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ABSTRACT: Novel asymmetric/symmetric supramolecular dendrimers were constructed by two kinds of (single/double) H-bonded acceptor chromophores, i.e., pyridyl/bispyridyl acceptor emitters, encapsulated with (one or two) 1,3,4-oxadiazole (OXD) donor dendrons in proper acceptor/donor molar ratios. These acceptor emitters were also complexed with another type of dendritic donor cores to form exterior emitting shells reverse to the previous system (with emitting cores) via self-assembly of complementary H-bonded moieties. Because of the shielding effect of bulky OXD dendritic shells in H-bonded donors, the supramolecular dendrimers are able to prevent acceptor emitters from spatial aggregation, and thus to induce glass-forming properties (with \( T_g \)) and show stronger emission intensities via H-bonds. Besides, the dendritic donors act as efficient light-harvesting antennae capable of transferring light energy from their peripheral OXD arms to their emitting acceptors, where the chromophore luminescence induced by energy transfer is more efficient than that by direct excitation of the emitting cores. Compared with analogous dendritic mixtures without H-bonds, higher quantum yields were observed in the supramolecular dendrimers because of better energy transfer from OXD units. Therefore, compared with acceptor emitters, not only can the emission wavelength be tuned (up to 100 nm of red-shift) by H-bonds, but also much higher emission efficiencies of the H-bonded complexes were induced by reduced aggregation and energy transfer from the OXD donor dendrons.

Introduction

In the past decade, electroluminescent materials have attracted significant attention since the first contribution of small molecular organic light-emitting diodes (OLED) by Tang et al. and polymeric light-emitting diodes (PLED) by Friend et al. Because of their enormous potential applications in flat panel displays, great efforts have been paid to develop novel electroluminescent materials with intense luminescent efficiencies, good thermal/electrical/optical stabilities, and desirable film morphology.1–7

The luminescent quantum efficiencies of \( \pi \)-conjugated materials are substantially lower in the solid state than those in the solution state because of intermolecular interactions, such as aggregation and excimer formation, which lead to a self-quenching process of excitons.8,9 A very attractive way to solve this problem is to encase chromophores within dendritic architectures.10,11 By connecting bulky dendrons around a central dye moiety, it has been used to prevent the self-aggregation of chromophores in the solid state12,13 and also define the color of the light emission.14 Furthermore, chromophore-core dendrimers may be potentially useful as multifunctional emissive materials in OLED devices. For example, the proper charge transporting functionalities are incorporated at the periphery of the dendritic wedges. This may result in the improvement of imbalanced charge characters in organic luminescent materials.15,16 In light-harvesting antennae, the peripheral donor units can collect photons, and transfer excitation energy through bonds to the cores or focal points of the acceptors, thus to enhance luminescence efficiencies considerably. In addition, a special benefit is that the amorphous phase of chromophores can be significantly induced by well-defined dendritic structures which prevent from crystallization of chromophores to develop high quality films by spin-coating technique. It is important because melting and recrystallization, caused by heat or short-circuit currents, often result in device damages.17–19

Another route to overcome the \( \pi-\pi \) stacking phenomenon is the utilization of branching systems. In a previous report, oligo-(p-phenylenevinylene) (OPVs) have been oriented in a tetrahedral framework to minimize the intramolecular stacking.20 These tetrahedral arrays do not crystallize and thus form stable amorphous phases. However, it is very difficult to obtain branched systems because of their complicated synthetic routes and low yields. Supramolecules as well as supramolecular polymers can be prepared from two complementary components that are appropriately substituted with functional H-bonded donor and acceptor groups.21–23 The simpler synthetic molecules through supramolecular self-assembly often possess specific and useful chemical, physical, or optical properties due to the collective behavior of each other. Upon hydrogen-bonded (H-bonded) complexation with dendritic acceptors, the supramolecular dendrimers showed a significantly higher PL emission than those individual emitting OPVs alone, due to the three-dimensional orientation of the OPV emitting molecules.24

In our previous work,25 we have completed several series of H-bonded liquid crystalline trimers and H-bonded polymer networks, which were constructed by complexation of two complementary components containing various bifunctional photoluminescent (PL) acceptor cores and monofunctional proton donors (or donor polymers). These supramolecular trimers and H-bonded polymer networks demonstrate that different wavelengths of PL emissions and liquid crystalline phases can be achieved by introducing nonphotoluminescent proton donors (or donor polymers).
In this report, the design, synthesis, and optical properties of highly efficient light emitting H-bonded dendrimers with single/double H-bonds, i.e., symmetric/symmetric supramolecules as shown in Figure 2, are presented. A new strategy involving two complementary segments which contain monofunctional/bifunctional photoluminescent acceptor cores and dendritic donor wedges (bearing OXD segments) are explored. The key structural elements in the dendritic H-donors are various generations of functional poly(aryl ether) dendrons bearing outward OXD arms and a focal point of benzoic acid. This self-assembly of dendritic framework is expected to be effective for the construction of light-harvest of OXD arms and site-isolation of emitting cores. The absorption and emission spectra, as well as energy transfer of the H-bonded dendrimers are also studied to gain insight into the effect of dendritic wedges on the photoluminescent cores. Significantly, by choosing different generations of H-donors, the color of PL emission can be tuned. Even more, stronger fluorescence emission from OXD excitation can be obtained by reduced aggregation and energy transfer from OXD wedges in these supramolecular dendrimers. On the other hand, dendritic donor cores of poly(aryl ether) were also synthesized to form another chromophore-shelled dendrimers by complexation with the same emitting acceptors (as the peripheral emitting shells) in comparison with the previous chromophore-cored dendrimers. Hopefully, this study is expected to be helpful and constructive for the forthcoming researches about light-emitting dendrimers.

**Experimental Section**

**Measurements and Characterization.** ¹H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using CDCl₃ or DMSO-d₆ solvent with tetramethylsilane as reference. Elemental analyses were performed on a HERAEUS CHN-OS RAPID elemental analyzer. MALDI–TOF spectra were measured on a Biflex III (Bruker) time-of-flight mass spectrometer utilizing a 5-methoxysaliclyclic acid matrix. Fourier transform infrared (FTIR) spectra were performed a Nicolet 360 FT-IR spectrometer. Phase transition temperatures were determined by differential scanning calorimetry (Perkin-Elmer Diamond) with a heating and cooling rate of 10 °C/min and polarizing optical microscopy (Leica DMLP) equipped with a hot stage. UV–visible absorption spectra were recorded in dilute THF solutions (10⁻⁶ M) on a HP G1103A spectrophotometer, and photoluminescence (PL) spectra were obtained on a Hitachi F-4500 spectrophotometer. Thin films of UV–vis and PL measurements were spin-coated on a quartz substrate from THF solution with a concentration of 1 wt %. The fluorescence quantum yields (Φₚₗ) of the chromophores and H-bonded dendrimers were determined relative to a standard film of 9,10-diphenylanthracene dispersed in PMMA (Φ = 0.83).²⁶

**Materials.** Chemicals and solvents were reagent grades and purchased from Aldrich, ACROS, TCI, and Lancaster Chemical Co. Dichloromethane and THF were distilled to keep anhydrous before use. The other chemicals were used without further purification. All H-bonded dendrimers were prepared by slow evaporation of THF solution containing the mixtures of the acceptor and donor moieties, followed by drying in vacuo. All H-bonded complexes are made up of appropriate (fully H-bonded) molar ratios of acceptor and donor moieties in THF.

**Synthesis.** Compounds 1–3 and 10 were obtained by following the previous literature.²⁷-²⁸ The synthetic procedures of all donor dendrimers of various generations containing OXD moieties are described in Schemes 1 and 2. Besides, Scheme 3 shows dendritic donor cores, which are H-bonded with emitting acceptor shells. Synthesis and characterization of all mono-pyridyl and bis-pyridyl acceptor chromophores PBBPEC-OCS (17), PBBCN-OCS (18), PBB-OC₈ (19), PBBP-Me-OC₈ (20), and their intermediates (as shown in Figure 1) are described in the Supporting Information.

**General Synthetic Procedures of Dendritic Benzoic Acid Methy1Esters(G1COOCH₃(4),G2COOCH₃(5),andG3COOCH₃(6)).** A mixture of 1, 2, or 3 (2.1 equiv), 3,5-dihydroxybenzoate (1 equiv), K₂CO₃ (2.5 equiv), and 18-crown-6 (0.2 equiv) in dry THF was heated to reflux and stirred under nitrogen for 24 h. The mixture was evaporated to dry under reduced pressure, and the residue was partitioned between water and CH₂Cl₂. Later on, the aqueous layer was extracted with CH₂Cl₂, and the organic layer was dried over MgSO₄. Consequently, the crude products G1COOCH₃ (4), G2COOCH₃ (5), and G3COOCH₃ (6) were purified as outlined in the following text.

G1COOCH₃ (4), G1COOCH₃ (4) was purified by column chromatography with EA/CH₂Cl₂ (1:10) to get a white solid. Yield: 63%. ¹H NMR (ppm, CDCl₃): δ 0.86–0.95 (m, 12H), 1.23–1.54 (m, 16H), 1.70–1.76 (m, 2H), 3.90–3.91 (overlap, 7H), 5.15 (s, 4H), 6.81 (s, 1H), 7.00 (d, J = 9 Hz, 4H), 7.30 (s, 2H), 7.57 (d, J = 8.4 Hz, 4H), 8.04 (d, J = 9 Hz, 4H), 8.13 (d, J = 8.4 Hz, 4H). MS (MALDI–TOF): m/z [MH⁺] 1861.92. Calcld m/z [MH⁺] 1861.23; calcd m/z [MH⁺] 1861.23.

G2COOCH₃ (5), G2COOCH₃ (5) was purified by column chromatography with EA/CH₂Cl₂ (1:8) to get a white solid. Yield: 73%. ¹H NMR (ppm, CDCl₃): δ 0.92–0.97 (m, 24H), 1.33–1.53 (m, 32H), 1.74–1.81 (m, 4H), 3.88–3.92 (overlap, 11H), 5.02 (s, 4H), 5.10 (s, 8H), 6.57 (s, 2H), 6.69 (s, 4H), 6.74 (s, 1H), 7.00 (d, J = 8.4 Hz, 8H), 7.26 (s, 2H), 7.55 (d, J = 8.1 Hz, 8H), 8.04 (d, J = 8.1 Hz, 8H), 8.10 (d, J = 7.5 Hz, 8H). MS (MALDI–TOF): m/z [MH⁺] + 1861.23; calcd m/z [MH⁺] 1861.23.

G3COOCH₃ (6), G3COOCH₃ (6) was purified by column chromatography with THF/CH₂Cl₂ (1:8) to get a white solid. Yield: 70%. ¹H NMR (ppm, CDCl₃): δ 0.91–0.96 (m, 48H), 1.32–1.54 (m, 64H), 1.70–1.76 (m, 8H), 3.85 (s, 3H), 3.89 (d, J = 5.7 Hz, 16H), 4.96–5.04 (overlap, 28H), 6.50 (s, 2H), 6.52 (s, 4H), 6.62 (s, 4H), 6.65 (s, 8H), 6.71 (s, 1H), 6.98 (d, J = 9 Hz, 16H), 7.23 (s, 2H), 7.50 (d, J = 8.1 Hz, 16H), 8.00 (d, J = 9 Hz, 16H), 8.06 (d, J = 8.4 Hz, 16H). MS (MALDI–TOF): m/z [MH⁺] 3800.23; calcd m/z [MH⁺] 3800.39.

G1COOH (7). To a solution of G1COOCH₃ (4) (1.0 equiv) in THF was added KOH (5 equiv) dissolved in water. A small amount of methanol was then added to the two-phase mixture to afford a homogeneous solution. The reaction was heated at reflux for 24 h. After the solution was cooled to room temperature, hydrochloric acid was added to precipitate the product G1COOH (7), which was isolated by filtration, washed with water and dried overnight in a vacuum oven. Yield: 80%. ¹H NMR (ppm, DMSO-d₆): δ 8.05–0.90 (m, 12H), 1.28–1.45 (m, 16H), 1.68–1.74 (m, 2H), 3.92
G2COOH (8). This compound was prepared from G2COOHCl (5) by the same synthesized procedure as that of G1COOH (8). Yield: 85%. 1H NMR (ppm, CDCl3): δ 0.90–0.95 (m, 24H), 1.32–1.53 (m, 32H), 1.71–1.75 (m, 4H), 3.86 (d, J = 5.4 Hz, 8H), 5.00 (overlap, 12H), 6.50 (s, 2H), 6.65 (s, 4H), 6.75 (s, 1H), 6.96 (d, J = 8.7 Hz, 8H, 7.31 (s, 2H), 7.49 (d, J = 8.1 Hz, 8H), 7.99 (d, J = 8.7 Hz, 8H), 8.05 (d, J = 8.1 Hz, 8H). MS (MALDI–TOF): m/z [MH+]+ 1848.88; calcld m/z [MH+]+ 1849.22. Anal. Calcld for C113H122N8O16: C, 73.43; H, 6.65; N, 6.06. Found: C, 73.04; H, 6.74; N, 6.42.

G3COOH (9). This compound was prepared from G3COOHCl (6) by the same synthesized procedure of G1COOH (9). Yield: 82%. 1H NMR (ppm, CDCl3): δ 0.90–0.95 (m, 48H), 1.26–1.55 (m, 64H), 1.71–1.75 (m, 8H), 3.86 (d, J = 5.4 Hz, 16H), 4.91–4.98 (overlap, 28H), 6.50 (overlap, 6H), 6.56–6.70 (overlap, 13H), 6.95 (d, J = 8.7 Hz, 16H), 7.27 (t, J = 8.4 Hz, 16H), 7.97 (d, J = 9 Hz, 16H), 8.02 (d, J = 8.4 Hz, 16H). MS (MALDI–TOF): m/z [MH+]+ 3787.14; calcld m/z [MH+]+ 3787.57. Anal. Calcld for C231H256N16O16: C, 73.91; H, 6.65; N, 5.92. Found: C, 73.63; H, 6.51; N, 6.04.

11. Sodium hydride (3 equiv) in anhydrous THF was slowly added into a stirred solution of compound 10 (1 equiv) in dry THF under nitrogen. After 10 min of stirring, 1,6-dimethoxyhexane (5 equiv) was added. After being stirred overnight, the reaction mixture was quenched with water. The mixture was evaporated to dry under reduced pressure, and the residue was partitioned between water and CH2Cl2. Then, the aqueous layer was extracted with CH2Cl2, and the organic layer was dried over MgSO4. Finally, the crude product was purified by column chromatography with CH2Cl2/Hexane (1:2) to get a white oil. Yield: 67%. 1H NMR (ppm, CDCl3): δ 1.27 (m, 12H), 1.55–1.57 (m, 2H), 1.82–1.87 (m, 2H), 3.35–3.44 (overlap, 4H), 4.41 (s, 2H), 5.08 (s, 4H), 6.46 (s, 1H), 6.57 (s, 2H), 7.51 (d, J = 8.1 Hz, 4H), 7.65 (d, J = 8.1 Hz, 4H).

12. The previous procedure was followed using sodium hydride (3 equiv), compound 10 (1 equiv), and 1,6-dimethoxy-decane (5 equiv). The crude product was purified by column chromatography with CH2Cl2/Hexane (1:2) to get a white oil. Yield: 67%. 1H NMR (ppm, CDCl3): δ 1.27 (m, 12H), 1.55–1.57 (m, 2H), 1.82–1.87 (m, 2H), 3.35–3.44 (overlap, 4H), 4.41 (s, 2H), 5.08 (s, 4H), 6.46 (s, 1H), 6.57 (s, 2H), 7.51 (d, J = 8.1 Hz, 4H), 7.65 (d, J = 8.1 Hz, 4H).

Figure 2. Schematic representation of asymmetric encapsulation of single H-bonded acceptor emitter PBBN-OCA (18) and symmetric encapsulation of double H-bonded acceptor emitter PBP-OCA (19) with different generations (G1-G3) of dendritic donors.

General Synthetic Procedures of Dendritic Trialkylated Donor Cores (13 and 14). A mixture of 11 or 12 (3.1 equiv), 1.11-tris(4-hydroxyphenyl)ethane (1.0 equiv), K2CO3 (4.0 equiv), and 18-crown-6 (0.3 equiv) in dry THF was heated to reflux and stirred vigorously under nitrogen for 24 h. The mixture was evaporated to dry under reduced pressure, and the residue was partitioned between water and CH2Cl2. Then, the aqueous layer was extracted with CH2Cl2, and the organic layer was dried over MgSO4. Consequently, the crude products 13 or 14 were purified as outlined in the following text.

13. Compound 13 was purified by column chromatography with EA/CH2Cl2 (1:10) to get a slight yellow oil. Yield: 51%. 1H NMR (ppm, CDCl3): δ 1.26–1.43 (m, 12H), 1.57–1.63 (m, 6H), 1.72–1.78 (m, 6H), 2.03 (s, 3H), 3.43 (t, 6H), 3.90 (t, 6H), 4.41 (s, 6H), 5.07 (s, 12H), 6.45 (s, 3H), 6.57 (s, 6H), 6.73 (d, J = 9 Hz, 6H), 6.94 (d, J = 8.4 Hz, 6H), 7.50 (d, J = 8.1 Hz, 12H), 7.65 (d, J = 8.4 Hz, 12H).

14. Compound 14 was purified by column chromatography with EA/CH2Cl2 (1:10) to get a slight yellow oil. Yield: 42%. 1H NMR (ppm, CDCl3): δ 1.23–1.40 (m, 36H), 1.55–1.59 (m, 6H), 1.70–1.75 (m, 6H), 2.07 (s, 3H), 3.42 (t, 6H), 3.88 (t, 6H), 4.41 (s, 6H), 5.08 (s, 12H), 6.45 (s, 3H), 6.57 (s, 6H), 6.74 (d, J = 9 Hz, 6H), 6.95 (d, J = 9 Hz, 6H), 7.50 (d, J = 8.4 Hz, 12H), 7.65 (d, J = 8.4 Hz, 12H).

G1-C16(COOH)6 (15). This compound was prepared from 13 by the same synthesized procedure of G1-COOH (7). Yield: 77%. 1H NMR (ppm, DMSO-d6): δ 1.34 (m, 12H), 1.47–1.49 (m, 6H), 1.65 (m, 6H), 1.96 (s, 3H), 3.33 (t, 6H), 3.86 (t, 6H), 4.35 (s, 6H), 5.14 (s, 12H), 6.57 (overlap, 9H), 6.76 (d, J = 8.7 Hz, 6H), 6.85 (d, J = 8.7 Hz, 6H), 7.51 (d, J = 8.1 Hz, 12H), 7.94 (d, J = 7.8 Hz, 12H), 12.94 (broad, COOH). MS (MALDI–TOF): m/z [M+K]+ 1817.14; calcld m/z [M+K]+ 1816.08. Anal. Calcld for C215H184O65K6: C, 72.28; H, 6.12. Found: C, 71.95; H, 6.31.

G1-C16(COOH)6 (16). This compound was prepared from 14 by the same synthesized procedure of G1-COOH (7). Yield: 80%. 1H NMR (ppm, DMSO-d6): δ 1.21 (m, 36H), 1.44 (m, 6H), 1.61 (m, 6H), 1.97 (s, 3H), 3.31 (t, 6H), 3.84 (t, 6H), 4.33 (s, 6H), 5.14 (s, 12H), 6.57 (overlap, 9H), 6.75 (d, J = 8.7 Hz, 6H), 6.86 (d, J = 9 Hz, 6H), 7.51 (d, J = 8.1 Hz, 12H), 7.94 (d, J = 8.1 Hz, 12H), 12.94 (broad, COOH). MS (MALDI–TOF): m/z [M+K]+ 1985.31; calcld m/z [M+K]+ 1984.40. Anal. Calcld for C194H164O54K6: C, 73.44; H, 6.84. Found: C, 73.14; H, 6.76.
Results and Discussion

Synthesis and Characterization. As shown in Schemes 1—3, all H-bonded donors were synthesized via a previously reported convergent method. In the presence of K2CO3 with THF at reflux, 3,5-dihydroxy-benzoic acid methyl ester reacted with various corresponding generations of dendrons (1, 2, and 3) to obtain G1COOCH3 (4), G2COOCH3 (5), and G3COOCH3 (6), which were followed by hydrolysis reaction with KOH in methanol/THF at reflux to give G1COOH (7), G2COOH (8), and G3COOH (9). Another series of dendrimers (13 and 14) were prepared by coupling dendritic wedges to a polyfunctional core and followed by hydrolysis reaction to give G1-C6-(COOH)6 (15) and G1-C10-(COOH)6 (16) as shown in Scheme 3. The polyfunctional core chosen in this case was 1,1,1-tris-(4'-hydroxyphenyl)ethane, and the resulting molecules were characterized by NMR spectroscopy, MALDI–TOF mass spectroscopy, and elemental analysis.

All H-bonded complexes are made up of appropriate (fully H-bonded) molar ratios of acceptor and donor moieties in THF. Thus, symmetric supramolecular dendrimers were produced by complexation of double H-bonded acceptor emitters PBP-OC8 (19) and PBBBP-Me-OC8 (20) with dendritic donors G1COOH (7), G2COOH (8), and G3COOH (9) in a molar ratio of 1:2, respectively; and asymmetric supramolecular dendrimers were generated by complexation of single H-bonded acceptor emitters PBBOC8-OC8 (17) and PBBCN-OC8 (18) with dendritic donors G1COOH (7), G2COOH (8), and G3COOH (9) in the molar ratio of 1:1, respectively. Furthermore, the single H-bonded acceptor emitters PBBOC8-OC8 (17) and PBBCN-OC8 (18) were complexed with another type of dendritic donor cores G1-C6-(COOH)6 (15) and G1-C10-(COOH)6 (16) in the molar ratio of 6:1 to form exterior emitting shells. In addition, the double H-bonded acceptor emitters PBP-OC8 (19) and PBBBP-Me-OC8 (20) (as H-bonded cross-linkers) were also complexed with
dendritic donor cores G1-C16-(COOH)₆ (15) and G1-C₁₆-(COOH)₆ (16) in the molar ratio of 6:2 to form cross-linked H-bonded emitting shells. The three-dimensional dendritic scaffolding of H-bonded dendrimer design provides the desired amorphous films without crystallization and leads to good film qualities by spin-coating. The resulting supramolecular H-bonded assemblies were investigated with respect to their photophysical and thermal properties.

The existence of hydrogen bonds in the H-bonded complexes can be characterized by IR spectra. Therefore, the IR spectra of PBBCN-OC₈ (18), G1COOH (7), and H-bonded complex of PBBCN-OC₈/G1COOH (18/7) shown in Figure 3 are compared to analyze the hydrogen bonds. In contrast to the O–H band of pure G1COOH (7) (H-bonded dimer) at 2604 cm⁻¹, the weaker O–H band observed at 1911 and 2500 cm⁻¹ in the H-bonded complex PBBCN-OC₈/G1COOH (18/7) is indicative of stronger hydrogen bonding between the pyridyl group of PBBCN-OC₈ (18) and the carboxylic acid of G1COOH (7) in the H-bonded complex. On the other hand, a C=O stretching vibration appeared at 1710 cm⁻¹ in the H-bonded complex PBBCN-OC₈/G1COOH (18/7), which show that the carbonyl group was in a less associated state than that in pure G1COOH (7) (H-bonded dimer) with weaker C=O stretching vibration appeared at 1695 cm⁻¹. Both results suggest that hydrogen bonds formed between PBBCN-OC₈ (18) and G1COOH (7) in the solid state of the H-bonded complex PBBCN-OC₈/G1COOH (18/7). The other H-bonded complexes discussed in this study should have similar consequences as the demonstrated complexes.³⁰

Thermal Properties. To elucidate the H-bonding effect on the thermal properties of the H-bonded dendrimers, all compounds were characterized by differential scanning calorimetry (DSC). Polarizing optical microscopy (POM) demonstrated that no phase separation took place between donors and acceptors in the H-bonded dendrimers. In addition, the third-generation (G3) of H-bonded dendrimers containing G3COOH (9) have higher isotropization temperatures (Tᵢ) than the lower generations of H-bonded dendrimers. As shown in Table 1, it is observed that dendritic donors G1COOH (7), G2COOH (8), and G3COOH (9) possess the glass transition temperatures (T₉) at

![Scheme 2](https://example.com/scheme2.png)
51, 63, and 72 °C, respectively. Because of higher molecular weights in the higher generations of dendrimers, the glass transition temperatures of the H-bonded dendrimers with higher generations were observed to increase monotonically. The behavior is consistent with the trends of the glass transition temperatures in earlier studied dendrimers.31,32 As for the acceptor, PBP-OC8 (19) exhibits a melting temperature at 137 °C without Tg, indicating the crystalline nature of the molecule. However, H-bonds have a strong effect on the thermal properties by the introduction of OXD dendritic donors (bearing benzoic acids) to the emitting acceptor PBP-OC8 (19) via H-bonded self-assembly. Symmetric H-bonded dendrimers PBP-OC8/G1COOH (19/7), PBP-OC8/G2COOH (19/8), and PBP-OC8/G3COOH (19/9) reveal distinct glass transition temperatures at 26, 48, and 65 °C, respectively, which are lower than their corresponding dendritic donors (owing to the formation of H-bonded dimers by two dendritic acids). Similar phenomena were observed in the other H-bonded dendrimers (see Table 1). The incorporation of OXD dendrons into the supramolecular structures shows no melting (only observed in POM) and crystallization peaks in DSC measurements, but Tg only. This clearly indicates that the OXD bulkly wedges in these H-bonded dendrimers effectively suppress the crystallization and reduce the chain aggregation of the emitting cores.

Another interesting trend is that all generations of dendritic analogues have the same order of transition temperatures in Tg and T1 for the H-bonded dendrimers containing the following emitting acceptors: PBBBP-Me-OC8 (20) > PBP-OC8 (19) > PBBCN-OC8 (18) > PBBOC8-OC8 (17). The result of higher Tg and T1 in symmetric supramolecular dendrimers (H-bonded
trimers) containing PBBBP-Me-OC₈ (20) and PBP-OC₈ (19) than asymmetric supramolecular dendrimers (H-bonded dimers) containing PBBCN-OC₈ (18) and PBBOC₆-OC₈ (17) may be explained by the higher molecular weights of H-bonded trimers in the symmetric supramolecular dendrimers. Higher $T_g$ and $T_i$ in H-bonded dendrimer containing PBBBP-Me-OC₈ (20) than that containing PBP-OC₈ (19) is due to the longer central core of PBBBP-Me-OC₈ (20). Besides, higher $T_g$ and $T_i$ in H-bonded dendrimer containing PBBBP-Me-OC₈ (20) than that containing PBBOC₆-OC₈ (17) is because of the dipole–dipole interaction of CN groups in PBBCN-OC₈ (18). In the reverse H-bonded dendrimers (containing emitting shells), e.g. PBBBP-Me-OC₈ (20), PBP-OC₈ (19), PBBCN-OC₈ (18), and PBBOC₆-OC₈ (17) were complexed with dendritic donor cores G1-C₆-(COOH)₆ (15) and G1-C₁₀-(COOH)₆ (16) in proper ratios, no phase transition peaks were found, which is probably due to the flexible chains of the polyfunctional cores in the H-bonded dendritic donors. Similar behavior in polypropylene dendrimers containing trialkoxybenzene wedges as mesogenic units was reported in the literature.²³–²⁴

**Optical Properties.** The absorption and PL spectral data of the pure chromophores (in THF and solid films) and all H-bonded dendrimers in solid films are summarized in Table 2. Figure 4a shows the absorption spectra of uncomplexed H-bond donors and acceptor PBBCN-OC₈ (18) in THF solutions. The series of H-bonded dendrimers show very similar absorption and emission characteristics in the solid films. Figure 4b shows various asymmetric H-bonded dendrimers containing single H-bonded acceptor emitter PBBCN-OC₈ (18) in solid films. In the asymmetric supramolecular complexes bearing dendriformically mono-encapsulated chromophores, i.e., PBBCN-OC₈/G1COOH (18/7), PBBCN-OC₈/G2COOH (18/8), and PBBCN-OC₈/G3COOH (18/9), the absorption peak at 305 nm was attributed to the transition absorption of OXD groups and the longer absorption peak at 423 nm was attributed to the characteristic absorption of emitter PBBCN-OC₈ (18). By increasing the generation of the dendritic donors in the H-bonded complexes, the absorbance of OXD units at 305 nm is proportional to the generation number of the dendrimers. In view of Figure 5, the PL emission spectrum of PBBCN-OC₈ (18) showed a characteristic peak at 470 nm in THF, which is red-shifted to 512 nm in solid films due to the formation of π–π stacking and molecular aggregation. In contrast to the single H-bonded acceptor emitter PBBCN-OC₈ (18) alone, the asymmetric supramolecular dendrimers PBBCN-OC₈/G1COOH (18/7), PBBCN-OC₈/G2COOH (18/8), and PBBCN-OC₈/G3COOH (18/9) exhibit red-shifted PL emissions with values of $\lambda_{max}$ at 554, 541, and 531 nm excited at 423 nm, respectively. This result is similar to our previous work,²⁵ where the photoluminescent H-bonded trimers containing bifunctional bis-pyridyl acceptors complexed with monofunctional carboxylic acids show red-shifted PL spectra as the acceptor emitters are H-bonded to donors with smaller pKa values. As well-known that pH values of aqueous solutions may affect photoluminescence properties of polyelectrolytes containing pyridine units. Therefore, the H-bonded dendritic donors G1COOH (7), G2COOH (8), and G3COOH (9) bearing benzoic acid groups can be regarded as acidic solvents, so the PL spectra reveal red-shifted PL emissions compared with that of emitter PBBCN-OC₈ (18) in THF. Interestingly, different generations of asymmetric H-bonded dendrimers containing single H-bonded acceptor emitter PBBCN-OC₈ (18) appeared to have different degrees of red-shifted PL emissions. The red-shifts of PL emissions in asymmetric H-bonded dendrimers PBBCN-OC₈/G1COOH (18/7), PBBCN-OC₈/G2COOH (18/8), and PBBCN-OC₈/G3COOH (18/9) are 84, 71, and 61 nm, respectively, where the higher generations of the H-bonded dendrimers have smaller red-shifted PL emissions than the lower generations of the H-bonded dendrimers. It clearly indicates that larger dendritic wedges have higher site-isolation or dendron dilution effect than smaller dendritic ones, so the higher generations of dendrimers efficiently reduce the aggregation extent of the emitting cores. The opposite type of H-bonded dendritic complexes containing poly(alkyl aryl ether) dendrimers (dendritic donor core) complexed with a single H-bonded acceptor emitter PBBCN-OC₈ (18) at the periphery; i.e., PBBCN-OC₈/G1-C₆-(COOH)₆ (18/7), PBBCN-OC₈/G2COOH (18/8), and PBBCN-OC₈/G3COOH (18/9)
Table 2. Photophysical Properties of H–Bonded Acceptors and Dendritic Complexes

<table>
<thead>
<tr>
<th>Compound or H-bonded complex</th>
<th>PL, sol (nm)</th>
<th>PL,film (nm)</th>
<th>ΦPL,film</th>
<th>RFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBBOC8-OC8 (17)</td>
<td>463</td>
<td>468 (495)</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>PBBOC8-OC8/G1COOH (17/7)</td>
<td>569</td>
<td>569</td>
<td>0.11</td>
<td>0.87</td>
</tr>
<tr>
<td>PBBOC8-OC8/G2COOH (17/8)</td>
<td>562</td>
<td>562</td>
<td>0.19</td>
<td>1.14</td>
</tr>
<tr>
<td>PBBOC8-OC8/G3COOH (17/9)</td>
<td>555</td>
<td>555</td>
<td>0.23</td>
<td>2.16</td>
</tr>
<tr>
<td>PBBOC8-OC8/G1-C6-(COOH)14 (17/15)</td>
<td>570</td>
<td>570</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>PBBOC8-OC8/G1-C10-(COOH)14 (17/16)</td>
<td>558</td>
<td>558</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>PBBCN-OC8 (18)</td>
<td>470</td>
<td>512</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>PBBCN-OC8/G1COOH (18/7)</td>
<td>556</td>
<td>556</td>
<td>0.20</td>
<td>0.73</td>
</tr>
<tr>
<td>PBBCN-OC8/G2COOH (18/8)</td>
<td>543</td>
<td>543</td>
<td>0.26</td>
<td>0.97</td>
</tr>
<tr>
<td>PBBCN-OC8/G3COOH (18/9)</td>
<td>532</td>
<td>532</td>
<td>0.32</td>
<td>1.97</td>
</tr>
<tr>
<td>PBBCN-OC8/G1-C6-(COOH)14 (18/15)</td>
<td>556</td>
<td>556</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>PBBCN-OC8/G1-C10-(COOH)14 (18/16)</td>
<td>550</td>
<td>550</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>PBP-OC8 (19)</td>
<td>460</td>
<td>482 (506)</td>
<td>0.08</td>
<td></td>
</tr>
<tr>
<td>PBP-OC8/G1COOH (19/7)</td>
<td>545</td>
<td>545</td>
<td>0.20</td>
<td>1.27</td>
</tr>
<tr>
<td>PBP-OC8/G2COOH (19/8)</td>
<td>539</td>
<td>539</td>
<td>0.26</td>
<td>2.33</td>
</tr>
<tr>
<td>PBP-OC8/G3COOH (19/9)</td>
<td>522</td>
<td>522</td>
<td>0.33</td>
<td>4.50</td>
</tr>
<tr>
<td>PBP-OC8/G1-C6-(COOH)14 (19/15)</td>
<td>539</td>
<td>539</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>PBP-OC8/G1-C10-(COOH)14 (19/16)</td>
<td>533</td>
<td>533</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>PBP-OC8/G1-C10-(COOH)14 (19/4)</td>
<td>482 (506)</td>
<td>482 (506)</td>
<td>0.13</td>
<td>0.55</td>
</tr>
<tr>
<td>PBP-OC8/G2COOCH3 (19/5)</td>
<td>499</td>
<td>499</td>
<td>0.18</td>
<td>1.04</td>
</tr>
<tr>
<td>PBP-OC8/G3COOCH3 (19/6)</td>
<td>506</td>
<td>506</td>
<td>0.19</td>
<td>1.27</td>
</tr>
<tr>
<td>PBBP-Me-OC8/G1COOH (20/7)</td>
<td>511</td>
<td>535 (567)</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>PBBP-Me-OC8/G2COOH (20/8)</td>
<td>607</td>
<td>607</td>
<td>0.16</td>
<td>0.39</td>
</tr>
<tr>
<td>PBBP-Me-OC8/G3COOH (20/9)</td>
<td>588</td>
<td>588</td>
<td>0.22</td>
<td>1.06</td>
</tr>
<tr>
<td>PBBP-Me-OC8/G1-C6-(COOH)14 (20/15)</td>
<td>568</td>
<td>568</td>
<td>0.32</td>
<td>1.61</td>
</tr>
<tr>
<td>PBBP-Me-OC8/G1-C10-(COOH)14 (20/16)</td>
<td>610</td>
<td>610</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>PBBP-Me-OC8/G1-C10-(COOH)14 (20/16)</td>
<td>602</td>
<td>602</td>
<td>0.10</td>
<td></td>
</tr>
</tbody>
</table>

* The relative fluorescent intensities (RFI) were calculated by the ratio of the core emission intensities excited at the OXD unit and the core absorption peaks.

Figure 4. UV–vis absorption spectra of (a) uncomplexed H-bond donors and acceptor PBBCN-OC8 (18) in THF solutions and (b) PBBCN-OC8 (18) and its H-bonded dendrimers in solid films, which are normalized at the absorption peak of PBBCN-OC8 (18) at 423 nm. The relative fluorescent intensities (RFI) were calculated by the ratio of the core emission intensities excited at the OXD unit and the core absorption peaks.

15) and PBBOC8-OC8/G1-C10-(COOH)14 (18/16), also both exhibit red-shifted emission peaks at 556 and 550 nm, respectively, compared with that of PBBCN-OC8 (18) in THF. With respect to PBBCN-OC8/G1-C6-(COOH)14 (18/15), the relative 6 nm blue-shift of PL emission in PBBCN-OC8/G1-C10-(COOH)14 (18/16) may be explained by that the longer flexible alkyl chains (as solid solvents) in the dendritic donor cores result in higher dilution effect for emitting acceptors. It is worthy noticing that the PL emission spectra of PBBCN-OC8/G1-C6-(COOH)14 (18/15) and PBBCN-OC8/G1-C10-(COOH)14 (18/16) are similar to that of PBBCN-OC8/G1COOH (18/7), which means that poly(alkyl aryl ether) dendritic acid cores in the reverse form of the previous H-bonded dendrimers affect PL emission behavior of PBBCN-OC8 (18) in a similar way as the lower generation of G1COOH (7). Figure 6 shows the PL emission characteristics of emitter PBP-OC8 (19) and its double H-bonded dendrimers with symmetric structures. All PL emission data are summarized in Table 2, which demonstrate similar trends as those of single H-bonded acceptor emitter PBBBCN-OC8 (18) and its asymmetric H-bonded dendrimers. Compared with single H-bonded dendrimers, no further red-shifted PL emissions were observed in the double H-bonded dendrimers due to the weaker H-bonded effect of the second H-bonds on the conjugated structures of double H-bonded acceptors and the double dilution effect from double amount of donor acids.

Because of significant overlap in the absorption spectra of the representative chromophores (compounds 17, 18, 19, and 20) and the emission spectrum of model compound 1 in Figure 7, the energy transfer from the OXD dendritic groups to the central emitters can be expected, which was also probed by photoluminescent excitation (PLE) spectra of H-bonded dendrimers containing PBP-OC8 (19) as shown in Figure 8. Similar spectral features of PLE spectra appear to match those of the corresponding absorption spectra, where both peaks (ca. 300 and 425 nm) exist, indicating that the peripheral OXD units in such supramolecular dendrimers possess light-harvesting capability. Hence, the functionalized OXD dendron units or the emitting core PBP-OC8 (19) can be independently addressed by changing the excitation wavelength. By excitation of the dendrons and the cores selectively, it provides a window to study
the photoinduced energy transfer between H-bonded donors and acceptors. As shown in Figure 9, when the dendritic OXD groups were excited at 305 nm, the symmetric H-bonded dendrimers containing PBP-OC$_8$ (19), i.e., PBP-OC$_8$/G1COOH (19/7), PBP-OC$_8$/G2COOH (19/8), and PBP-OC$_8$/G3COOH (19/9), emit fluorescence at wavelengths of 545, 539, and 522 nm, respectively. The photoexcitation of H-bonded dendrimers at the maximum absorption wavelength of OXD units apparently generated identical predominant emission peaks as those excited at the maximum absorption of PBP-OC$_8$ (19). Whereas, no luminescence was detected from the major emission of OXD dendron, and thus the energy transfer of OXD emission from the dendritic wedges to the central emitting cores is confirmed. In addition, the values of relative fluorescent intensities (RFI) were calculated from the intensity ratio of core emissions by respective excitations at the maximum absorption peaks of the OXD dendrons and the emitting cores (ca. 300 and 425 nm, respectively). The values of RFI from H-bonded G1 to G3 dendrimers are 1.27, 2.33, and 4.50, respectively. The results indicate that the intensity of the sensitized emission (by energy transfer from OXD dendritic absorption at 300 nm) is even stronger than that of the direct core emission (by core absorption at 425 nm) in the H-bonded dendrimers. Therefore, sensitization by the telechelic antennae is more efficient than direct excitation at the maximum absorption of the chromophore. The increasing tendency from H-bonded G1 to G3 dendrimers unambiguously suggests that the more number of grafted OXD units (higher generations) in the dendrons, the higher capability of light-harvest. However, in contrast to symmetric H-bonded (G1-G3) dendrimers containing double H-bonded acceptor emitter PBP-OC$_8$ (19), where all RFI values are larger than 1 in all generations of H-bonded dendrimers, the enhancement of the core emission in the asymmetric H-bonded dendrimers containing single H-bonded acceptor emitter PBBCN-OC$_8$ (18) (as

Figure 5. Normalized PL spectra of mono-pyridyl (single H-bonded) acceptor emitter PBBCN-OC$_8$ (18) and its H-bonded dendrimers.

Figure 6. Normalized PL spectra of bis-pyridyl (double H-bonded) acceptor emitter PBP-OC$_8$ (19) and its H-bonded dendrimers.
excited at the maximum absorption of OXD dendron) only occurred in the third generation of H-bonded dendrimers PBBCN-OC8/G3COOH as shown in Figure 10. One of the major reasons should be attributed to that single H-bonded acceptor emitter PBBCN-OC8 is complexed only with one H-bonded donor (energy-transfer donor) in the molar ratio of 1:1 to result in the relatively lower enhancement of fluorescent intensity, as compared with double H-bonded acceptor emitter PBP-OC8 complexed with two H-bonded donor (energy-transfer donor) in the molar ratio of 1:2.

The possible behavior of supramolecular aggregation might be explained as shown in Figure 11. To balance the contribution of the number of OXD units in asymmetric/symmetric H-bonded dendrimers, the complexation of G1 donors with double H-bonded acceptor emitters should be comparable with the complexation of G2 donors with single H-bonded acceptor emitters as shown in Figure 11b–d, which all possess four OXD units in each asymmetric/symmetric H-bonded dendrimer. Interestingly, comparing asymmetric H-bonded dendrimers with four OXD units on one donor side of asymmetric ones and two
bonded dendrimers containing single H-bonded acceptor emitters PBBOC8-OC8 (17) and PBBCN-OC8 (18), both acceptor emitters are encapsulated by single-side dendrons, but, as shown in Figure 11d, PBBCN-OC8 (18) in H-bonded dendrimers is further aggregated by the dipole–dipole interaction of CN groups. However, comparing symmetric H-bonded dendrimers PBP-OC8/G1COOH (19/7) and PBP-OC8/G2COOH (19/8) in Figure 11a,b, not only the number of the OXD units but also the distance between OXD units and the central acceptor emitter is of major concern for the energy transfer regarding the RFI value. In general, the energy transfer is highly dependent on a number of factors, including the extent of aggregation, the relative orientation of the transition dipoles, the extent of the spectral overlap, and the distance between the donor and acceptor moieties. For instance, the overlap extent between the absorption spectra of the representative chromophores PBP-OC8 (19), PBBOC8-OC8 (17), and PBBCN-OC8 (18) and the emission spectrum of model compound 1 are approximately similar in Figure 7. In corresponding study of the H-bonded dendrimers containing double H-bonded acceptor emitter PBBBP-Me-OC8 (20) with longer conjugation length (Figure 12), PBBBP-Me-OC8/G2COOH (20/8) and PBBBP-Me-OC8/G3COOH (20/9) excited at the peripheral dendritic OXD units exhibit higher fluorescent intensities than those excited at direct PBBBP-Me-OC8 (20) absorption, except for the lowest generation of H-bonded dendrimer PBBBP-Me-OC8/G1COOH (20/
of OXD dendrons and the absorption of PBBBP-Me-OC \(_8\) (PBP-OC \(_8\)) emitter. Compared with H-bonded dendrimers containing acceptor PL spectra of symmetric supramolecular dendrimers Figure 12. Wu and Lin containing double H-bonded acceptor emitter PBBBP-Me-OC \(_8\) (20) in H-bonded G1-G3 dendrimers (at 450, 446, 439 nm, respectively, for solid symbols).

7). Compared with H-bonded dendrimers containing acceptor emitter PBP-OC \(_8\) (19), the less spectral overlap in the emission of OXD dendrons and the absorption of PBBBP-Me-OC \(_8\) (20) in Figure 7 seems to explain the min reason for lower energy transfer (i.e., lower RFI values) of OXD units to chromophores in H-bonded counterparts containing acceptor emitter PBBBP-Me-OC \(_8\) (20).

In all H-bonded dendrimers containing emitting cores, the PL efficiencies are higher than pure chromophores and the values are much enhanced (the maximum value of 4 times larger) in the higher generation of H-bonded dendrimers, which is in accordance with the results obtained previously. This improvement of PL efficiencies should be attributed to the bulky OXD dendrons refraining from the aggregation of chromophores. These results consistently indicate that the dendritic wedges play an important role of shielding/isolating effects among the cores. However, the PL efficiencies are not obviously improved by the complexation of chromophores with functionalized poly(aryl acyl ether) donor dendrimers containing peripheral carboxylic acid units to form exterior emitting shells (reverse to the previous system with emitting cores). Therefore, the supramolecular anchoring of chromophores on the dendritic surface by H-bonds to form exterior emitting shells seems to be inefficient to solve the intermolecular aggregation of chromophores. Thus, the RFI values strongly depend on the types of emitters (including single/double H-bonded sites and dipole moments) and the generation number of OXD dendrons (including the number of OXD units in the H-bonded donors along with the distance between OXD units and chromophores).

To evaluate the H-bonding effect on the efficiency of energy transfer within H-bonded dendrimers, analogous dendritic mixtures without H-bonds were prepared by the esterification of the dendritic acids and then mixing with corresponding chromophores. Because of the lack of H-bonds between two components, the simple mixtures of PBP-OC \(_8\)/G1COOH \(_8\) (19/4), PBP-OC \(_8\)/G2COOCH \(_3\) (19/5), and PBP-OC \(_8\)/G3COOCH \(_3\) (19/6) (molar ratio = 1:2, shown in Figure 13) showed similar emission spectra in contrast to PBP-OC \(_8\) (19) in solid films (Figure 6). These mixed systems (without H-bonds) reveal a lower ratio (the ratio of the core emissions excited at dendritic OXD units and at the core) of PL emission enhancement in comparison with those of H-bonded dendritic counterparts.

Hence, PBP-OC \(_8\)/G1COOCH \(_3\) (19/4), PBP-OC \(_8\)/G2COOCH \(_3\) (19/5), and PBP-OC \(_8\)/G3COOCH \(_3\) (19/6) have the relative fluorescent intensities (RFI) values of 0.55, 1.04, and 1.27, respectively. Therefore, they exhibited lower fluorescence quantum yields and RFI values than their H-bonded dendritic counterparts. The results indicate that better energy-transfer properties and higher fluorescence quantum yields are obtained as the dendritic donors are H-bonded to the emitting acceptors, where the better energy transfer is caused by higher pairing ratio and closer molecular distance between donors and acceptors through H-bonds.

Conclusions

In summary, several series of novel H-bonded dendrimers were constructed by encapsulation of chromophores with dendrimers or by complexation of functionalized poly(aryl ether) dendrimers with peripheral chromophores via supramolecular self-assembly. Various degrees of red-shifted PL emissions are expected in the H-bonded dendrimers as benzoic acids are H-bonded to the H-bonded acceptor emitters. The emission wavelengths of the mono-/bis-pyridyl (single/double H-bonded) chromophores can be easily adjusted by their surrounding H-donors. As a result, the larger (higher generation) dendritic size can afford stronger site-isolation and dendron-dilution effect, and thus the better energy transfer and higher fluorescence quantum efficiencies can be achieved. Moreover, the peripheral OXD dendrons have specific capabilities of light-antennae and enhanced core luminescence by energy transfer from OXD dendrons. Overall, the energy transfer in the supramolecular dendrimers depends on the types of H-bonded acceptors and donors, including single/double (asymmetric/symmetric) H-bonded structures, dipole moments, dendritic generations, and the overlap ratio of the OXD emission spectra and the emitter absorption spectra. Owing to the efficient shielding effect and energy transfer of the donor dendrimers, high fluorescence quantum yields of these supramolecules have the potential to be utilized in molecular electrooptical devices.

Acknowledgment. We are thankful for the financial support from the National Science Council of Taiwan (ROC) through NSC 93-2113-M-009-011, and the instrumental support from Prof. Yu-Chie Chen (MALDI-TOF mass spectroscopy) at the Department of Applied Chemistry, National Chiao Tung University (in Taiwan).
Supporting Information Available: Text and a scheme giving procedures for the synthesis and purification of all mono-/bis-pyridyl acceptor emitters :PBBCN-OC$_8$ (17), PBBCN-OC$_8$ (18), PBP-OC$_8$ (19), PBBBP-Me-OC$_8$ (20), and their intermediates. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes


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