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Synthesis of 1,4-Bis[2,2-bis(4-alkoxyphenyl)vinyl]benzenes and Side Chain Modulation of Their Solid-State Emission

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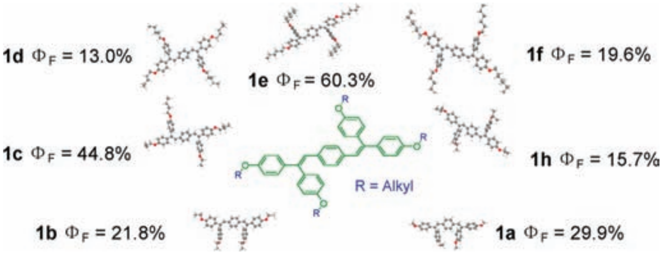
ABSTRACT



A series of 1,4-bis[2,2-bis(4-alkoxyphenyl)vinyl]benzene molecules with aggregation-induced emission (AIE) activity were synthesized. The conformations and packing arrangements of these molecules in the solid state can be adjusted by changing the side chains, which subsequently modulates their solid-state emission. The fluorescence quantum yield of 1e with the n-C_6H_{13} side chain in the solid state could reach up to 60.3% in the solid state.

The development of efficient organic fluorescent materials has met with increasing interest because of their widespread and direct applications.[1] The enhancement and manipulation of the light emission of organic fluorophores in the solid state attracts much attention because these materials are commonly used as thin films in their real-world applications.[2] In the solid state, the light emission of the luminogenic molecules can be quenched by chromophore aggregation relative to that in the solution, which is known as the aggregation-caused quenching (ACQ) effect.[2b,3] However, the aggregation can positively restrict intramolecular rotation (IMR), which exhibits aggregation-induced emission (AIE):[4] an unusual phenomenon in which nonemissive π-conjugated molecules in solution emit efficiently in the solid state, such as thin films, nanoparticles, powder, and crystals.[5] Whether the aggregation weakens or strengthens light emission is decided by the competition between these two antagonistic physical effects, which is internally determined by the chemical structures of the luminogenic molecules.[6]

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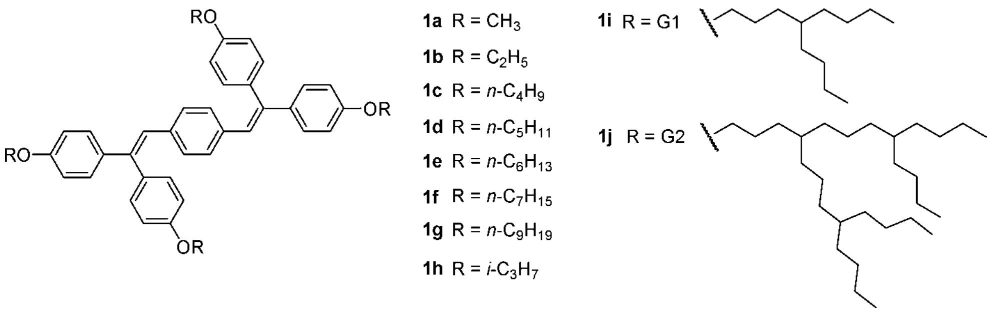
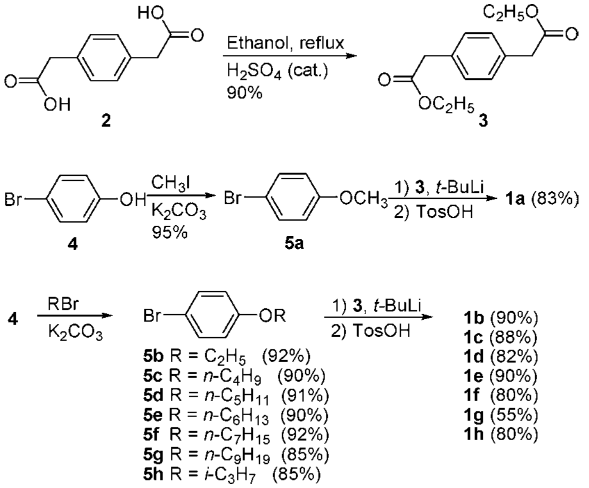


Figure 1. Structures of substituted 1,4-bis(2,2-bis(4-alkoxyphenyl)vinyl)benzene molecules.

At the same time, introduction of appropriate substituent groups to organic fluorophores is an important method to obtain better AIE molecules with desired emission behaviors.[7] The diversity in size and polarity of substituents can affect the three-dimensional aggregation of molecules to modulate the light emission in the solid state.[8] However, a systematic understanding of how side chains modulate the fluorescence emission of the chromophore in the solid state is still lacking. In this paper, a series of 1,4-bis[2,2-bis(4-alkoxyphenyl)vinyl]benzene molecules with different alkyl side chains (Figure 1) were synthesized, which enables the length and steric effects of side chains on the solid-state optical properties to be revealed for the first time. It was found that the packing arrangement and the emission property of these molecules in the solid state could be efficiently modulated by the side alkyl groups.

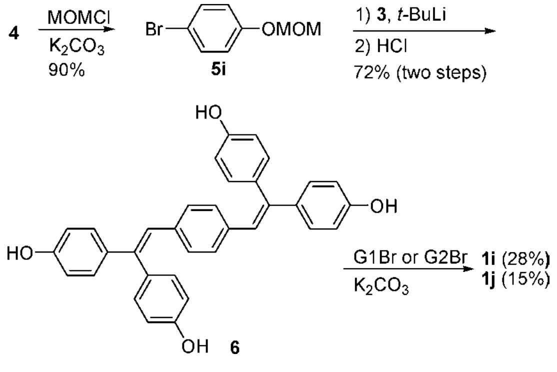
The synthesis of **1a**−**h** proceeded according to Scheme 1. First, the diester **3** was obtained from 1,4-phenylenediacetic acid by esterification with ethanol (cat. H_2SO_4) in 90% yield. Subsequently, the 4-bromophenol (**4**) was transformed into the corresponding methyl ether to afford **5a** by reaction with iodomethane in the presence of K_2CO_3 in 95% yield. Then **5a** was first reacted with *t*-BuLi through lithium−halogen exchange, followed by treatment with diester **3** in THF to give a tertiary alcohol, which was then dehydrated in the presence of 4-methylbenzenesulfonic acid (cat.) in CH_2Cl_2 to give **1a**[9] in 83%. Likewise, **4** was treated with different RBr in the presence of K_2CO_3 in acetone to afford compounds **5b**−**5h** in high yield, which were subjected to the same connecting protocol (**3**, *t*-BuLi, then TosOH) to provide the desired compounds **1b**−**1h** in the appropriate yield.

Scheme 1. Synthesis of **1a**−**h**



For the synthesis of **1i** and **1j** (Scheme 2), the core **6** was first prepared for avoiding the steric hindrance of the dendrons, thus 4-bromophenol (**4**) was converted to its MOM ether by treatment with MOMCl in the presence of K_2CO_3 in acetone to provide **5i** in 90% yield. The bromo group in **5i** was exchanged for lithium and then reacted with diester **3**, followed by the removal of the MOM group and dehydration which were carried out simultaneously in the presence of 6 N HCl (cat.) in CH_3OH. Thus, the core **6** was obtained in 72% overall yield for two steps. With the requisite **6** in hand, the aliphatic dendrons (G1 and G2)[10]

Scheme 2. Synthesis of **1i** and **1j**



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were attached to the phenol groups to give compounds **1i** and **1j** in 28% and 15% yield, respectively. By incorporation of dendrons, the undesired intramolecular rotation can be minimized with the retention of the electronic factor in the conjugate core. The detailed synthetic procedures and characterization data of ^{1}H and ^{13}C NMR, HRMS, or MS and elemental analysis are shown in the Supporting Information.

To assess the influence of side chains on the fluorescence of the aromatic core, the synthesized molecules were characterized by UV−vis spectroscopy and fluorescence spectroscopy (Table 1). Dilute THF solution of **1a**−**j** revealed absorption peaks (λ_{ab}), all at approximately 369 nm, and emission peaks at nearly 476 nm, which suggests that the incorporation of various side chains does not bring about changes to the electronic structure of the conjugated core in the solution. All compounds emit weakly in the diluted solutions with the fluorescence quantum yields (Φ_F) around 0.5−1.3%, but the Φ_F are somewhat higher than the classical hexaphenylsilole (HPS) (0.1%).[5b]

Table 1. Absorption and Emission Characteristics of the Samples in Solution[a] and Amorphous[b]

	λ_{ab} [nm]	λ_{em} [nm]		Φ_F [%][c]	
samples	solution	solution	amorphous	solution	amorphous
1a	369	476	477	1.0	29.9
1b	369	476	463	1.2	21.8
1c	369	477	499	0.8	44.8
1d	369	476	492	1.1	13.0
1e	369	475	490	1.2	60.3
1f	370	475	500	1.1	19.6
1g	368	474	499	1.3	19.2
1h	370	475	485	1.1	15.7
1i	368	475	485	0.5	1.4
1j	360	483	478[d]	0.9	2.5[d]

[a] Measured in THF (10 μM). [b] Measured using a powder. [c] Absolute quantum yield. [d] Measured using a thin film.

Compared to the weak fluorescence of all the compounds in THF solution, the solid-state fluorescence spectra are distinctly different. The amorphous power of **1c**, **1e**, and **1g** fluoresces at 499, 490, and 499 nm, which exhibits an obvious red-shift compared to **1a** (λ_{em} at 477 nm). The emission peak of **1b** shows an exceptional 14 nm blue-shift compared to **1a**. The emission efficiencies of **1a**−**j** are all significantly enhanced in the solid state because the aggregation positively restricts IMR, and the degree of enhancement is strongly dependent on the structure of the side chains.

The conjugated core and the alkyl side chains play different roles in the solid-state packing arrangement of these molecules. Due to its highly conjugated structure, the $\pi-\pi$ stacking of the core could facilitate ordered stacking with strong intermolecular interaction, and ACQ is generally expected. The steric hindrance of the side chains could increase the distance of the neighboring molecules and could reduce the ACQ effect. Meanwhile, the long or branched side chains may also induce significant disorder in the packing arrangement, which could weaken the emission. Therefore, an optimum size of the side chain is expected to give the most favored molecular packing arrangement for solid-state emission. In this work, the n-C_6H_{13} chain was found to have an optimal effect on the solid-state emission, as molecule **1e** shows sharp and strong emission with the highest quantum yield of 60.3%. It is interesting to note that compounds **1i** and **1j**, which have branched alkyl dendrons as side chains, show very weak emission in the series. The Φ_F of **1i** and **1j** in the solid state are only slightly higher than those in solution, indicating that though the aggregation restricts IMR they are probably in an oil-like state because of the enwrapping of the dendritic alkyl substituents, which have better motions, vibrations, and rotations than **1a**−**1h** in the solid state. In fact, the melting point of **1i** is only at 64−68 °C, and **1j** is an oil at room temperature.

In an effort to understand the effect of the side chains on the molecular conformation and packing arrangements, the crystal structures of compounds **1a**−**f** and **1h** were determined. As can be seen from the single-crystal structures shown in Figure 2 (the large packing arrangement images of **1a**−**f** and **1h** are shown in Supporting Information), a little structural change, the same core with different side chains, brings obvious variety of molecular conformation and packing arrangement in the solid state. When the chains are short (**1a** and **1b**), the conformations tend to be *cis*-geometric structure (the two benzene rings are on the same side of the nonplanar conjugated structure as the chromophore which consists of three benzene rings and two double bonds). As the length of the side chains is beyond three carbons, the molecular conformations exhibit *anti*-geometric structures and tend to be centrosymmetric structures. The packing arrangements of these compounds are also different. The molecules of **1e** have strong head-to-face interactions between the conjugated structures, which give so-called *J*-aggregates[11] extending on the long axis direction of the molecule, which are generally considered to be good emitters. The molecules of compounds **1a**, **1b**, and **1h** have one conformational molecule in the crystals like **1e**, but they exhibit different packing arrangements. The molecules of **1a** exhibit interlaced *H*-aggregates. The conjugation system of **1b** is almost coplanar, and the plane of one molecule is almost vertical on that of the neighboring molecule (the dihedral angel $\theta = 73.9°$). In the crystal of **1h**, the molecules are packed in the form of two neighboring back to back molecules as a unit. There are two conformational molecules in the crystals of compounds **1c**, **1d**, and **1f**, which exhibit *J*-aggregates in more than one extending direction. In addition, the CH/π hydrogen bond plays a crucial role in the packing arrangement in the crystals and is also important in terms of the conformations of these compounds. As an example shown in Figure 2, a CH/π hydrogen bond ($d_1 = 2.63$ Å) is formed between two phenyl rings in neighboring molecules of **1e**. A CH/π hydrogen bond ($d_2 = 3.00$ Å) is

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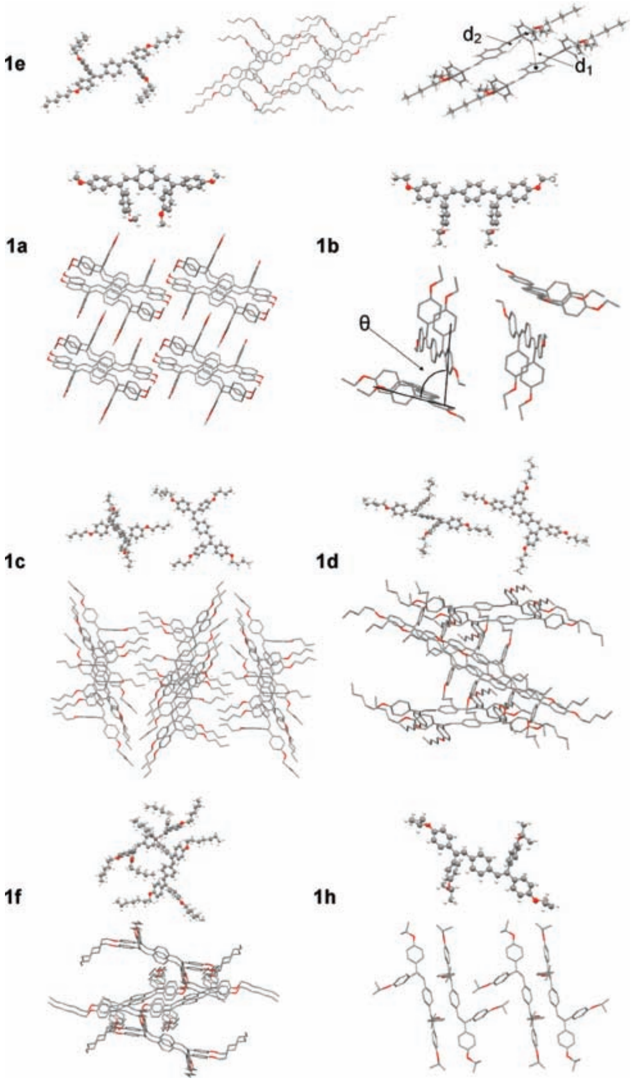

Figure 2. Molecular structures and stacking images of **1a**−**f** and **1h** in single crystals.

also formed between two phenyl rings in the same molecule. The CH/π hydrogen bonds in the crystals of other compounds are shown in Supporting Information.

Similar to the other AIE-fluorophores, the AIE activity can be observed from the fluorescence spectra in a mixed solvent of THF and water. As can be seen from the example shown in Figure 3, **1e** was dissolved in the mixture of THF and water. The higher the water content, the stronger the light emission will become, and a red-shifted phenomenon will be observed. When the amount of water was 20% and the slit width was 6 nm, there was almost no emission intensity. Although the slit width was reduced to 4 nm, the light emission was still enhanced when the amount of water increased (f_w = 40, 60, 80, 90). The result verified that the emission of this kind of structure became stronger by aggregate formation because the water is a nonsolvent of these molecules. A similar emission-enhanced effect was observed in other long-chain molecules.

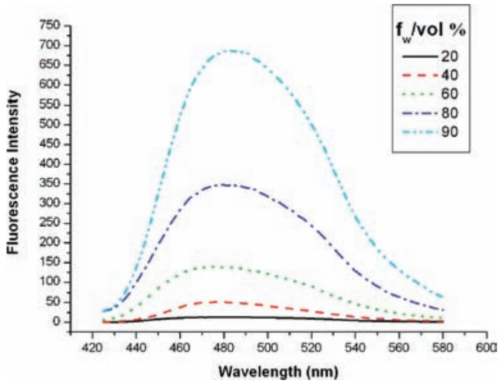

Figure 3. Emission spectra of **1e** in THF/water mixtures with different fractions of water (f_w) and excitation wavelength at 410 nm.

In summary, we have synthesized a series of 1,4-bis[2,2-bis(4-alkoxyphenyl)vinyl]benzene molecules using a concise route, all of which exhibit aggregation-induced emission. These compounds were easy to prepare in powder or crystal, the solid-state emissions of which were tunable by changing the length and shape of the side chains. The fluorescence quantum yields (Φ_F) are distributed from 13.0% to 60.3%. Also, when the large steric dendrons were induced, the emission became weak in the solid state. The successful synthesis of these molecules provides opportunities to gain insight into the effect of the alkyl side substituents on the solid-state optical properties of the AIE-fluorophores.

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Supporting Information Available: Experimental procedure and characterization for compounds **1a**−**j** and **6**, and ^{1}H, ^{13}C NMR, and DEPT 135 spectra of them; absorption and emission spectra of **1a**−**j**; X-ray crystallographic files in CIF format for **1a**−**f** and **1h**; and the table of CH/π hydrogen bonds in their crystals and the packing arrangement images of them. This material is available free of charge via the Internet at http://pubs.acs.org.

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