Solid-Phase Synthesis of Unsymmetrical *trans*-Stilbenes

Chul-Hee Cho, Chul-Bae Kim, and Kwangyong Park*

School of Chemical Engineering and Materials Science, Chung-Ang University, 221 Heukseok-Dong, Dongjak-Gu, Seoul 156-756, Korea

A small library of fluorescent and unsymmetrical *trans*-stilbene compounds was efficiently produced by a solid-phase synthetic approach using the sulfonate-based traceless linker system. Nickel(0)-catalyzed cleavage/ cross-coupling of polymer-bound stilbenesulfonates with aryl Grignard reagents generated the desired *trans*-stilbenes at high yield by the multifunctional release facilitating the additional diversification of the library. The luminescent properties of *trans*-stilbenes are assessed, and the influence of alkyl substituents on their photophysical properties is discussed.

Introduction

Organic fluorescent materials have attracted attention because of their various potential applications such as fluorescent dyes for labeling biomolecules,[1] fluorescent tracers,[2] fluorescent sensors and switches,[3] fluorochromes in dental restorations,[4] and optical brighteners.[5] Recently, they have gained particular interest for application in organic light-emitting diodes (OLEDs), in which the emissive layer is composed of organic fluorescent compounds.[6]

Stilbene derivatives, which are famous because of their wide range of biological activities,[7] are attracting much attention for application in OLEDs. Stilbene derivatives have been widely investigated as short subunits of poly(*p*-phenylenevinylene), which was the first light-emitting polymer to be discovered,[8] to gain an understanding of the emission mechanism and the relationship between the substitution on the conjugated skeleton and the emitted light.[9] Moreover, stilbene and aminostilbene derivatives exhibit blue photoluminescence[10] and hole transport[11] properties. Stilbene dendrimers have recently attracted considerable attention as efficient luminescent materials.[12]

Dimerization reaction has been the most popular method for the preparation of symmetrical stilbenes. The oxidative dimerization of methylarenes,[13] eliminative dimerization of benzyl halides,[14] and reductive dimerization of benzaldehydes[15] have been reported for preparing symmetrical stilbenes. On the other hand, unsymmetrical stilbenes have often been prepared by the Wittig[16] or Horner−Wadsworth−Emmons (HWE) reactions[17] of substituted benzaldehydes with benzyl phosphonium ylides or phosphonates. The Heck reaction has also been applied for the synthesis of stilbene derivatives.[18] We have previously reported our efforts in applying the nickel-catalyzed coupling reaction of neopentyloxysulfonylarenes with arylmagnesium halides to the synthesis of unsymmetrical stilbene derivatives.[19]

Organic fluorescent materials with high quantum efficiency and longtime stability are required for OLED fabrication.

However, the systematic relationship between the luminescent properties of materials and their chemical structure remains unclear. Therefore, it is important to prepare and characterize a variety of structurally similar luminophores to elucidate the influence of chemical modifications on the photophysical properties. During the course of our studies on the development of organic fluorescent materials emitting blue light for OLEDs, we became interested in developing an efficient synthetic methodology for preparing a stilbene library. A combinatorial strategy was necessary to produce a large array of different stilbene derivatives quickly.

Combinatorial synthesis, coupled with high-throughput screening and integrated data management systems, is a powerful tool to produce large and diverse libraries of structurally related compounds. The combinatorial approach, which has played an important role in the search for lead molecules in the pharmaceutical industry,[20] is now widely utilized to accelerate the discovery of new materials.[21] Inorganic luminescent[22] and magnetic[23] materials, catalysts,[24] organic/inorganic sensor materials,[25] and organometallic[26] and polymeric luminescent materials[27] have been investigated through the use of combinatorial approaches. The parallel/ combinatorial preparation of organic fluorescent materials has also been reported.[28]

Polymer-supported parallel/combinatorial synthesis is the most popular synthetic strategy for the combinatorial preparation of large libraries of organic substrates. A library of hydroxystilbene analogues has also been prepared by this method and characterized to investigate their biological activities.[29] During the polymer-supported reaction process, substrates are usually linked to the polymeric support through an ether, ester, or amide bond.[30] Accordingly, most organic compounds prepared by this approach are destined to possess a functional moiety, typically hydroxyl, amino, or carboxyl group, that is the trace of the former linkage with the support. However, a majority of blue emitting organic materials are nonfunctionalized hydrocarbons.[31] Therefore, the polymer-supported preparation of a fluorescent stilbene library for OLEDs requires the efficient traceless linker technology[32]

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* To whom correspondence should be addressed. E-mail: kypark@ cau.ac.kr.

Scheme 1. Library Design for Stilbene Compounds **6**
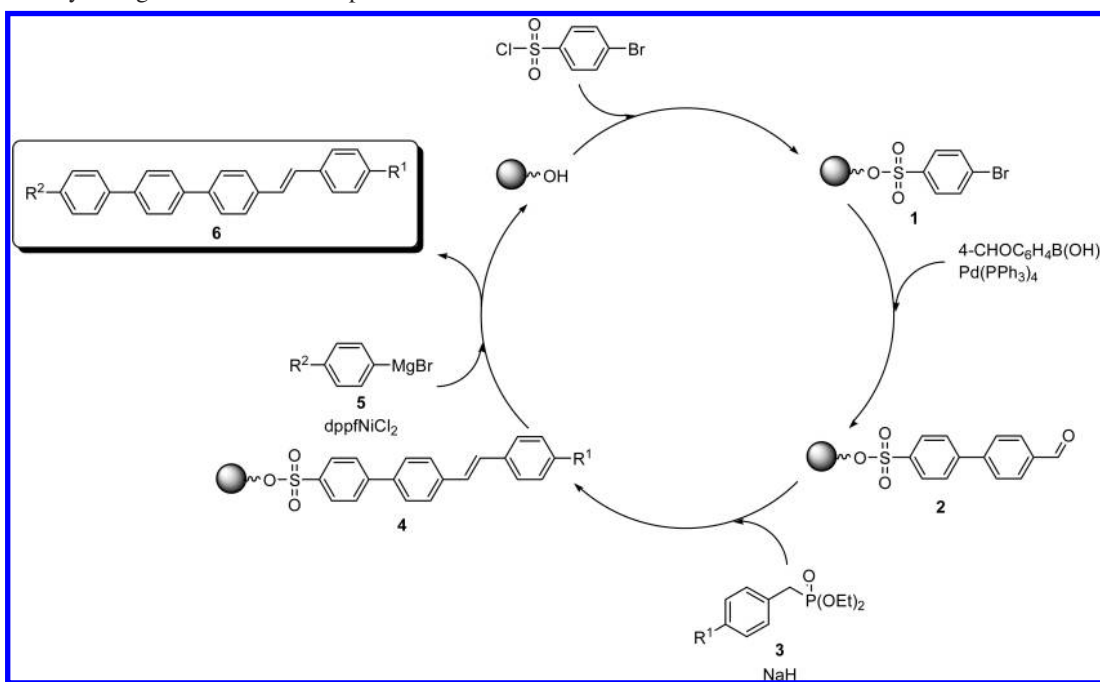
that enables the release of unfunctionalized stilbenes from the support. In addition, a multifunctional cleavage strategy[33] is highly desirable to facilitate the additional diversification of the library with the release of the target compound. However, difficulties have been experienced in trying to isolate the known synthetic strategy appropriate for our purpose.

Herein, we present the novel parallel syntheses and photophysical studies of fluorescent unfunctionalized stilbene derivatives. The sulfonate-based traceless and multifunctional linker system[34] was applied for the solid-phase synthesis of unsymmetrical *trans*-stilbene derivatives **6** via the nickel(0)-catalyzed cleavage/cross-coupling reaction of polymer-bound *trans*-stilbenesulfonates **4** with aryl Grignard reagents **5** (Scheme 1). Polymer-supported synthesis of unfunctionalized stilbenes has not previously been reported to the best of our knowledge. The results of this study are presented and discussed below.

Result and Discussion

Polymer-supported 4-bromobenzenesulfonate **1** was prepared by treating hydroxyethylmethyl resin[34] with 4-bromobenzenesulfonyl chloride in the presence of Et_3N for 48 h.[35] The yield of **1** was calculated as 91% based on the loading level of the resin, which was determined by elemental analysis. The remaining hydroxyl group was converted into a methoxy group by treatment with excess CH_3I. Polymer-bound 4-formylbiphenylsulfonate **2** was prepared by the Suzuki−Miyaura coupling of **1** with 4-formylphenylboronic acid in the presence of $Pd(PPh_3)_4$. The liberation of arenesulfonate via the catalytic cleavage of the C−O bond by the Pd(0) catalyst was not observed by our standard analysis. Formylbiphenylsulfonate **2** was allowed to react with benzylphosphonates **3** to form polymer-bound stilbenesulfonates **4** by constructing the central vinyl moiety of the stilbene skeletons. All intermediates **1**, **2**, and **4** could be isolated by

simple filtration and underwent the next step without any further purification.

The progress of all of the solid-phase reactions employed in these sequences was monitored by using FT-IR spectroscopy (Figure 1). Sulfonylation and the subsequent methylation of the hydroxyethylmethyl resin were identified by the disappearance of the IR bands corresponding to the hydroxy group at 3583 and 3455 cm^{-1}, and by the appearance of new bands corresponding to the sulfate group of **1** at 1362 and 1182 cm^{-1}. The presence of a strong new band at 1705 cm^{-1} and the absence of the absorption band at 1576 cm^{-1} corresponding to the C−Br bond clearly demonstrated the efficient substitution of the Br group by formyl group in **2**. Solid-phase HWE reaction of **2** with diethyl benzylphosphonate was confirmed by the complete disappearance of the formyl band on the IR spectrum of **4**{*1*}.

Stilbene derivatives **6** were generated by the traceless multifunctional cleavage/cross-coupling reactions of stilbenesulfonates **4** with aryl Grignard reagents **5** using a Ni(0) catalyst. Treatment of a mixture of **4** and [1,1′-bis(diphe-
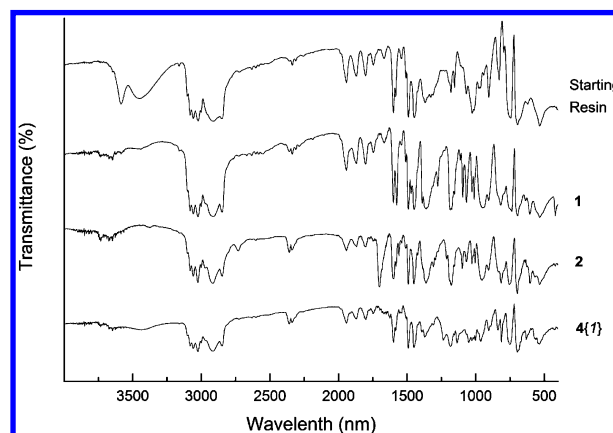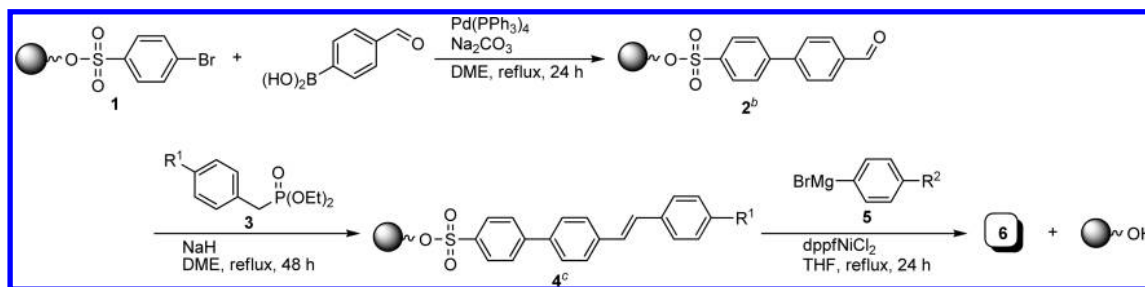

Figure 1. FT-IR analysis of the polymer-bound intermediates **1**, **2**, and **4**{*1*}.

Table 1. Solid-Phase Preparation of Unsymmetrical *trans*-Stilbenes **6**[a]

entry	phosphonate 3 (R¹)	Grignard reagent 5 (R²)	product 6		yield (%)[d]
1	H	H		6{1}	38
2	H	Me		6{2}	37
3	H	*t*-Bu		6{3}	43
4	Me	H		6{4}	48
5	Me	Me		6{5}	46
6	Me	*t*-Bu		6{6}	50
7	*t*-Bu	H		6{7}	43
8	*t*-Bu	Me		6{8}	45
9	*t*-Bu	*t*-Bu		6{9}	47

[a] Reactions between **4** (0.282 mmol) and **5** (1.97 + 1.41 mmol) in THF (6 mL) were carried out at 66 °C (6 mL) in the presence of dppfNiCl₂ (0.113 mmol). [b] Reactions between **1** (10.4 mmol) and boronic acid (34.2 mmol) in DME (230 mL) were carried out at 85 °C in the presence of Pd(PPh₃)₄ (0.933 mmol) and aqueous Na₂CO₃ (0.0900 mmol). [c] Reactions between **2** (1.86 mmol) and **3** (7.44 mmol) DME (40 mL) were carried out at 85 °C in the presence of NaH (7.07 mmol). [d] The calculated overall yields of **6** from **1** are based on the loading level of **1**.

nylphosphino)ferrocene]dichloronickel (dppfNiCl₂) with 15 equiv of **5** produced the desired unsymmetrical stilbenes **6** via the nucleophilic aromatic substitution of the alkyloxysulfonyl group by aryl nucleophiles. The reactions were performed in tetrahydrofuran (THF) at 66 °C for 60 h. Stilbenes **6** were isolated as reasonably pure white solids by simple precipitation using methanol after the standard workup. Even though a large amount of biphenyls derived by the dimerization of **5** was produced in these reactions, these biphenyls were easily removed by washing with methanol during the precipitation process. The catalytic substitution of arenesulfonates by nucleophiles[36] was not observed by gas chromatography (GC) and nuclear magnetic resonance (NMR) analyses. Crude products were purified

further by column chromatography for more precise calculation of isolated yields and characterization of structures.

All reactions resulted in good overall yields (Table 1), which were calculated on the basis of the initial loading of **1**. Isolated yields of 37−50% for three steps are compatible or better than the theoretical combined yields of the corresponding solution-phase syntheses.[19] Overall yields were dependent more on the type of phosphonates than on the type of Grignard reagents. The use of different kinds of phosphonate **3** induced a 7−10% variation in the overall yields (entries 1, 4, and 7 and entries 3, 6, and 9), while a change of Grignard reagents **5** generated only a 4−6% variation (entries 1−3 and entries 4−6). Only *trans*-stilbenes were obtained within the limits of the NMR analysis, as

Table 2. Absorption and Emission Specifications of Stilbene Derivatives **6**

entry	product	solution[a]				solid		
		$\lambda_{abs}{}^{b}$ (nm)	$\lambda_{em}{}^{c}$ (nm)	stokes shift (nm)	$\Phi_F{}^{d}$	λ_{em} (nm)	chromaticity	mp (°C)
1	**6{*1*}**	327	399	72	0.31	441	x: 0.1470 y: 0.1437	315−317
2	**6{*2*}**	333	400	67	0.49	442	x: 0.1487 y: 0.1297	326−328
3	**6{*3*}**	333	400	67	0.75	447	x: 0.1492 y: 0.1205	281−283
4	**6{*4*}**	336	400	64	0.38	460	x: 0.1451 y: 0.1616	314−316
5	**6{*5*}**	335	402	67	0.39	466	x: 0.1496 y: 0.1684	329−330
6	**6{*6*}**	336	402	66	0.57	477	x: 0.1484 y: 0.1709	299−301
7	**6{*7*}**	335	401	66	0.48	465	x: 0.1426 y: 0.1186	293−294
8	**6{*8*}**	335	404	69	0.49	459	x: 0.1574 y: 0.0784	313−315
9	**6{*9*}**	339	402	63	0.54	450	x: 0.1484 y: 0.1344	307−309

[a] Solution of **6** in chloroform solution. [b] λ_{abs} represents the maximum absorption wavelength of **6**. [c] λ_{em} represents the maximum fluorescence wavelength of **6**. [d] The quantum yields were determined using 4-phenyl-*trans*-stilbene in cyclohexane as the reference standard ($\Phi_F = 0.60$).
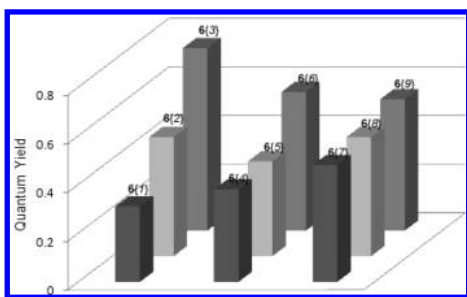
Figure 2. Quantum yields of **6** in chloroform.

expected. The coupling constants of a pair of doublets generated by two vinylic protons of **6{*4−9*}** were 16−17 Hz, which is the typical coupling constant between two *trans* vicinal vinylic protons, in the ^{1}H NMR spectra. The vinylic protons of **6{*1−3*}** formed a singlet in the ^{1}H NMR spectra.

The absorption and emission properties of stilbenes **6** were characterized and are summarized in Table 2. All of **6** dissolved in CHCl₃ displayed similar spectra with the absorption λ_{max} between 333 to 339 nm and the emission λ_{max} between 399 and 404 nm. The absorption and emission λ_{max} spectra of the solution slightly increased with the addition of the alkyl substituents, within a small margin.[31,37] However, there was no consistency in Stokes shifts of the solutions with substituents. The fluorescence quantum yields for **6** in CHCl₃ were calculated from the steady-state spectroscopic measurements using the techniques described by Demas and Crosby.[38] The values are given in Table 2 and graphically illustrated in Figure 2. The quantum efficiency was considerably enhanced with the addition of an alkyl group on the terphenyl moiety, while the substitution on the phenyl moiety had no discernible effect. Especially, the presence of a *tert*-butyl group on the terphenyl side remarkably increased the quantum yield (entries 3, 6 and 9). Dramatic red shifts, which are generally attributed to $\pi-\pi$ stacking, of about 47−75 nm were observed in the emission maximum of the solid-state stilbenes relative to their solutions.[39] While the emission λ_{max} spectra of the solids also increased in the presence of alkyl substituents as the solution, the methyl group on the phenyl moieties had a greater

influence on the red shift of fluorescence wavelength (entries 4−6). The methyl group also considerably increased the y value of chromaticity of the fluorophore.[31]

Conclusions

A small library of fluorescent *trans*-stilbene compounds was produced and characterized by employing a solid-phase parallel synthetic approach. The unsymmetrical and unfunctionalized *trans*-stilbene derivatives **6** were generated in good yield by the nickel(0)-catalyzed cleavage/cross-coupling of polymer-bound *trans*-stilbenesulfonate **4** with aryl nucleophile **5**. The luminescent properties of **6** were assessed, and the influence of the alkyl substituents on their photophysical properties was discussed. The efficiency of the sulfonate-based traceless and multifunctional linker system was demonstrated in the preparation of various unfunctionalized hydrocarbons by facilitating the additional diversification of the library with the traceless release of the final products. We expect this approach to be useful for the rapid parallel or combinatorial synthesis of conjugated hydrocarbon libraries for various purposes.

Experimental Section

Preparation of Polymer-Bound Formylbiphenylsulfonate 2. Polymer-bound bromobenzenesulfonate **1** (0.691 mmol/g, 15 g) and Pd(PPh₃)₄ (0.933 mmol, 1.08 g) were swollen in DME (230 mL) under Ar atmosphere for 30 min at room temperature. 4-Formylphenylboronic acid (34.20 mmol, 5.13 g) dissolved in a minimum amount of EtOH/DME (1:1) and 2 M aqueous Na₂CO₃ (30 mL) were added to the reactor, and the reaction mixture was stirred at 85 °C for 24 h. The resin was filtered, washed with DME, 1% aqueous HCl, water, and MeOH, and dried in vacuo. The terminal functional group was determined by FT-IR analysis. FT-IR (KBr) 2912, 1705, 1596, 1491, 1448, 1362, 1176, 949, 814, 754, 696.

General Procedure for the Preparation of Polymer-Bound Stilbenesulfonates 4. A mixture of polymer-bound formylbiphenylsulfonate **2** (2.5 g, 1.0 equiv), benzyl phos-

phonate **3** (3.08 mmol), and sodium hydride (124 mg, 60% dispersion in oil, 3.10 mmol) in DME (40 mL) was swollen under Ar atmosphere. The brown mixture was heated at 85 °C for 48 h. The resin was filtered, washed with DME, 1% aqueous HCl, water, and MeOH, and dried in vacuo. In the qualitative analysis, the carbonyl group was determined by FT-IR analysis to have disappeared.

General Procedure for Cross-Coupling Reaction of 4 with 5. To a stirred solution of **4** (0.282 mmol) and dppfNiCl$_2$ (0.113 mmol, 77.4 mg) in THF (6 mL), was slowly added Grignard reagent **5** (2.830 mmol) at room temperature under Ar atmosphere. The reaction mixture was stirred at 66 °C of THF for 36 h and cooled to room temperature. An additional 5.0 equiv of **4** (1.415 mmol) was added to the solution, which was heated for 24 h. The resin was filtered and washed with THF, 1% aqueous HCl, water, and excess CH$_2$Cl$_2$. The drained solution mixture was poured into a separatory funnel containing CH$_2$Cl$_2$ and 1% aqueous HCl. The combined organic layer was washed with water, dried over MgSO$_4$, and concentrated in vacuo. To precipitate the product **6**, MeOH was added to the concentrated mixture. The suspension was filtered through a small pad of silica gel on a sintered glass filter. The solid remaining on the silica gel was washed with MeOH, collected by elution with CH$_2$Cl$_2$, and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using *n*-hexane/CHCl$_3$ as the eluent system to afford the corresponding products **6**.

Supporting Information Available. ^{1}H NMR for compounds **6**{*1−9*} and ^{13}C NMR for compounds **6**{*3−4*}; UV-absorption and emission spectra of **6**{*1−9*}. This material is available free of charge via the Internet at http://pubs.acs.org.

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