecular interaction is carefully controlled.

New communication techniques and devices can be created using photons as information carrier manipulated at micro-to-nano scale.^[22,23] Organic materials are advantageous over conventional inorganic materials in such fields, because of their cost-effectiveness, easy molecular modification, flexibility and lightweight.^[24] To attain transmitting light both in active and passive modes, organic materials should have highly ordered, crystalline structure to transport photonic carriers.^[25,26]

Herein, we synthesized DDT and its derivatives to investigate their optical properties and optical waveguiding application. DDT had two hydroxyl groups that were hydrogen-bonded inter- and intramolecularly with carbonyl groups. The hydroxyl and carbonyl groups acted as electron-donating and -withdrawing groups in the benzene ring, respectively, affecting the high fluorescence of DDT. The intramolecular hydrogen bond provided enhanced ring planarity, resulting in the delocalization of electrons. It was revealed that the presence of hydroxyl groups was essential for the fluorescence of DDT, and thus this fluorescence of DDT was easily altered by the protection and deprotection of the hydroxyl groups. It was found that



Scheme 1. Synthesis of DDT and its derivatives. Inset photographs were taken in their chloroform solutions under UV lamp (365 nm).

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DDT easily and facilely crystallized, in which strong intermolecular interactions including the π - π interaction and the hydrogen bond between the molecules played an important role in crystal packing. The resulting DDT crystal could serve as efficient 1D waveguide, which can transmit light in active mode, because of the unique optical property in its crystal form. It has been also reported that the push-pull structure in a benzene ring including DDT was able to provide strong fluorescence based on X-shaped tetrafunctionalities.[27] They, however, investigated simple spectroscopic properties of DDT including UV-vis absorption, emission, and fluorescence lifetime, because they thought that stronger electron-donating diamine compound was more attractive than DDT. We were to investigate the detailed origin of DDT fluorescence in various solvents. Moreover, we conjectured such hydroxyl groups would be helpful in rapid crystallization via intermolecular hydrogen bond.

Results and Discussion

A blue-emissive fluorophore, DDT, was synthesized by the Fischer esterification of DHT with ethanol (Scheme 1). After recrystallization from ethanol, the synthesized DDT was a highly emissive needle-like crystal. DDT has been reported as the intermediate for oxadiazole derivatives, but its optical properties have been rarely studied.^[28] To investigate the main cause of fluorescence in DDT, the spectroscopic properties of DDT were compared with those of DHT, which was similar to DDT in structure, having two hydroxyl groups adjacent to carbonyl groups, but DHT had carboxylic acid groups. DDT showed UV absorption around 365 to 378 nm in various solvents used, but the fluorescence emission was shown at 451 nm, in which the solvent effect was not observed (Fig. 1a,b). No significant difference in the emission wavelengths of DDT was found in organic solvents with different polarity and thus the fluorescence



Fig. 1. (a) UV-vis and (b) fluorescence spectra of DDT and (c) UV-vis and (d) fluorescence spectra of DHT in various solvents. [DDT] = 0.07 mM; [DHT] = 0.05 mM.

of DDT did not originate from ESIPT. The fluorescence of ESIPTactive molecules should vary according to the solvent polarity, because of the alteration in intramolecular hydrogen bonding.^[17,29,30]

The UV-vis spectra of DHT showed absorption at 375 nm, similar to that of DDT (Fig. 1c). However, the fluorescence spectra of DHT varied according to the solvent used (Fig. 1d). DHT showed short wavelength emission (452 nm) in THF, but a distinctive long wavelength emission was observed around 510 nm in DMF and DMSO, which had higher dipole moments (3.96 and 3.86 D, respectively) than THF (1.75 D). Moreover, the fluorescence spectra in protic solvents such as ethanol and methanol differed from THF and DMF, because the intramolecular hydrogen bond of DHT was disturbed in the protic solvents. Thus, it might be concluded that unlike DDT, the fluorescence of DHT dominantly resulted from ESIPT.^[31] The same phenomenon of ESIPT was found in salicylic acid, which has half the DHT structure (a hydroxyl and a carboxylic acid groups).^[32] To ensure that the fluorescence of DDT was not related to ESIPT, trifluoroacetic acid (TFA) was added to DDT to protonate the hydroxyl groups of DDT in THF, indicating negligibly small changes in UV-vis absorption and emission shift of DDT (Fig. S1). Therefore, it was evident that ESIPT did not occur in the DDT molecule.^[16] 2,5-Bis(methylsulfonyl)-1,4-diaminobenzene showed green emission that resulted from a push-pull structure, assisted by an intramolecular hydrogen bonding interaction.^[33] As such, we supposed that DDT showed efficient fluorescence based on the push-pull system by the presence of electron-donating and withdrawing groups. DDT has two hydroxyl groups acting as donors and two carbonyl groups acting as acceptors, which would meet the requirement of the push-pull system in a single benzene.

To investigate the effect of the electron push-pull structure on the optical properties of DDT, the optimized structures in the ground and excited states were obtained by density functional theory (DFT) calculations at the B3LYP/6-31G(d) level. DDT had a structure in which electrons were mainly located in the central benzene ring in the highest occupied molecular orbital (HOMO) level and were evenly distributed throughout the molecule in the ester groups in the lowest unoccupied molecular orbital (LUMO) level (Fig. S2a). The HOMO-LUMO structure suggests that the push-pull system occurred in a benzene ring. On the while, ethyl salicylate, which has half the DDT structure (one hydroxyl and one ester group) showed intense fluorescence, and its fluorescence varied according to the solvents with different polarity (Fig. S3). The changes in the DDT fluorescence were investigated to verify the presence of the



Fig. 2. (a) Fluorescence spectra and (b) photographs of DDT in chloroform solution, film, and crystal (from left to right). Photographs were taken under UV irradiation (365 nm).

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substitution effect of the hydroxyl groups. DDT-A and DDT-T were synthesized, in which the hydroxyl groups were protected with the acetyl and tert-butyloxycarbonly (t-Boc) groups, respectively (Scheme 1). Upon protection, the UV-vis absorption was blue-shifted (Fig. S4a) and the fluorescence of DDT-A and DDT-T was hardly observed in the solutions (inset photographs in Scheme 1 and Fig. S4b), and the relative quantum yields (QYs) of DDT-A and DDT-T were found to be much lower than that of DDT (Table S1). It is suggested that the hydroxyl groups were essential for the fluorescence of DDT via electron-donation and intramolecular hydrogen bonding. To strengthen electron-donating ability of the hydroxyl groups in DDT, deprotonation from the hydroxyl groups was performed using tetrabutylammonium fluoride (TBAF). The emission wavelength was shifted to longer wavelength (562 nm) by the formation of O⁻ group (DDT-F⁻), which became a stronger donor in the benzene ring (Fig. S5). Taking into account that the electrondonating ability of oxygen anion is much higher than that of hydroxyl group,^[34,35] the long-wavelength emission band in DDT-F⁻ could be attributed to its phenolate anion species via facilitated intramolecular charge transfer, as reported earlier.[36]

To elucidate the effect of alkyl chain length of ester groups, various numbers of alkyl groups were introduced to the C=O groups in DDT. Dibutyl- (DT-C4), dihexyl- (DT-C6), dioctyl- (DT-C8), didecyl- (DT-C10), and didodecyl 2,5-dihydroxyterephthalate (DT-C12) were



Fig. 3. Crystal structure of DDT: top view (a); molecular packing structures along the crystallograpic *b* axis (b); and between *b* and *c* axes. CCDC 128054 (DDT) contains the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

synthesized using the same method for DDT. As the number of alkyl groups did not affect the electron-withdrawing ability of the ester groups, the absorption and emission spectra of DT-Cn were the same as those of DDT in chloroform (Fig. S6 and Table S2). The electron distribution, band gap, and HOMO-LUMO levels of DT- C6 were almost identical to those of DDT, indicating that the effect of the number of alkyl groups on optical properties was negligible (Fig. S2b). DT-Cn crystals, however, tended to show a red shift in the fluorescence emission wavelength, compared with those in solution and film state (Fig. S6). It should be noted that such a red shift of the emission wavelength became larger with a smaller n and was maximized in DDT (25 nm of red shift). Among these derivatives, DDT showed most rapid crystallization with largest crystal size. It suggests that the alkyl group affected the crystal packing and, finally, the fluorescence wavelength of their crystals (Table S2). on

DDT exhibited various fluorescence wavelengths depending on its states including solution, film, and crystal, in which the blue fluorescence was observed in its solution and film and greenish blue emission was found in its crystal (Fig. 2). It appears that the red shift of the fluorescence of crystalline DDT resulted from the planarization-induced intermolecular π - π interaction of the rings. To verify the planarization, the crystal structure of DDT was determined using a single crystal diffractometer (Fig. 3 and Table S3). DDT had intramolecular hydrogen bonds (H3-O2; bond length: 1.906 Å) between the oxygen atom at the carbonyl group and the hydrogen



Fig. 4. Planar optical wave-guiding effects in 1D DDT crystal (designated as solid rectangle). (a) Color CCD images of unguided and five waveguided emissions in 1D DDT crystal with various distinct propagation distances. Circled numbers denote incident laser positions, and dashed ellipse indicates detector positions where guided PL spectra were measured. Inset: Optical microscope image of the 1D DDT crystal. (b) Comparison of unguided black line) and waveguided fluorescence spectra from (a). The unguided black line was out of range, but illustrated for comparison. (c) Intensity ratio including single exponential fitting curve with respect to the propagation distance. Excitation wavelength = 405 nm.

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atom at hydroxyl group, which affected the planarization of the molecule.^[1] Moreover, strong intermolecular hydrogen bonds (H3-O2 in adjacent molecule; bond length: 2.348 Å) provided a π - π interaction-induced high crystallinity and enhanced fluorescence in the crystalline state. The DDT crystal showed a herringbone packing structure. The packing structure affected the crystal to have an absolute QY of 34%, determined with an integrating sphere. It was already reported that the molecular packing considerably affected fluorescence efficiency.^[37]

Different from conventional waveguiding phenomena observed in optical fiber that satisfy total internal reflection of axially incident photons, crystalline organic small molecular microstructures exhibited planar optical waveguiding effects, which normally incident photons were propagated laterally.³⁷⁻⁴⁰ The color CCD images show optically active fluorescence waveguiding of 1D DDT crystal (Fig. 4a,b and Fig. S7). Bright blue luminescent spots in color CCD images indicate excitation positions, which were moved from right edge of the 1D DDT crystal to left designated positions (1) to (5) with distances of 2.2, 3.4, 4.6, 5.8, and 7.0 µm, respectively. All the color CCD images show that internally waveguided photon energies were re-emitted as pale blue lights at both edges, indicating an important evidence of planar optical waveguiding effect. For quantitative comparison, unguided and waveguided fluorescence spectra were compared (Fig. 4c). The initial unguided fluorescence spectrum as well as guided spectra (1) to 5) were observed at about 465 nm, suggesting that they reflected same emission colors from the corresponding spots. However, the emission intensity of the guided fluorescence spectra (Iguided) gradually decreased with increase in the propagation distances (d). The changes in the intensity ratio (I_{guided} / $I_{unguided}$) as a function of d including single exponential fitting curve can be described as: Iguided / Iunguided = Aexp(-Rd), where A is a constant and R is an optical loss coefficient (Fig. 4d).^{25,40} The R value was determined to be 0.158 dB/µm, which was comparable and even better than previous reports on the highly crystalline organic microstructures (0.9~1.6 dB/mm).[25,26,38-41] The present work elucidates the related photophysics in a simple benzene-based, organic system, providing an important paradigm of organic integrated photonics.

Conclusions

In summary, a single benzene fluorophore was prepared, which showed high fluorescence both in solution and in the solid state. According to photophysical and DFT studies, the fluorescence of DDT originated from the presence of functional groups of electronwithdrawing and -donating. Therefore, the presence of hydroxyl groups was necessary to provide strong fluorescence of DDT. The intermolecular hydrogen bonding in DDT was versatile so that DDT showed rapid crystallization with unique packing, exhibiting strong fluorescence in the solid state. Such fluorescence from crystallized DDT showed successful optical waveguiding, indicating that DDT is a promising candidate for optoelectronic transportation devices

Experimental Section

Synthesis of DDT. 2,5-Dihydroxyterephthalic acid(DHT) (5 g, 25 mmol) was dissolved in ethanol (200 mL) charged in a three-necked flask (500 mL) under argon atmosphere. Sulfuric acid (13 mL, 0.25 mol) was slowly added and then the mixture was stirred at 80 °C for 24 h. The mixture was cooled to room temperature and the precipitate was isolated by filtration. The product was recrystallized from ethanol. A greenish needle-like crystal was obtained (yield 5.52 g, 87 %). ¹H NMR (300 MHz, CDCl₃): δ = 10.1 (s, 2H), 7.4 (s, 2H), 4.4 (m, 4H), 1.4 ppm (t, 6H).

Synthesis of DDT-A. DDT (1 g, 3.9 mmol) was dissolved in acetonitrile (60 mL) charged in a 100 mL three-necked flask. Acetic anhydride (1.48 mL, 15.6 mmol) was added to the solution, and the mixture was stirred at 80 °C for 10 min. Cesium carbonate (1.91 g, 5.85 mmol) was added to the mixture and then the mixture was stirred for 4 h. After cooling, the solution was washed with chloroform three times and with brine solution, and dried over MgSO4. The solvent was recrystallized from ethyl acetate. The colorless diamond-shaped crystal was obtained (yield 1.2 g, 89 %). ¹H NMR (300 MHz, CDCl₃): δ = 7.7 (s, 2H), 4.3 (m, 4H), 2.3 (s, 6H), 1.3 ppm (t, 6H).

Synthesis of DDT-T. To a 250 mL three-necked flask was added DDT (0.615 g, 2.4 mmol), di-tert-butyl dicarbonate (1.27 g, 5.82 mmol), and tetrahydrofuran (THF, 100 mL). DMAP (15 mg, 0.12 mmol) was added to the solution and then the mixture was stirred overnight. The solution was poured into water and the precipitate was isolated by filtration. A white powder was obtained (yield 1.03 g, 94 %). ¹H NMR (300 MHz, CDCl₃): δ = 7.8 (s, 2H), 4.3 (m, 4H), 1.5 (s, 18H), 1.4-1.3 ppm (t, 6H).

Synthesis of DT-Cn (n = 4, 6, 8, 10, and 12). DHT (1.0 g, 5.0 mmol) was dissolved in n-butanol (40 mL) for DT-C4 synthesis; in n-hexanol (50 mL) for DT-C6 synthesis; in n-octanol (60 mL) for DT-C8 synthesis; in n-decanol (50 mL) for DT-C10 synthesis; in n-dodecanol (70 mL) for DT-C12 synthesis in the presence of sulfuric acid catalyst. Subsequent procedures are the same as those used for the DDT synthesis. In the cases of DT-C8, DT-C10, DT-C12, the crude product was purified by recrystallization from 1-propanol.

Preparation of DDT crystals. Highly crystalline DDT was fabricated by using solvent-assisted self-assembly method. Briefly, DDT was dissolved in THF and the solution was drop-cast on a glass slide. As vaporizing the solvent at room temperature, the nucleation as well as self-assembly of DDT molecules occurred resulting in various forms of DDT crystals. Among them, 1D DDT crystal was chosen to investigate planar optical waveguiding phenomena.

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Optical Waveguiding. Optical properties of 1D DDT crystal, including color charge-coupled device (CCD) images and fluorescence spectroscopy, were measured using a home-made laser confocal microscope (LCM) system with high spatial resolution (≤200 nm). In order to characterize planar optical waveguiding effects, the LCM system should be modified as separating the positions of the incident laser from those of the detector. Especially, the irradiating positions of the incident laser were precisely controlled with an aid of the piezoelectric 2D positioning system (Albatross, Nanofocus Inc.). The excitation wavelength (λ_{ex}) was set to 405 nm for both luminescent color CCD images and fluorescence spectra, which were recorded by GF-033C-IRF (Allied Vision) and SR-303I-B (Andor), respectively. The power density of the incident laser was carefully chosen to minimize photobleaching of the crystal sample.

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Keywords: benzene-based fluorophore • crystals • fluorescence spectroscopy • hydrogen bonds • optical waveguiding

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