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Triarylethene-Based Extended π-Systems: Programmable Synthesis and Photophysical Properties

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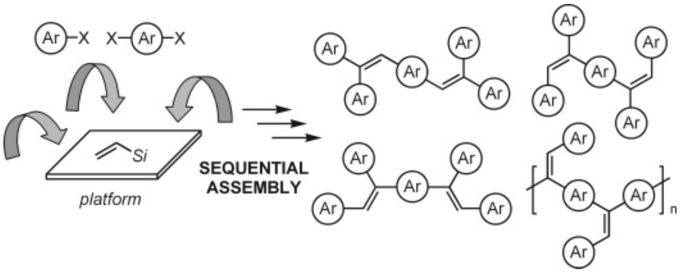

On the basis of an efficient Pd-catalyzed triarylation to a vinylsilane platform, four types of structurally well-defined triarylethene-based extended π-systems have been prepared very rapidly. From a compound library constructed by the present method, it was possible to find a number of interesting fluorescent materials, as well as interesting fluorescent properties such as aggregation-induced enhanced emission. A useful method for the rapid synthesis and property evaluation has also been developed.

Introduction

The carbon−carbon double bond (C═C) is a minimal unit in π-systems. Therefore, an extended π-system equipped with π-systems such as aryl groups on the minimal π-unit C═C (arylethene-based extended π-system) would be an interesting target as a functional material (Figure 1). Although some of the π-systems within this family, such as stilbene derivatives and poly(arylene vinylene)s (1,2-diarylethene-based π-systems), have already established their utility as functional materials,[1] we felt that an important object still remains in this class of extended π-systems, namely, exploring the chemistry (synthesis and properties) of π-systems based on a highly substituted C═C core (tri- and tetraarylethene-based extended π-systems). Since such an investigation is subject to the establishment of a general synthetic scheme for multisubstituted olefins, which has been a formidable challenge for chemists for years, the chemistry is extremely challenging as a whole.

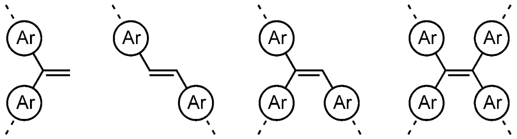

FIGURE 1. Arylethene-based extended π-systems.

We herein describe a simple but powerful strategy that enables rapid and systematic assembly of small π-systems into structurally well-defined triarylethene-based extended π-systems in a programmable and diversity-oriented format. By following this strategy, we succeeded in rapidly making chemical libraries of extended π-systems, in which a number of interesting fluorescent organic materials as well as interesting fluorescence properties were found.

Recently, we have initiated a program directed toward the development of a programmable and diversity-oriented synthesis of multisubstituted olefins[2] and reported such a synthetic scheme for diarylethenes and triarylethenes using vinyl(2-pyridyl)silane (**1a**) as a platform (eq 1).[2c] We first reported that the otherwise difficult Mizoroki−Heck reaction (MHR) of vinylsilanes[3,4] was efficiently promoted by appending a catalyst-directing 2-pyridyl group on silicon.[2a,5−8] The suitably positioned nitrogen atom of the pyridyl group might accelerate the rate-determining C═C π-complexation and

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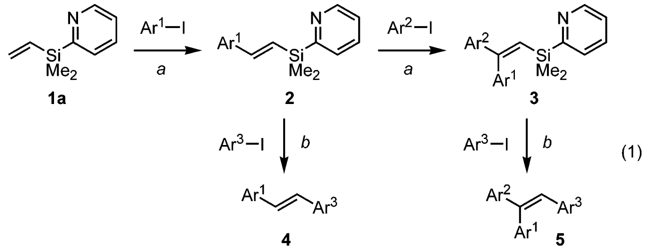
successive carbopalladation (insertion) events in MHR.[2c] Moreover, because of the strong directing effect of the 2-pyridyl group, a hard-to-achieve double-MHR has been accomplished (**1** → **2** → **3**), which allows us to install two aryl groups at two β-C−H bonds in one pot.[2c,9] We also found that the resultant alkenyl(2-pyridyl)silanes (**2** and **3**) undergo an efficient Hiyama-type silicon-based cross-coupling reaction (CCR)[10] with aryl iodides producing diarylethenes **4** and triarylethenes **5** in a regio- and stereoselective manner (eq 1).[2b,c] Noteworthy features are that (i) all aryl groups assembled stem from readily available aryl iodides (Ar-I), (ii) the installation at the desired position can be achieved by the addition of aryl iodides in the appropriate order, and (iii) simple alteration of addition order in the sequence results in the production of all possible regio- and stereoisomers of multisubstituted olefins.



a) $Pd_2(dba)_3$, P(2-furyl)$_3$, Et_3N, THF, 60 °C. b) $PdCl_2(PhCN)_2$, Bu_4NF, THF, 60 °C

This represents a new synthetic strategy that permits assembly of π-systems, such as aryl groups, onto a C=C core in a programmable and diversity-oriented format.[11] Clearly, the programmability of the synthesis is attributed to the inherent stereo-electronic bias of the vinylsilane platform (differentiated reactivity of C−H and C−Si bonds) as well as the aid of catalyst-directing (coordinating) groups. It should be noted that this

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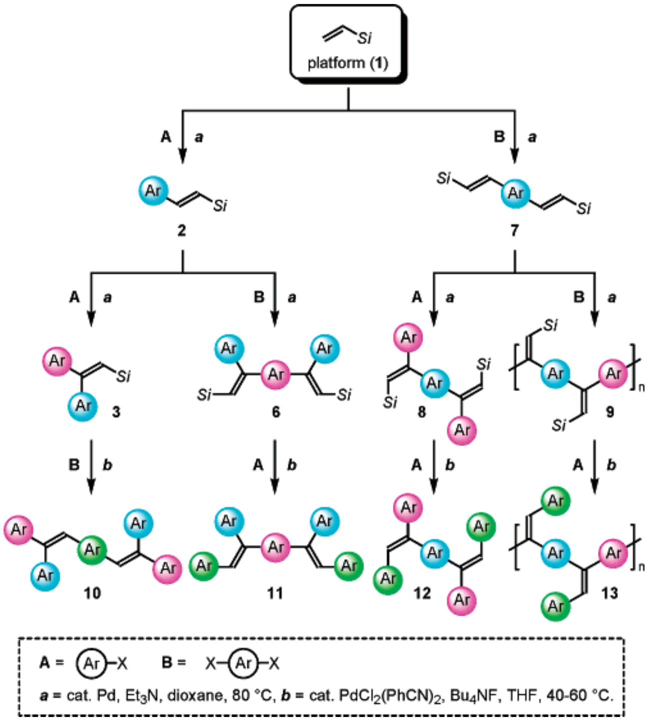
SCHEME 1. Programmable and Diversity-Oriented Construction of Triarylethene-Based Extended π-Systems



A = Ar–X B = X–Ar–X

a = cat. Pd, Et_3N, dioxane, 80 °C, *b* = cat. $PdCl_2(PhCN)_2$, Bu_4NF, THF, 40-60 °C.

platform strategy differs from the classical olefin synthesis as exemplified by the Wittig reaction and its analogues, which connect two components with the creation of a C═C bond, where the selectivity (stereoselectivity) depends inevitably on the existing substituent(s).

Because π-assembling sites are programmed in our synthesis, we envisaged that the strategic use of bifunctional aryl units (ArX_2) in place of a monofunctional unit (ArX) in the reaction sequence described in eq 1 would result in the selective production of various types of triarylethene-based extended π-systems, which are otherwise difficult to construct. The programmable and diversity-oriented synthetic scheme for triarylethene-based extended π-systems is shown in Scheme 1. For example, the CCR of β,β-diarylvinylsilane **3** (double-MHR product of **1**) with aryl dihalides (ArX_2) under the influence of a Pd catalyst and Bu_4NF results in the production of the interesting extended π-system **10**. When the double-MHR/CCR sequence is performed with the addition order of ArX/ArX_2/ArX (**1** → **2** → **6** → **11**) and ArX_2/ArX/ArX (**1** → **7** → **8** → **12**), extended π-systems of interesting structure (**11** and **12**) are selectively produced. Moreover, when double-MHR is performed with ArX_2 alone, an unprecedented type of polymerization takes place (**1** → **7** → **9**). The successive CCR with ArX then affords the novel cross-conjugated polymer **13**, which is otherwise difficult to construct. The power of this synthetic strategy is apparent, as all of these extended π-systems can be selectively prepared at will by using common platforms (**1**),[12] common reactions (MHR and CCR), and common reagents (ArX and ArX_2).

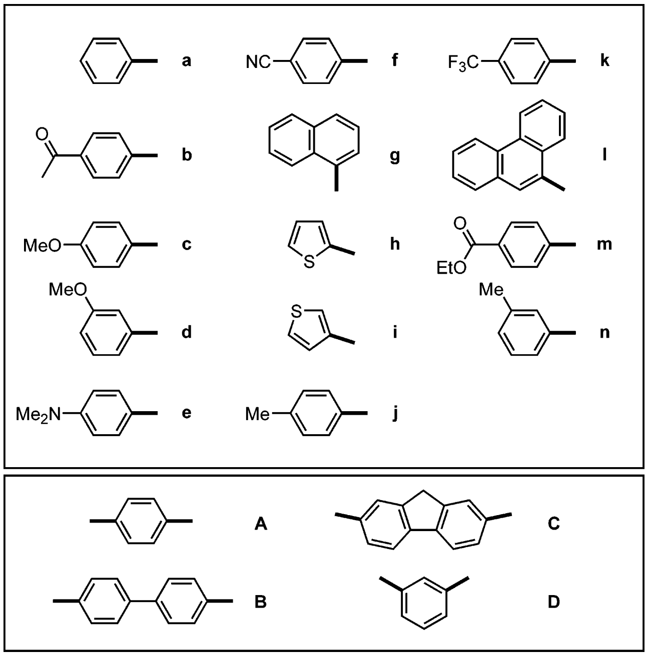


FIGURE 2. Aryl groups (π-units) used in this study.

Results and Discussion

1. Assignment of Aryl Groups. In this study, we used the following 18 aryl groups (or π-units) for the construction of the triarylethene-based extended π-systems. For simplicity, we assigned them alphabetically as described in Figure 2 and used them in compound assignment.

2. Improved Conditions for Installing Two Aryl Groups at β-C−H Bonds of Vinylsilanes. Before initiating this study, we were aware of the need for a reliable method of installing two aryl groups at β-C−H bonds of vinylsilanes. Although we have already reported in our previous paper that the Mizoroki−Heck reaction (MHR) of vinyl(2-pyridyl)silanes is useful for such a purpose, this method suffers from limited reaction scope. For example, by using our previous catalytic conditions [$Pd_2(dba)_3$, P(2-furyl)$_3$, Et_3N, THF, 60 °C], the efficient double-MHR (**1** → **2** → **3**) of dimethyl(2-pyridyl)vinylsilane (**1a**) occurs only with iodobenzene, 2-iodothiophene, and 3-iodothiophene.[2c]

After extensive reinvestigation of catalysts as well as substrates, we established more general and reliable procedures for the double-MHR of vinylsilanes. We found that the use of P(t-Bu)$_3$[13] or P[OC_6H_3(t-Bu)$_2$-2,4]$_3$[14] as supporting ligand to palladium substantially broadens the scope of double-MHR of **1a** (eq 2).[15,16] Not only aryl iodides but also aryl bromides as well as heteroaryl halides and alkenyl halides can be used as substrates when the Pd/P(t-Bu)$_3$ system is used.[17] When aryl iodides were used as arylating agents, the $Pd_2(dba)_3$/P[OC_6H_3(t-Bu)$_2$-2,4]$_3$ catalyst was as effective as the Pd/P(t-Bu)$_3$ catalyst in many cases.[15] Moreover, we found dimethyl-

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[12] Dimethyl(2-pyridyl)vinylsilane (**1a**) is now commercially available from Tokyo Kasei Kogyo Co., Ltd (TCI), catalog no. D2935.

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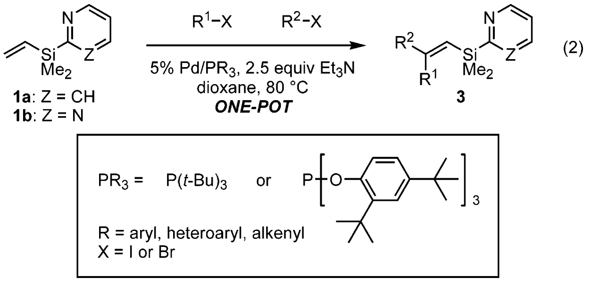
(2-pyrimidyl)vinylsilane (**1b**) to be another excellent substrate for MHR.[15] Depending on the reaction sequence, one can choose either **1a** or **1b** as a platform in our synthesis.



3. Synthesis of Triarylethene-Based Extended π-Systems.

3.1. Synthesis of Extended π-System 10.

3.1.1. Synthesis of 3 through Double Mizoroki-Heck Reaction of 1 with Aryl Halides (1 → 2 → 3). Having established the effective catalysts and substrates, we investigated the one-pot double-MHR of dimethyl(2-pyrimidyl)vinylsilane (**1b**) with various aryl halides (Scheme 2). Under the influence of Pd[P(t-Bu)$_3$]$_2$ catalyst (5 mol %) and Et_3N (2.5 equiv), the double-MHR of **1b** proceeded with various electronically and structurally diverse aryl halides (2.5 equiv) at 80 °C in dioxane to give β,β-diarylvinylsilanes **3** in excellent yields. It was found that not only aryl iodides but also aryl bromides can be used as substrates (**3b-ee** and **3b-ff**). Most of these aryl groups cannot be introduced (doubly) by our previous method using the $Pd_2(dba)_3$/P(2-furyl)$_3$ catalyst.[2c] Heteroaryl iodides (**h** and **i**) were again found to be applicable. Moreover, it should also be mentioned that the yields of **3** were greater than 95%, except for the case of 4-iodoanisole (86%). Use of the $Pd_2(dba)_3$/P[OC_6H_3(t-Bu)$_2$-2,4]$_3$ catalyst instead of Pd[P(t-Bu)$_3$]$_2$ was beneficial for this case, giving the desired β,β-diarylvinylsilane **3b-cc** in 93% yield.

Moreover, it is also possible to install different aryl groups selectively onto **1b** by adding two different aryl iodides in a stepwise fashion. Thus, a solution of **1b** (1.0 equiv), first aryl iodide (1.0 equiv), Et_3N (2.5 equiv), and Pd[P(t-Bu)$_3$]$_2$ (5 mol %) was stirred at 80 °C to afford monoarylated vinylsilane in situ. Thereafter, the second aryl iodide (1.2 equiv) was added to the mixture and further heating of the mixture at the same temperature afforded the unsymmetrical β,β-diarylvinylsilane. For example, the employment of 4-iodoacetophenone/4-iodoanisole (first/second) afforded **3b-bc** in quantitative yield. The stereochemistry was determined to be 98% E by NMR analysis of the crude product. Importantly, by simply changing the addition order of the two aryl iodides in the reaction sequence, the stereoisomer **3b-cb** could be obtained in quantitative yield with 97% stereoselectivity.

3.1.2. Synthesis of 10 through Hiyama-Type Coupling of 3 with Aryl Diiodides (3 → 10). With an efficient method of installing two aryl groups at β-C–H bonds of vinylsilanes established, we subsequently examined the Hiyama-type CCR of the resultant alkenylsilanes **3** (Scheme 3). Gratifyingly, under our standard conditions [5% $PdCl_2(PhCN)_2$, 1.5 equiv Bu_4NF, THF, 60 °C],[2b] **3** underwent efficient CCR with aryl diiodides affording an interesting triarylethene-based extended π-system **10** in moderate to excellent yields (Scheme 3).[18]

For property comparison (vide infra), unsymmetrically substituted analogues **10′**, which bear two different diarylvinyl groups on the central aryl units, were needed. We found that these π-systems can be prepared by one-pot sequential CCR of aryl dihalides with two different β,β-diarylvinylsilanes **3**. For example, the selective mono-CCR of **3b-bb** with 1-bromo-4-iodobenzene (at the Ar-I bond) afforded mono-alkenylated bromobenzene in situ. The subsequent addition of **3b-cc** and Bu_4NF (1.5 equiv each) to the mixture then gave the desired π-system **10′bcA** in 45% yield (Scheme 4).

3.2. Synthesis of Extended π-System 11.

3.2.1. Synthesis of 6 through Mizoroki–Heck Reaction of 2 with Aryl Diiodides (2 → 6). The use of aryl diiodides in the second β-C–H arylation results in the production of aryl-linked bis-alkenylsilanes **6**. For these reactions, we found that both Pd[P(t-Bu)$_3$]$_2$ and $Pd_2(dba)_3$/P[OC_6H_3(t-Bu)$_2$-2,4]$_3$ are effective as catalyst. The results using the $Pd_2(dba)_3$/P[OC_6H_3(t-Bu)$_2$-2,4]$_3$ catalyst in combination with Et_3N are shown in Scheme 5. The stereoselectivities were virtually complete, as in the cases of using simple aryl halides (Scheme 2).

3.2.2. Synthesis of 11 through Hiyama-type Coupling of 6 with Aryl Iodides (6 → 11). The resultant bis-alkenylsilanes **6** underwent CCR with aryl iodides to furnish another type of triarylethene-based π-system **11** (Scheme 6). However, under our standard conditions (Scheme 3), substantial amounts of protodesilylation products were obtained. After reinvestigation of CCR

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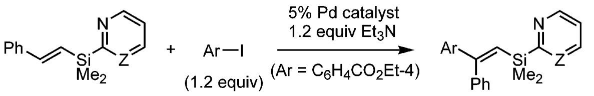
[15] Representative results using P(2-furyl)$_3$, P(t-Bu)$_3$, and P[OC_6H_3(t-Bu)$_2$-2,4]$_3$ ligands in the Mizoroki–Heck reaction of styryl(2-pyridyl)silane and styryl(2-pyrimidyl)silane are shown below.



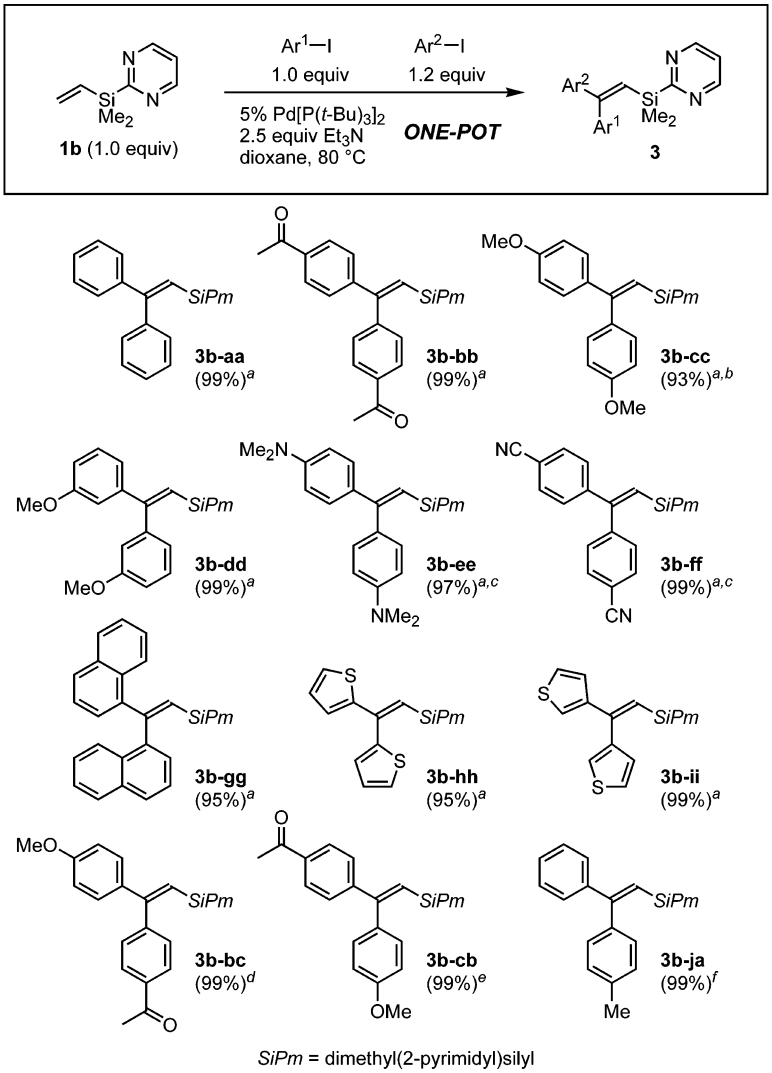
Z	Pd catalyst	yield (%)	
		THF, 50 °C	dioxane, 80 °C
CH (pyridyl)	$Pd_2(dba)_3$/P(2-furyl)$_3$	22	64
CH (pyridyl)	Pd[P(t-Bu)$_3$]$_2$	67	95
N (pyrimidyl)	Pd[P(t-Bu)$_3$]$_2$	85	>99
N (pyrimidyl)	$Pd_2(dba)_3$ /P[OC_6H_3(t-Bu)$_2$-2,4]$_3$	-	98

[16] Currently, we assume that the exceptionally high reactivity exerted by P(t-Bu)$_3$ and P[OC_6H_3(t-Bu)$_2$-2,4]$_3$ might be attributed to their propensity to dissociate from Pd to form highly reactive mono- or nonligated Pd complexes in the olefin coordination step and/or carbopalladation (insertion) step. (a) Stambuli, J. P.; Bühl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346. (b) Galardon, E.; Ramdeehul, S.; Brown, J. M.; Cowley, A.; Hii, K. K.; Jutand, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1760.

[17] Unfortunately, aryl chlorides were found not to be applicable in our system even using highly reactive Pd/P(t-Bu)$_3$ catalyst.

[18] Very recently, we found that vinylboronate pinacol ester can also be used as a platform for triarylethene-based extended π-systems such as **10**. However, because the double-MHR step is not stereoselective, the boron-based method can only be used in the synthesis of "symmetrical" **10** where all four terminal aryl groups (Ar^1 and Ar^2) are same. Therefore, the selective synthesis of "unsymmetrical" **10** (such as **10bcA** and **10cbA**) as well as the structural isomers of **10** (**11** and **12**) is not possible with the boron-based method. Itami, K.; Tonogaki, K.; Ohashi, Y.; Yoshida, J. *Org. Lett.* **2004**, *6*, 4093.

SCHEME 2. Synthesis of 3 through Double Mizoroki-Heck Reaction of 1b with Aryl Halides[a]



SiPm = dimethyl(2-pyrimidyl)silyl

[a] Employing 2.5 equiv of aryl iodides. [b] The reaction was carried out with $Pd_2(dba)_3$ (2.5%) and $P[OC_6H_3(t\text{-Bu})_2\text{-}2,4]_3$ (5%) instead of $Pd[P(t\text{-Bu})_3]_2$. [c] Aryl bromides were used. [d] The stereochemistry was determined to be 98% E by NMR analysis. [e] The stereochemistry was determined to be 97% *Z* by NMR analysis. [f] The stereochemistry was determined to be 96% *Z* by NMR analysis.

conditions, we found that the slow addition of Bu_4NF as well as lowering the reaction temperature (60 → 40 °C) had a beneficial effect on cross-coupling. Under these conditions, **11** was obtained in reasonable yield (Scheme 6).

3.3. Synthesis of Extended π-System 12.

3.3.1. Synthesis of 7 through Mizoroki−Heck Reaction of 1 with Aryl Diiodides (1 → 7). The use of aryl diiodides in the first β-C−H arylation results in the production of aryl-linked bis-alkenylsilanes **7** (Scheme 7). However, when highly reactive $Pd[P(t\text{-Bu})_3]_2$ or $Pd_2(dba)_3/P[OC_6H_3(t\text{-Bu})_2\text{-}2,4]_3$ catalyst was used for the reaction of **1a** and 1,4-diiodobenzene, an undesirable double-Mizoroki−Heck-type polymerization took place (vide infra). After careful reinvestigation of MHR conditions for this particular reaction, we found that the use of our original $Pd_2(dba)_3/P(2\text{-furyl})_3$ catalyst is most effective, furnishing the desired **7a-A** in 94% yield (Scheme 7).

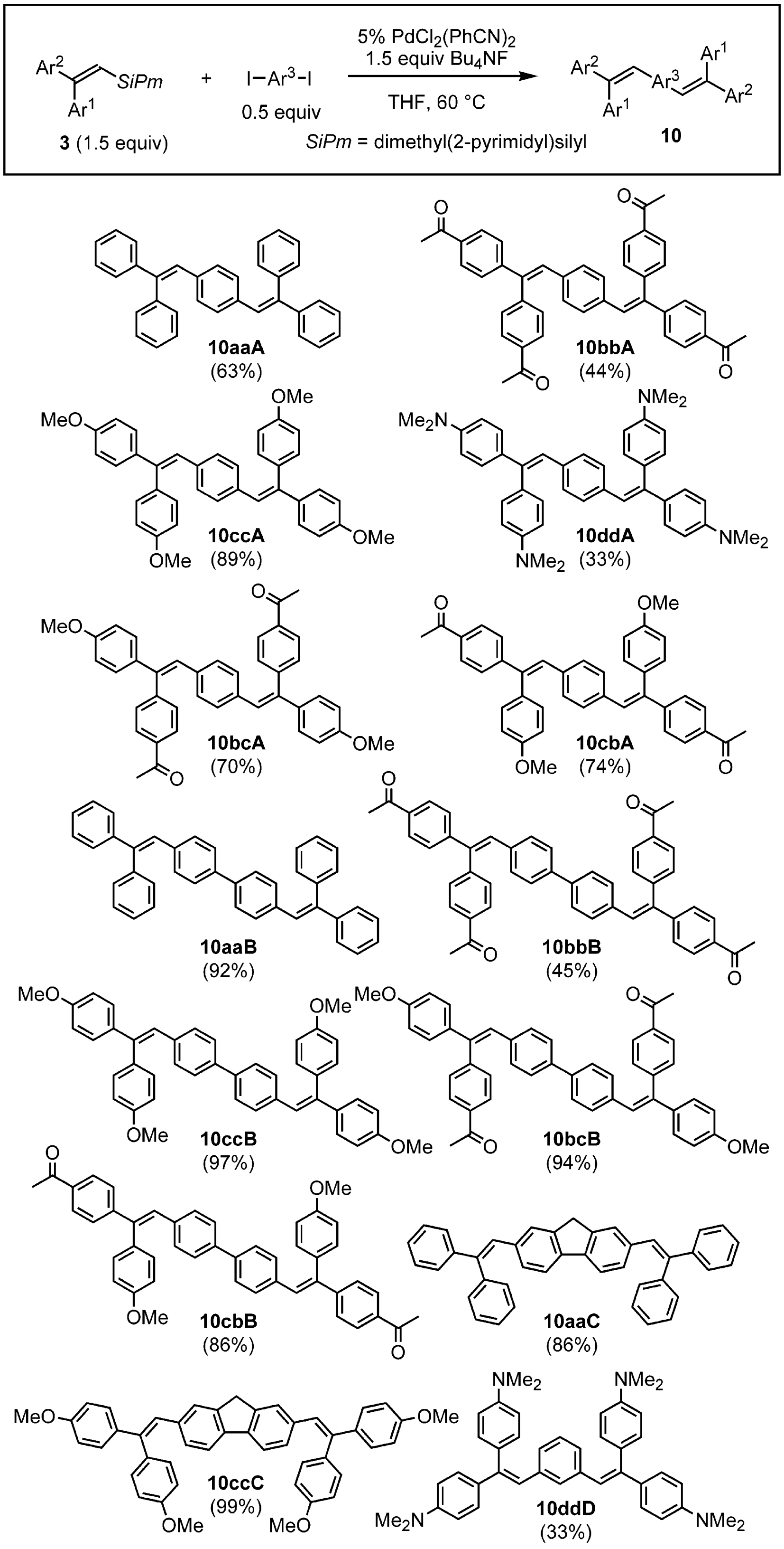
3.3.2. Synthesis of 8 through Mizoroki−Heck Reaction of 7 with Aryl Iodides (7 → 8). The second MHR of the resultant **7** with aryl iodides then gave another type of aryl-linked bis-alkenylsilanes **8** (Scheme 8). The $Pd_2(dba)_3/P[OC_6H_3(t\text{-Bu})_2\text{-}2,4]_3$ system was found to be suitable for these substrates. Even using equimolar quantities of each substrate, **8** could be obtained in high yields with virtually complete stereoselectivities under these conditions (Scheme 8).

3.3.3. Synthesis of 12 through Hiyama-type Coupling of 8 with Aryl Iodides (8 → 12). The final end-capping CCR of **8** with aryl iodides then furnished the extended π-system **12** (Scheme 9). As in the cases using **6**, the slow addition of Bu_4NF as well as lowering the reaction temperature (40 °C) had a beneficial effect on cross-coupling efficiency, giving **12** in good yields except for the sterically congested **12Alb** (25%).

3.4. Synthesis of Extended π-System 13.

3.4.1. Synthesis of 9 through Double Mizoroki−Heck Reaction of 1 with Aryl Diiodides (1 → 9). When double-MHR of **1** was performed with ArX_2 alone, double Mizoroki−Heck-type polymerization took place (**1** → **7** → **9**) to afford novel polymers **9** in high yields

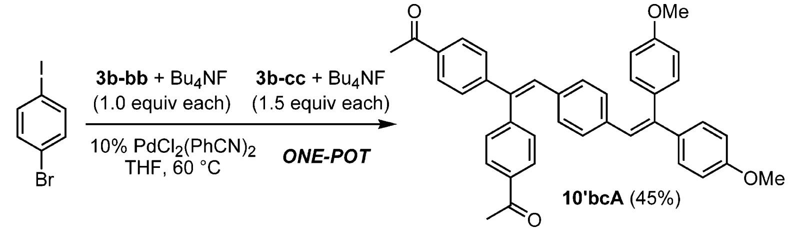
SCHEME 3. Synthesis of 10 through Hiyama-Type Coupling of 3 with Aryl Diiodides



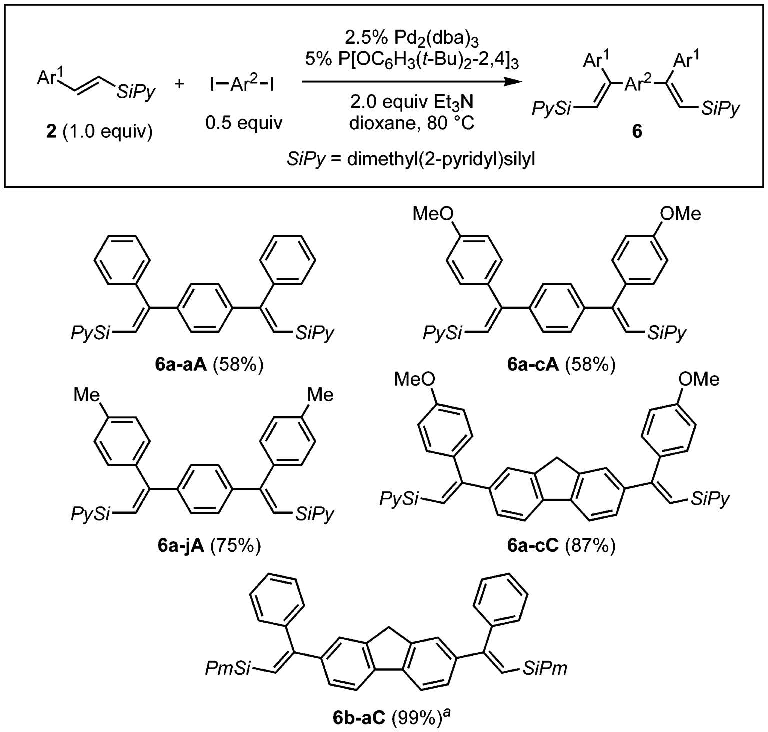
(Scheme 10). It should be noted that such a type of double arylative polymerization is unprecedented.[19]

3.4.2. Synthesis of 9 through Mizoroki−Heck Reaction of 7 with Aryl Diiodides (7 → 9). Although a new type of polymer can be prepared by the above-mentioned procedure, a similar type of polymer having different aryl units on the backbone should also be intriguing to prepare. It was found that such copolymers could be obtained when two different ArX_2 were sequentially employed in the double-MHR of **1**. Although one-

SCHEME 4. Synthesis of π-System 10′ through Sequential Cross-Coupling of Two Different 3 with Aryl Dihalide



SCHEME 5. Mizoroki−Heck Reaction of 2 with Aryl Dihalides



[a] Reaction carried out using styryl(2-pyrimidyl)silane **2b-a**.

pot reactions of this type were not possible because of the difficulty in the selective production of mono-arylated **7** with Pd[P(t-Bu)$_3$]$_2$ catalyst, the stepwise MHR of **7a-A** with 1,3-diiodobenzene yielded the desired copolymer **9a-AD** in 85% yield (Scheme 11).

3.4.3. Synthesis of 13 through Hiyama-Type Coupling of 9 with Aryl Iodides (9 → 13). The successive CCR of the resultant polymers **9** with aryl iodides in the presence of PdCl$_2$(PhCN)$_2$ catalyst and Bu$_4$NF finally produced novel cross-conjugated polymers **13** in good yields (Scheme 12). To our knowledge, this type of polymer has not been prepared previously. The molecular weight (M_n) and polydispersity (PD) of the polymers **13**, determined by size exclusion chromatography using polystyrene standards, are as follows: **13AAm** (M_n = 9235, PD = 2.06), **13DDb** (M_n = 7148, PD = 1.86), **13DDm** (M_n = 7804, PD = 2.03), **13ADb** (M_n = 7575, PD = 2.14), **13ADn** (M_n = 7661, PD = 3.03).

4. Photophysical Properties of Triarylethene-Based Extended π-Systems 10−13.

4.1. Photophysical Properties in CHCl$_3$. The photophysical properties (UV−vis and fluorescence) of the triarylethene-based extended π-systems **10**−**13** constructed (30 compounds) were first measured as their solution in degassed CHCl$_3$ (Table 1).

In the UV−vis absorption spectra, the absorption maxima (λ_{abs}) ascribed to the $\pi-\pi^*$ transitions depend on the nature of the aryl groups installed, as expected. For example, the λ_{abs} values increase as the phenyl group (**a**) is replaced by the p-acetylphenyl group (**b**) in the π-systems **10**, **11**, and **12**: **10aaA** (354 nm) → **10bbA** (377 nm); **10aaB** (353 nm) → **10bbB** (372 nm); **11aAa** (338 nm) → **11aAb** (360 nm); **12Aaa** (299 nm) → **12Aab** (327

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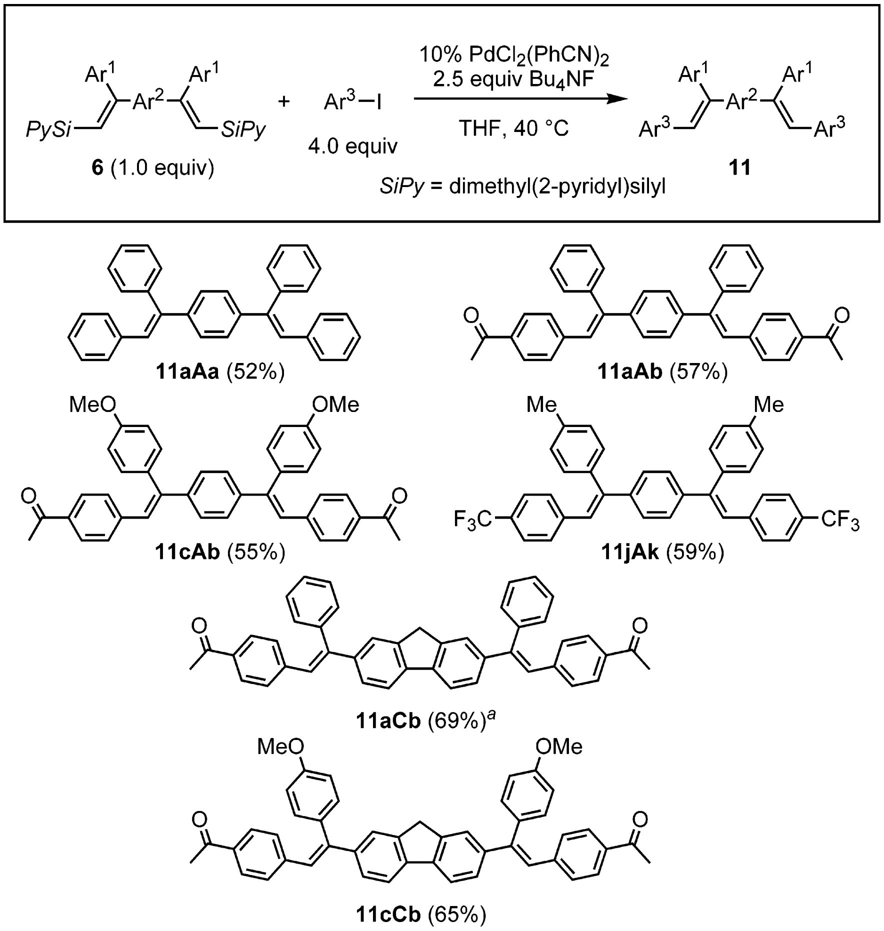
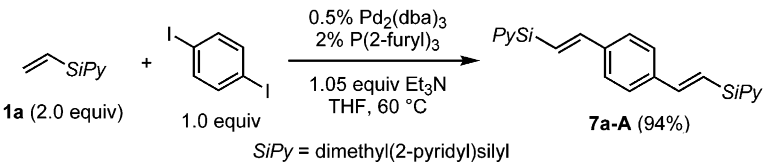
(19) Selected examples of Pd-catalyzed Mizoroki−Heck-type polycondensation of diolefins and dihalides: (a) Suzuki, M.; Lim, J.-C.; Saegusa, T. *Macromolecules* **1990**, *23*, 1574. (b) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281. (c) Pan, M.; Bao, Z.; Yu, L. *Macromolecules* **1995**, *28*, 5151. (d) Pasco, S. T.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **1999**, *32*, 6933. (e) Jung, S.-H.; Kim, H. K.; Kim, S.-H.; Kim, Y. H.; Jeoung, S. C.; Kim, D. *Macromolecules* **2000**, *33*, 9277. (f) Mikroyannidis, J. A.; Spiliopoulos, I. K.; Kulkarni, A. P.; Jenekhe, S. A. *Synth. Met.* **2004**, *142*, 113. (g) Kim, J. H.; Lee, H. *Synth. Met.* **2004**, *144*, 169. (h) Mikroyannidis, J. A.; Vellis, P. D.; Karastatiris, P. I.; Spiliopoulos, I. K. *Synth. Met.* **2004**, *145*, 87. (i) Mikroyannidis, J. A. *Synth. Met.* **2004**, *145*, 271. (j) Takagi, K.; Mori, K.; Kunisada, H.; Yuki, Y. *Polym. Bull.* **2004**, *52*, 125. (k) Jin, S.-H.; Kim, M.-K.; Koo, D.-S.; Kim, Y.-I.; Park, S.-H.; Lee, K.; Gal, Y.-S. *Chem. Mater.* **2004**, *16*, 3299. (l) Jin, S.-H.; Hwang, C.-K.; Gal, Y.-S.; Park, D.-K.; Cho, S.-J.; Shin, D.-M.; Lee, J.-W. *Eur. Polym. J.* **2004**, *40*, 1975. (m) Morisaki, Y.; Chujo, Y. *Macromolecules* **2004**, *37*, 4099.

SCHEME 6. Synthesis of 11 through Hiyama-Type Coupling of 6 with Aryl Iodides



[a] Reaction carried out using 2-pyrimidylsilane **6b-aC**.

SCHEME 7. Synthesis of 7 through Mizoroki−Heck Reaction of 1 with Aryl Diiodides



nm). Presumably this is a reflection of the effective extension of π-conjugation with terminal carbonyl groups. The olefinic isomers in π-system **10** (**10bcA/10cbA** and **10bcB/10cbB**) were found to possess similar absorption bands.

In the fluorescence spectra, many of these π-systems were found to have their emission bands in the visible region (blue to yellow). In addition to the emission color, the fluorescence quantum yields were also found to depend significantly on the attaching sites, as well as the nature of the aryl groups installed.

For example, the π-systems **10** emit light in the blue to yellow region, but their emission maxima (λ_{em}) and quantum yields (Φ_F) depend heavily on the nature and position of the aryl groups (vide infra). In this class of π-system, we detected an interesting substituent effect on the Stokes shifts. For example, when two terminal aryl groups (Ar^1 and Ar^2) are in a donor/acceptor (push/pull) relationship, larger Stokes shifts were observed (**10bcA** 130 nm, **10cbA** 122 nm) compared with those of the parent "symmetrical" π-systems (**10bbA** 109 nm, **10ccA** 101 nm). Such a donor/acceptor substitution can bring about the green emission (**10bcA** and **10cbA**) from otherwise blue-fluorescent **10aaA**. In comparison with the well-known blue-fluorescent DPVBi (**10aaB**; $\Phi_F = 6.0 \times 10^{-2}$), which has been used in organic electroluminescence devices,[20,21] **10aaC** was found to possess greater quantum yield (Φ_F = 0.30). The unsymmetrically substituted (at terminal olefinic carbons) π-systems **10bcA**,

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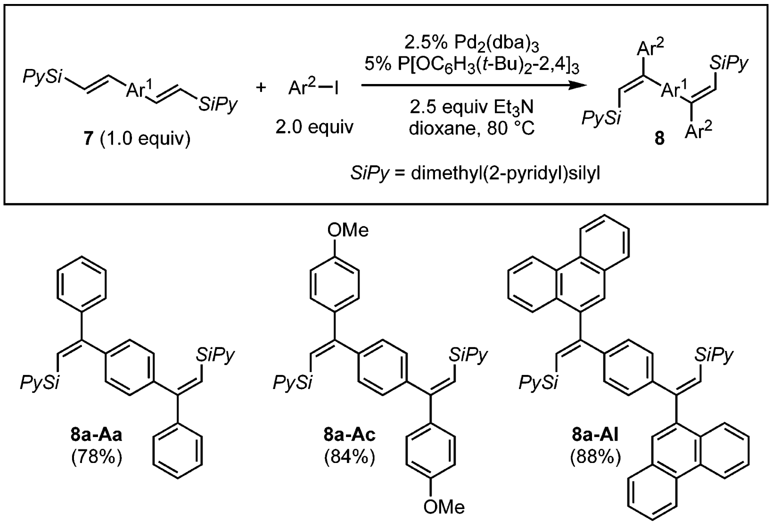
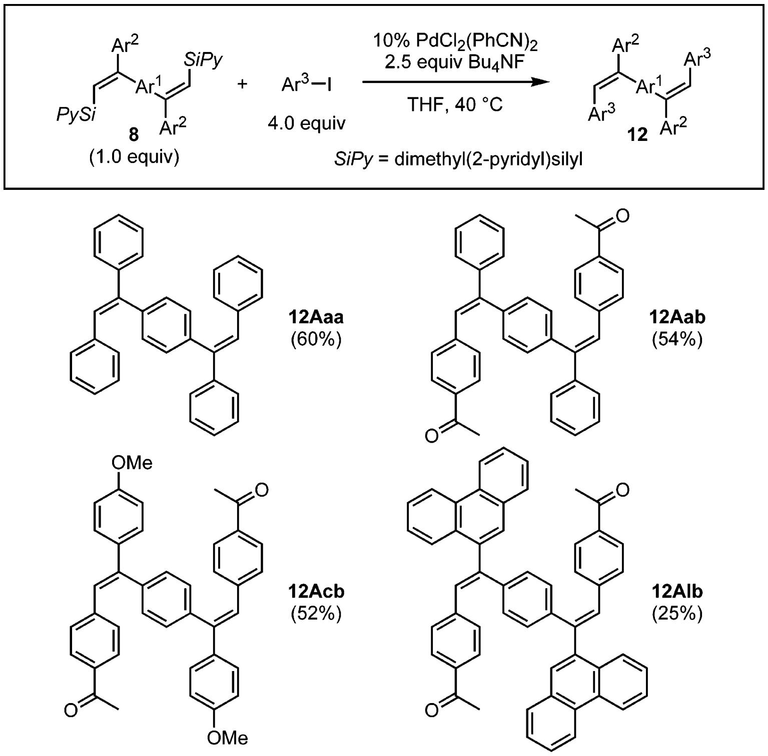
(20) Tokailin, H.; Hosokawa, C.; Kusumoto, T. Eur. Pat. Appl. EP387715, 1990; *Chem. Abstr.* **1990**, *115*, 123507. (b) Hosokawa, C.; Higashi, H.; Nakamura, H.; Kusumoto, T. *Appl. Phys. Lett.* **1995**, *67*, 3853. (c) Hosokawa, C.; Eida, M.; Matsuura, M.; Fukuoka, K.; Nakamura, H.; Kusumoto, T. *Synth. Met.* **1997**, *91*, 3. (d) Yang, J. P.; Jin, Y. D.; Heremans, P. L.; Hoefnagels, R.; Dieltiens, P.; Blockhuys, F.; Geise, H. J.; Van der Auweraer, M.; Borghs, G. *Chem. Phys. Lett.* **2000**, *325*, 251. (e) Savvate'ev, V.; Friedl, J. H.; Zou, L.; Shinar, J.; Christensen, K.; Oldham, W.; Rothberg, L. J.; Chen-Esterlit, Z.; Kopelman, R. *Appl. Phys. Lett.* **2000**, *76*, 1501. (f) Huang, Y.-S.; Jou, J.-H.; Weng, W.-K.; Liu, J.-M. *Appl. Phys. Lett.* **2002**, *80*, 2782.

(21) Shinar, J., Ed. *Organic Light-Emitting Devices: A Survey*; Springer-Verlag: New York, 2004.

SCHEME 8. Synthesis of 8 through Mizoroki–Heck Reaction of 7 with Aryl Iodides



SCHEME 9. Synthesis of 12 through Hiyama-Type Coupling of 8 with Aryl Iodides

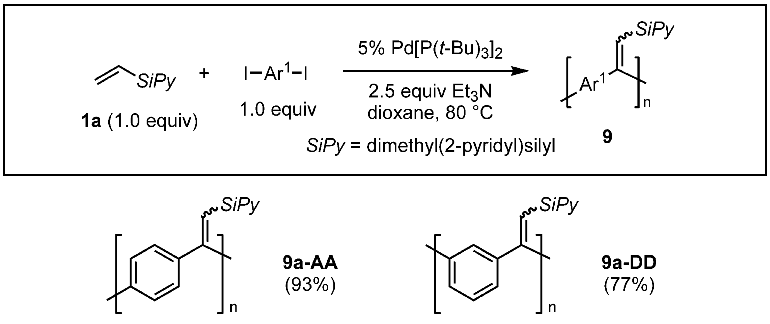


10cbA, **10bcB**, and **10cbB** also emit relatively intense light ($\Phi_F = 0.16-0.17$) in green region.

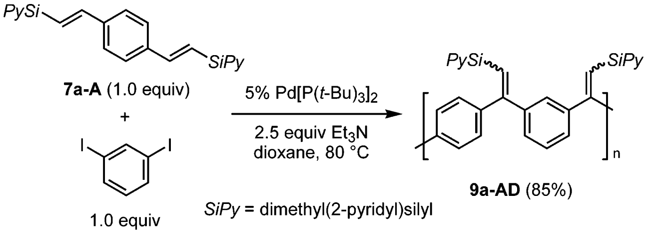
Interestingly, it was found that the π-systems **11** and **12** (the structural isomers of **10**) are almost nonfluorescent in solution (Table 1 and Figure 3). This is in a sharp contrast to the high fluorescence efficiencies obtained in **10**, which clearly indicates the importance of the attaching sites of aryl groups on photophysical properties. The polymeric π-systems **13** are also intriguing, not only because of their structural novelty but also because they are also fluorescent (green to yellow region).

4.2. Effect of Substituents on Fluorescence Efficiency. While constructing such fluorescent libraries, we were able to find interesting effects of substituents on fluorescence efficiency (Figure 4). For example, in the π-system **10**, the substitution of all terminal aryl groups with p-$MeCOC_6H_4$ or p-$MeOC_6H_4$ groups only had detrimental effects on emission efficiency (Φ_F 2.1×10^{-2} for **10bbA**, 3.5×10^{-3} for **10ccA**) compared with the parent phenyl group (**10aaA** $\Phi_F = 5.9 \times 10^{-2}$). The π-system **10′bcA** was also found to be weakly fluorescent ($\Phi_F = 5.4 \times 10^{-3}$). However, the unsymmetrical substitutions with these groups at terminal olefinic carbons resulted in a substantial increase in fluorescence quantum yield (Φ_F 0.16 for **10bcA** and **10cbA**) (Figure 4). These structure–property relationship analyses clearly showed the beneficial effect of the unsymmetrical substitutions at terminal olefinic carbons with an electron-accepting p-$MeCOC_6H_4$ group and an electron-releasing p-$MeOC_6H_4$ group on fluorescence efficiency.

SCHEME 10. Synthesis of 9 through Double Mizoroki−Heck Reaction of 1 with Aryl Diiodides



SCHEME 11. Synthesis of 9 through Mizoroki−Heck Reaction of 7 with Aryl Diiodides



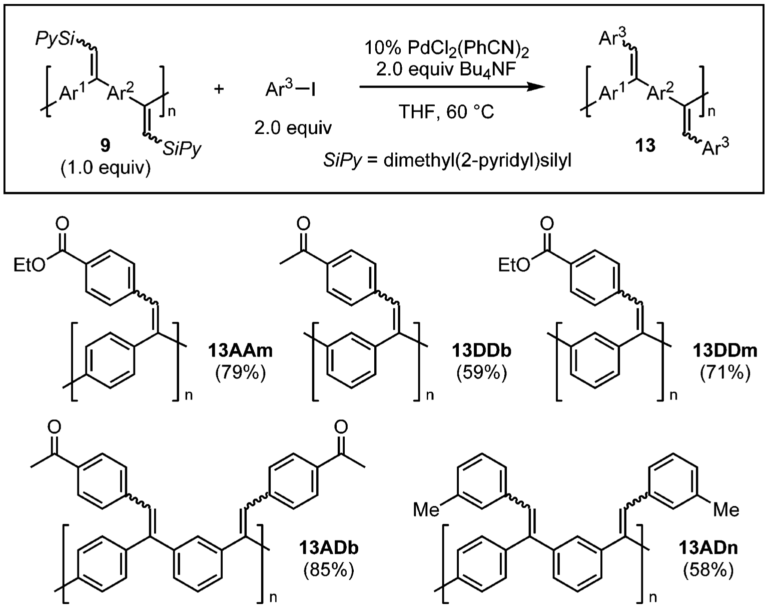
In addition to the increased chance of discovering new materials, the increased chance of discovering such interesting photophysical properties is clearly an advantage of programmable and diversity-oriented synthesis in fluorescent materials science, where the properties are often not predictable.[22] Currently, we are trying to clarify this interesting substituent effect on fluorescence efficiency.

4.3. Enhanced Emission in the Solid State. During the course of our investigation aimed at clarifying the controlling factors determining the fluorescence efficiency, we found that the fluorescence efficiency of these triarylethene-based extended π-systems **10**−**13** generally (and dramatically in many cases) increases in the solid state. As well as **10**, otherwise nonfluorescent π-systems such as **11** and **12** also became fluorescent in the solid state. The $\lambda_{\max}$ values of the solid-state emission were found to be similar to those obtained in chloroform solution (Table 1).

Because it has been assumed in many cases that the fluorescence efficiency of organic chromophores generally decreases in the solid state, mainly attributed to the intermolecular vibronic interactions that trigger nonradiative deactivation processes (fluorescence quenching),[23] we became interested in the enhanced emission of triarylethene-based extended π-systems in the solid state.

Currently, we assume this interesting fluorescence property of triarylethene-based extended π-systems is mainly attributed to their unique structure. On the basis of the X-ray crystal structure analysis[2e] and quantum calculations, we found that triarylethenes and triarylethene-based extended π-systems adopt a nonplanar structure as the result of a sterically congested environment around the C═C core. We suppose that such structural features of triarylethene-based extended π-systems would reduce the probability of effective intermolecular fluorescence-quenching interactions even in the solid state. If this is the case, then the aggregation (solidification) should lead to the reduced probability and amplitude of molecular motions such as twisting and out-of-plane bending motion, which might trigger radiationless transitions, thereby enhancing the fluorescence

SCHEME 12. Synthesis of 13 through Hiyama-Type Coupling of 9 with Aryl Iodides



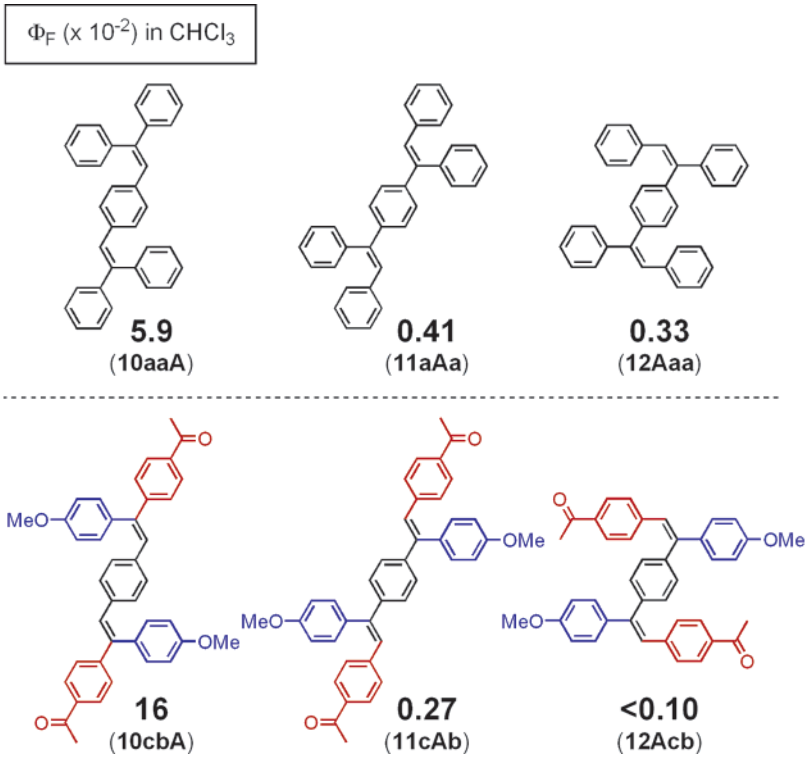


FIGURE 3. Effect of aryl-group attachment site on fluorescence efficiency.

TABLE 1. Photophysical Properties of Triarylethene-Based Extended π-Systems 10−13

	UV−vis[a]	fluorescence		
compd	λ_{abs} (log ϵ)	λ_{em}[a]	Φ_{F}[a,b]	$\lambda_{\text{em(solid)}}$[c]
10aaA	354 nm (4.54)	461 nm	5.9×10^{-2}	480 nm
10bbA	377 nm (4.63)	486 nm	2.1×10^{-2}	486 nm
10ccA	369 nm (4.59)	470 nm	3.5×10^{-3}	478 nm
10ddA	407 nm (4.63)	477 nm	$<1.0 \times 10^{-3}$	541 nm
10bcA	378 nm (4.49)	508 nm	0.16	515 nm
10cbA	383 nm (4.42)	505 nm	0.16	504 nm
10aaB	353 nm (4.71)	442 nm	6.0×10^{-2}	455 nm
10bbB	372 nm (4.63)	469 nm	2.0×10^{-2}	495 nm
10ccB	364 nm (4.71)	453 nm	5.6×10^{-3}	468 nm
10bcB	372 nm (4.67)	484 nm	0.17	481 nm
10cbB	375 nm (4.74)	482 nm	0.17	493 nm
10aaC	370 nm (4.74)	449 nm	0.30	460 nm
10ccC	380 nm (4.71)	460 nm	$<1.0 \times 10^{-3}$	479 nm
10ddD	354 nm (4.53)	nd	$<1.0 \times 10^{-3}$	nd
10′bcA	381 nm (4.53)	525 nm	5.4×10^{-3}	519 nm
11aAa	338 nm (4.57)	415 nm	4.1×10^{-3}	433 nm
11aAb	360 nm (4.58)	441 nm	3.9×10^{-3}	486 nm
11cAb	367 nm (4.56)	490 nm	2.7×10^{-3}	485 nm
11jAk	339 nm (4.53)	nd	7.7×10^{-4}	433 nm
11aCb	374 nm (4.68)	466 nm	6.1×10^{-3}	530 nm
11cCb	373 nm (4.65)	nd	1.1×10^{-3}	551 nm
12Aaa	299 nm (4.53)	nd	3.3×10^{-3}	451 nm
12Aab	327 nm (4.57)	nd	$<1.0 \times 10^{-3}$	469 nm
12Acb	343 nm (4.60)	nd	$<1.0 \times 10^{-3}$	463 nm
12Alb	302 nm (4.53)	450 nm	9.8×10^{-3}	481 nm
13AAm	335 nm (4.18)	492 nm	nd	nd
13DDb	330 nm (4.16)	463 nm	nd	nd
13DDm	322 nm (4.22)	452 nm	nd	nd
13ADb	330 nm (4.42)	498 nm	nd	nd
13ADn	303 nm (4.34)	469 nm	nd	nd

[a] Measured in degassed $CHCl_3$. nd = could not be detected. [b] Determined with reference to 9,10-diphenylanthracene (excited at 350 nm). nd = could not be detected. [c] Solid-state fluorescence. nd = could not be detected.

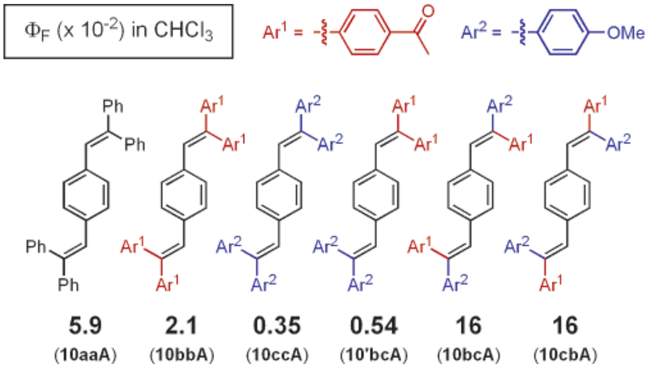


FIGURE 4. Effect of substituents on fluorescence efficiency.

efficiency as a whole.[24,25] Alternatively, an aggregation-induced planarization of the π-system might also be the reason for enhanced emission.

4.4. Aggregation-Induced Enhanced Emission. While investigating the enhanced emission of the triarylethene-based extended π-systems in the solid state, we became aware of the existence of several interesting organic fluorophores that show unique enhanced emission rather than a fluorescence quenching in the solid (aggregated) state.[26−34] For example, very recently, Tang

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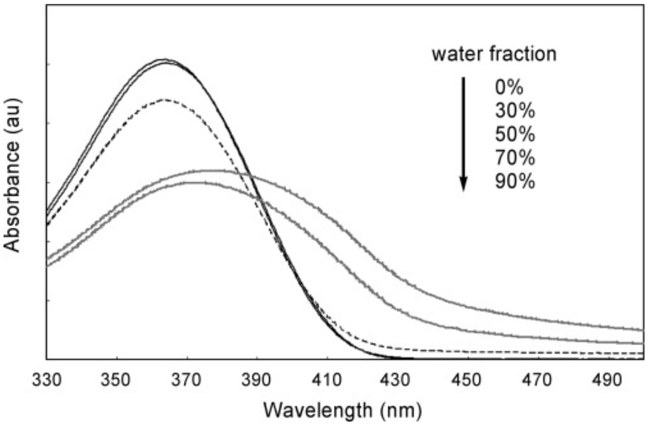

FIGURE 5. UV−vis spectra of **10ccB** in dioxane/water mixtures (10 μM).

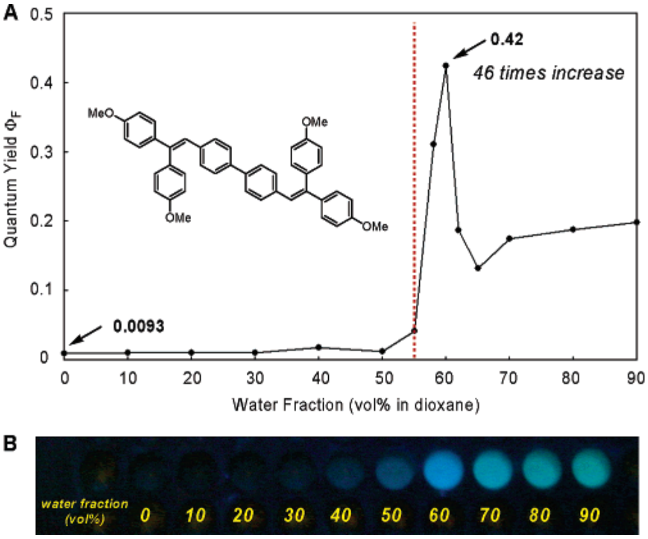

FIGURE 6. Aggregation-induced enhanced emission. (A) Fluorescence quantum yields (Φ_F) of **10ccB** depending on water fractions in dioxane. (B) Emissive behaviors of **10ccB** in dioxane/water mixtures under irradiation of light at 365 nm.

and co-workers reported that a series of siloles exhibit a strongly enhanced fluorescence emission in the solid state as well as in nanoparticles (nanoaggregates).[29,35] Thus, we decided to see whether such an aggregation-induced enhanced emission is also operating in our π-systems.

First, we measured the UV−vis absorption spectra of **10ccB** in various dioxane/water mixtures (Figure 5). Because **10ccB** does not dissolve in water, **10ccB** was expected to aggregate in dioxane/water mixtures with high water content. From 60% volume fraction of water, the maximum peaks in the absorption spectra are red-shifted with obvious level-off tailing (Figure 5). These spectral changes are commonly observed in nanoparticle suspensions.[29,30,35]

Next, we measured the fluorescence spectra of **10ccB** in various dioxane/water mixtures (Figure 6). As in chloroform (Table 1), **10ccB** exhibited an extremely low fluorescence quantum yield ($\Phi_F = 9.3 \times 10^{-3}$) in pure dioxane. Although **10ccB** showed similar Φ_F values up to 50% volume fraction of water, we observed an obvious and drastic increase of the Φ_F values from 60% volume fraction of water. In particular, the Φ_F value at this composition (dioxane/water = 40/60) is 46 and 70 times higher (Φ_F = 0.42) than that in pure dioxane and chloroform, respectively. The aggregation seems to be responsible for this dramatic increase in fluorescence efficiency. The formation of molecular aggregates was also indicated from the observation that the mixtures containing greater than 60% volume fraction of water exhibited an off-white turbidity due to light scattering. Interestingly, the Φ_F values were found to drop at higher water content (though they were still greater than that in pure dioxane). Although more in-depth experiments must be conducted, these results indicate the existence of additional aggregation effects, such as a size effect, on fluorescence properties.

To see the generality of aggregation-induced enhanced emission in the triarylethene-based extended π-systems, we measured the fluorescence spectra of representative compounds in a 20/80 dioxane/water mixture (Table 2). In all cases examined, the fluorescence quantum yields in such aggregated species (Φ_F^{agg}) were found to be greater than those of molecularly dissolved species in dioxane (Φ_F^{sol}). In particular, otherwise nonemissive π-systems such as **10′bcA**, **11aAa**, and **12Aaa** were found to fluoresce in the aggregation state (Φ_F^{agg} 0.15 for **10′bcA**, 0.18 for **11aAa**, 4.0×10^{-2} for **12Aaa**). The increase ($\Phi_F^{agg}/\Phi_F^{sol}$) observed was 21, 49, and 33 times, respectively. This aggregation-induced enhanced emis-

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TABLE 2. Fluorescence Efficiency of Representative Compounds in Dioxane/Water (20/80) Mixture[a]

compd	Φ_F^{agg}	Φ_F^{sol}	$\Phi_F^{agg}/\Phi_F^{sol}$
10aaA	0.44	8.7×10^{-2}	5.1
10aaB	0.31	0.21	1.5
10ccB	0.19	9.3×10^{-3}	20
10bcB	0.61	0.21	2.9
10′bcA	0.15	7.0×10^{-3}	21
11aAa	0.18	3.7×10^{-3}	49
12Aaa	4.0×10^{-2}	1.2×10^{-3}	33

[a] The Φ_F^{agg} values were determined in dioxane/water (20/80) mixture with reference to 9,10-diphenylanthracene. The Φ_F^{sol} values were determined in dioxane with reference to 9,10-diphenylanthracene.

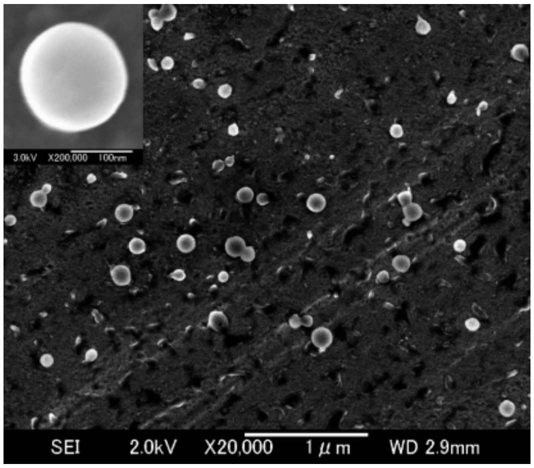

FIGURE 7. FE-SEM images of nanoparticles obtained from suspension of **10ccB** in 20/80 dioxane/water mixture (bar = 1 μm). Inset shows the magnified FE-SEM image (bar = 100 nm).

sion is also operative in highly fluorescent π-systems. For example, the Φ_F value of **10bcB** was found to rise to 0.61 from 0.21 obtained in pure dioxane. Overall, the formation of molecular aggregates in dioxane/water mixtures generally and dramatically boosts the emission efficiency of triarylethene-based extended π-systems.

The formation of molecular aggregates under these conditions (dioxane/water mixture) was indicated from many aspects, but direct evidence for it was lacking. Gratifyingly, dynamic light scattering (DLS) experiments on the suspension of **10ccB** in 20/80 dioxane/water mixture revealed the presence of molecular aggregates with average diameter of 240 nm. The shape of nanoparticles (nanoaggregates) was observed by field emission scanning electron microscopy (FE-SEM).[36] The FE-SEM images in Figure 7 show that the diameter of the nanoparticles is in a range of 100−250 nm, which agrees roughly with that determined by DLS experiments.

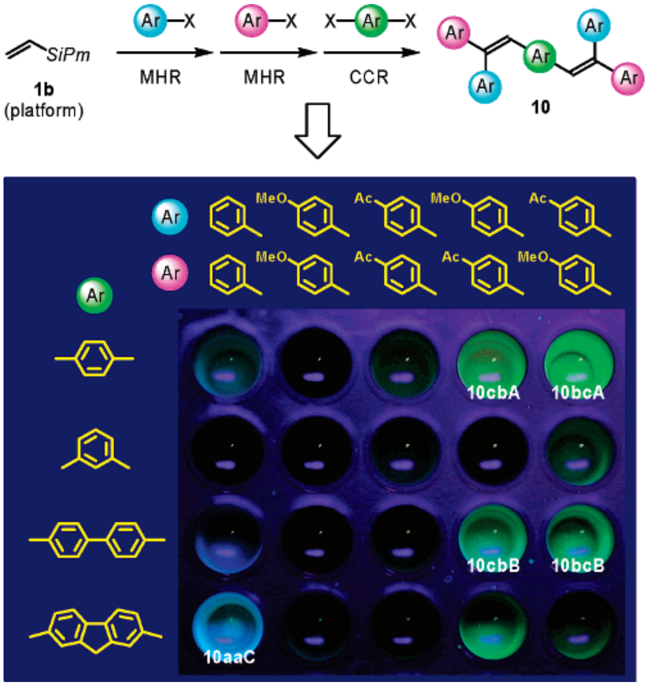

FIGURE 8. Rapid synthesis and property evaluation in the extended π-system **10**.

5. Rapid Synthesis/Evaluation Process. Through this study, we mainly focused our efforts on the conventional "one-at-a-time" synthesis/purification/evaluation process because the properties of the triarylethene-based extended π-systems that we dealt with were largely unknown. However, after obtaining a clearer picture of the photophysical properties of these π-systems, we are now in a position to take full advantage of the programmable and diversity-oriented nature of the present synthetic strategy for conducting rapid synthesis/evaluation process.[37] Although the execution of such experiments in a truly meaningful manner requires automated synthesis as well as high-throughput screening, we herein provide "proof-of-principle" (manual) experiments using our synthesis (Figure 8).

This was done as follows. The 20 compounds (**10**) with varied five aryl groups were synthesized in a parallel fashion and then placed in a microtiter plate directly from crude reaction solutions. Irradiation of this plate (at 365 nm) allowed us quickly to detect several fluorescent compounds from this crude library, as can be clearly seen from the picture in Figure 8. The emission color as well as relative emission efficiency was found to correlate with those of isolated samples. It should be noted that five highly fluorescent π-systems found in this study (**10aaC**, **10bcA**, **10cbA**, **10bcB**, and **10cbB**) were correctly detected by this method (Figure 8). We believe that this process not only serves as a first step toward our next goal (fully automated synthesis/evaluation of functional π-systems) but also is useful in its own right as a first-round qualitative manual screening method.

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Conclusions

In conclusion, we have developed a programmable and diversity-oriented synthetic method for the structurally well-defined triarylethene-based extended π-systems. By following the basic synthetic scheme developed, we succeeded in preparing a number of interesting triarylethene-based extended π-systems (four types, 30 compounds) very efficiently. The measurement of photophysical properties showed that many of these π-systems have their emission bands in the visible region (blue to yellow) and that the fluorescence quantum yields as well as emission color depend significantly on the attaching sites and the nature of the aryl groups attached. It was also found that many of the triarylethene-based extended π-systems prepared emit more intense light (do not quench their fluorescence) in the solid state. Moreover, such an aggregation-induced enhanced emission was also observed in dioxane/water mixtures with high water contents, where the formation of molecular aggregates such as nanoparticles has been indicated. A useful method for the rapid synthesis and property evaluation has also been developed.

The simple but powerful synthetic strategy described herein clearly benefits from the inherent stereo-electronic bias of the vinylsilane platform (differentiated reactivity of C−H and C−Si bonds) with the aid of catalyst-directing (coordinating) groups. The present successful application to functional extended π-systems speaks well for the potential of such an orchestrated interplay of organo-element chemistry (organosilicon chemistry herein, but not to be limited to silicon)[2e] and coordination chemistry in the development of other platforms[38] to construct versatile chemical libraries to face more challenging quest in materials science.

Experimental Section

Typical Procedure for Synthesis of 3 Where Two Aryl Groups Are the Same (Scheme 2). A mixture of dimethyl-(2-pyrimidyl)vinylsilane (**1b**; 173.5 mg, 1.06 mmol), iodobenzene (421.6 mg, 2.07 mmol), triethylamine (253.0 mg, 2.50 mmol), and Pd[P(t-Bu)$_3$]$_2$ (25.6 mg, 50.1 μmol) in dry dioxane (3.0 mL) was stirred at 80 °C for 8 h under argon. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The subjection of the crude mixture to gel permeation chromatography (CHCl$_3$) afforded **3b-aa** (330.6 mg, 99%) as a pale yellow oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.21 (s, 6H), 6.59 (s, 1H), 7.12−7.16 (m, 3H), 7.23−7.34 (m, 8H), 8.72 (d, J = 5.1 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ −2.2, 119.4, 125.6, 127.40, 127.44, 127.81, 127.83, 127.9, 129.5, 142.2, 142.8, 154.9, 159.0, 180.8; IR (neat) 1736, 1559, 1393 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{20}N_2Si$ 316.1396, found 316.1398.

Note: **3b-cc** was prepared using Pd$_2$(dba)$_3$ (2.5%) and P[OC$_6$H$_3$(t-Bu)$_2$-2,4]$_3$ (5%) instead of Pd[P(t-Bu)$_3$]$_2$.

Typical Procedure for Synthesis of 3 Where Two Aryl Groups Are Different (Scheme 2). A mixture of dimethyl-(2-pyrimidyl)vinylsilane (**1b**; 171.4 mg, 1.04 mmol), 4-iodoacetophenone (246.4 mg, 1.00 mmol), triethylamine (253.0 mg, 2.50 mmol), and Pd[P(t-Bu)$_3$]$_2$ (25.6 mg, 50.1 μmol) in dry dioxane (2.0 mL) was stirred at 80 °C for 5 h under argon. To this mixture was added 4-iodoanisole (286.1 mg, 1.22 mmol) and the resultant mixture was further stirred at 80 °C for 19 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The yield of **3b-bc** was estimated to be >99% (**3b-bc**/**3b-cb** = 98/2) by the ^{1}H NMR of the crude mixture. The subjection of the crude mixture to gel permeation chromatography (CHCl$_3$) afforded **3b-bc** (398.8 mg, 99%) as pale yellow oil: ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.20 (s, 6H), 2.59 (s, 3H), 3.76 (s, 3H), 6.51 (s, 1H), 6.77 (d, J = 9.3 Hz, 2H), 7.11 (t, J = 5.4 Hz, 1H), 7.18 (d, J = 9.3 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 8.66 (d, J = 5.4 Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$) δ −2.1, 26.5, 55.2, 113.3, 119.4, 124.2, 127.9, 128.6, 129.8, 134.7, 136.0, 147.5, 154.9, 157.2, 159.6, 180.4, 197.6; IR (neat) 1682, 1252 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{24}N_2O_2Si$ 388.1607, found 388.1604.

Typical Procedure for Synthesis of 10 (Scheme 3). To a mixture of **3b-aa** (95.6 mg, 0.30 mmol), 4,4′-diiodobiphenyl (41.1 mg, 0.10 mmol), and PdCl$_2$(PhCN)$_2$ (3.9 mg, 10.2 μmol) in dry THF (0.8 mL) was added a solution of Bu$_4$NF (0.30 mmol, 1.0 M) in THF at room temperature. The mixture was stirred at 60 °C for 4 h under argon. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The subjection of the crude mixture to gel permeation chromatography (CHCl$_3$) afforded **10aaB** (47.6 mg, 92%) as pale yellow solid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.98 (s, 2H), 7.03−7.06 (m, 4H), 7.21−7.24 (m, 4H), 7.29−7.35 (m, 20H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 126.2, 127.45, 127.50, 127.6, 127.7, 128.2, 128.7, 129.9, 130.3, 136.4, 138.6, 140.4, 142.6, 143.3; IR (KBr) 1495, 1441 cm^{-1}; HRMS (EI) m/z calcd for $C_{40}H_{30}$ 510.2348, found 510.2349.

Procedure for Synthesis of 10′bcA (Scheme 4). To a mixture of 1-bromo-4-iodobenzene (28.3 mg, 0.10 mmol), **3b-bb** (40.1 mg, 0.10 mmol), and PdCl$_2$(PhCN)$_2$ (3.9 mg, 10.2 μmol) in dry THF (0.5 mL) were added a solution of Bu$_4$NF (0.10 mmol, 1.0 M) in THF and additional THF (0.5 mL) at room temperature under argon. After stirring the mixture at 60 °C for 1 h, a solution of **3b-cc** (57.8 mg, 0.15 mmol) in THF (1.0 mL), a solution of Bu$_4$NF (0.15 mmol, 1.0 M) in THF, and additional THF (0.5 mL) were added to the mixture. The resultant mixture was further stirred at 60 °C for 3 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The subjection of the crude mixture to gel permeation chromatography (CHCl$_3$) afforded **10′bcA** (26.1 mg, 45%) as yellow solid: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.59 (s, 3H), 2.64 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 6.72 (s, 1H), 6.81−6.85 (m, 8H), 7.01 (s, 1H), 7.07 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.89 (d, J = 7.8 Hz, 2H), 7.93 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 26.6 (two carbons), 55.2, 55.3, 113.5, 113.9, 125.5, 127.6, 128.4, 128.8, 128.9, 129.2, 129.3, 130.7, 131.0, 131.5, 132.5, 134.2, 136.0, 136.18, 136.25, 137.4, 139.9, 142.5, 145.1, 147.4, 159.0, 159.3, 197.5, 197.7; IR (KBr) 1682, 1603, 1510 cm^{-1}; HRMS (FAB) m/z calcd for $C_{40}H_{34}O_4$ 578.2457, found 578.2452.

Typical Procedure for Synthesis of 6 (Scheme 5). A mixture of **2a-a** (1.15 g, 4.96 mmol), 1,4-diiodobenzene (824.4 mg, 2.50 mmol), triethylamine (1.01 g, 10.0 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (128.0 mg, 0.12 mmol), and tris(2,4-di-*tert*-butylphenyl)phosphite (161.0 mg, 0.25 mmol) in dry dioxane (5.0 mL) was stirred at 80 °C for 18 h under argon. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was chromatographed on silica gel (hexane/EtOAc) to afford **6a-aA** (797 mg, 58%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.18 (s, 12H), 6.58 (s, 2H), 7.07−7.12 (m, 6H), 7.17−7.24 (m, 6H), 7.22 (s, 4H), 7.37 (d, J = 7.6 Hz, 2H), 7.45 (td, J = 7.6, 1.6 Hz, 2H), 8.74 (d, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ −1.9, 122.1, 126.1, 126.7, 127.1, 127.5, 128.8, 129.2, 133.4, 141.7, 141.8, 149.6,

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[38] For a recent other example from our laboratory using such a platform strategy for the construction of pyrimidine-core extended π-systems, see: Itami, K.; Yamazaki, D.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 15396.

157.8, 167.4; IR (KBr) 1565, 1242 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{36}H_{36}N_2Si_2$ 552.2417, found 552.2418.

Typical Procedure for Synthesis of 11 (Scheme 6). To a mixture of **6a-aA** (53.6 mg, 0.10 mmol), iodobenzene (80.2 mg, 0.39 mmol), and $PdCl_2(PhCN)_2$ (3.7 mg, 9.6 μmol) in dry THF (1.0 mL) was slowly added a solution of Bu_4NF (0.25 mmol, 1.0 M) in THF by syringe pump (0.0167 mmol/min) at 40 °C under argon, and the resultant mixture was further stirred at 40 °C for 2 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The subjection of the crude mixture to gel permeation chromatography ($CHCl_3$) afforded **11aAa** (21.9 mg, 52%) as yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 7.03−7.06 (m, 4H), 7.12−7.18 (m, 6H), 7.23−7.26 (m, 4H), 7.29 (s, 4H), 7.33−7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 127.2, 127.3, 127.8, 127.9, 128.5, 129.4, 130.2, 137.2, 140.1, 142.0, 142.3; IR (KBr) 1445, 695 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{34}H_{26}$ 434.2034, found 434.2034.

Procedure for Synthesis of 7a-A (Scheme 7). To a solution of $Pd_2(dba)_3{\cdot}CHCl_3$ (41.2 mg, 0.04 mmol) and tri-2-furylphosphine (37.5 mg, 0.16 mmol) in THF (24 mL) were added 1,4-diiodobenzene (1.32 g, 4.00 mmol), dimethyl(2-pyridyl)vinylsilane **1a** (1.30 g, 8.00 mmol), and triethylamine (871.1 mg, 8.40 mmol) at room temperature under argon and the reaction mixture was stirred at 60 °C for 18 h. After cooling to room temperature, toluene (5 mL) was added to the reaction mixture. This mixture was extracted with 1 N aqueous HCl (6 × 10 mL). The combined aqueous phase was neutralized by adding $NaHCO_3$ and then was extracted with EtOAc (3 × 30 mL). Drying over Na_2SO_4 and removal of the solvents under reduced pressure afforded **7a-A** (1.51 g, 94%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.49 (s, 12H), 6.64 (d, J = 19.2 Hz, 2H), 6.99 (d, J = 19.2 Hz, 2H), 7.17−7.24 (m, 2H), 7.43 (s, 4H), 7.52−7.63 (m, 4H), 8.80 (dm, J = 5.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.4, 122.9, 126.3, 126.8, 129.5, 134.1, 138.0, 145.4, 150.3, 166.9; IR (KBr) 1603, 1574, 1557, 1509, 1451, 1420, 1248 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{24}H_{28}N_2Si_2$: 400.1791, found 400.1793.

Typical Procedure for Synthesis of 8 (Scheme 8). A mixture of **7a-A** (398.7 mg, 1.00 mmol), iodobenzene (408.5 mg, 2.00 mmol), triethylamine (253.0 mg, 2.50 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (23.4 mg, 0.025 mmol), and tris(2,4-di-*tert*-butylphenyl)phosphite (31.6 mg, 0.05 mmol) in dry dioxane (3.0 mL) was stirred at 80 °C for 20 h under argon. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The filtrate was evaporated and the residue was chromatographed on silica gel (hexane/EtOAc) to afford **8a-Aa** (429 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 12H), 6.54 (s, 2H), 7.10 (s, 4H), 7.17 (ddd, J = 7.6, 4.8, 1.6 Hz, 2H), 7.27−7.34 (m, 10H), 7.49 (dt, J = 7.2, 1.6 Hz, 2H), 7.54 (td, J = 7.6, 1.6 Hz, 2H), 8.78 (dt, J = 4.8, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.7, 122.3, 126.2, 127.2, 127.6, 127.7, 128.9, 129.0, 133.6, 141.3, 142.8, 149.8, 158.2, 167.5; IR (KBr) 1586, 1244, 857 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{36}H_{36}N_2Si_2$ 552.2417, found 552.2418.

Typical Procedure for Synthesis of 12 (Scheme 9). To a mixture of **8a-Aa** (56.3 mg, 0.10 mmol), iodobenzene (81.9 mg, 0.40 mmol), and $PdCl_2(PhCN)_2$ (3.7 mg, 9.6 μmol) in dry THF (1.0 mL) was slowly added a solution of Bu_4NF (0.25 mmol, 1.0 M) in THF by syringe pump (0.0167 mmol/min) at 40 °C under argon, and the resultant mixture was further stirred at 40 °C for 3 h. After cooling the reaction mixture to room temperature, the catalyst and salts were removed by filtration through a short silica gel pad (EtOAc). The subjection of the crude mixture to gel permeation chromatography ($CHCl_3$) afforded **12Aaa** (26.7 mg, 60%) as yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 7.15−7.24 (m, 10H), 7.21 (s, 4H), 7.30−7.43 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8, 127.5, 127.6, 127.9, 128.2 (two carbons), 129.6, 130.8, 137.4, 139.5, 142.4, 143.1; IR (KBr) 762, 695 cm^{-1}; HRMS (EI) *m/z* calcd for $C_{34}H_{26}$ 434.2034, found 434.2033.

Typical Procedure for Synthesis of 9 Where Two Aryl Units in the Polymer Backbone are the Same (Scheme 10). A mixture of **1a** (164.3 mg, 1.01 mmol), 1,4-diiodobenzene (329.6 mg, 1.00 mmol), triethylamine (253.0 mg, 2.50 mmol), and $Pd[P(t\text{-}Bu)_3]_2$ (25.0 mg, 50.0 μmol) in dry dioxane (2.0 mL) was stirred at 80 °C for 27 h under argon. After cooling the reaction mixture to room temperature, H_2O (2 mL) was added to the mixture. The mixture was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over Na_2SO_4. The subjection of the crude mixture to gel permeation chromatography ($CHCl_3$) afforded **9a-AA** (222.5 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.20−0.25 (br, 6H), 6.50−6.60 (br, 1H), 7.00−7.30 (m, 5H), 7.30−7.60 (m, 2H), 8.73 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.93, −1.88, 122.4, 122.5, 126.6, 126.8, 127.0, 129.1, 133.7, 133.8, 141.4, 141.5, 141.8, 142.1, 142.3, 149.9, 150.0, 157.8, 157.9, 167.6, 167.7; IR ($CHCl_3$) 1576, 1248, 1215 cm^{-1}.

Typical Procedure for Synthesis of 9 Where Two Aryl Units in the Polymer Backbone Are Different (Scheme 11). A mixture of **7a-A** (405.3 mg, 1.01 mmol), 1,3-diiodobenzene (333.6 mg, 1.01 mmol), triethylamine (98.0 mg, 2.50 mmol), and $Pd[P(t\text{-}Bu)_3]_2$ (25.7 mg, 50.0 μmol) in dry dioxane (3.0 mL) was stirred at 80 °C for 12 h under argon. After cooling the reaction mixture to room temperature, H_2O (2 mL) was added to the mixture. The mixture was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over $MgSO_4$. The subjection of the crude mixture to gel permeation chromatography ($CHCl_3$) afforded **9a-AD** (405.7 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (br, 12H), 6.49 (br, 2H), 6.90−7.20 (br, 9H), 7.30−7.60 (br, 5H), 8.73 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −1.7, 122.3, 125.5, 126.8, 127.2, 128.89, 128.95, 133.6, 141.3, 143.0, 149.8, 158.3, 167.5; IR ($CHCl_3$) 1217 cm^{-1}.

Typical Procedure for Synthesis of 13 (Scheme 12). To a mixture of **9a-AA** (92.8 mg, 0.39 mmol for unit), 4-iodobenzoic acid ethyl ester (214.0 mg, 0.78 mmol), and $PdCl_2(PhCN)_2$ (14.9 mg, 38.8 μmol) in dry THF (1.5 mL) was added a solution of Bu_4NF (0.78 mmol, 1.0 M) in THF at room temperature, and the resulting mixture was stirred at 60 °C for 5 h under argon. After cooling the reaction mixture to room temperature, the mixture was evaporated. The subjection of the crude mixture to gel permeation chromatography ($CHCl_3$) afforded **13AAm** (69.6 mg, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (br, 3H), 4.30 (br, 2H), 6.90−7.50 (m, 7H), 7.60−7.90 (m, 2H); IR ($CHCl_3$) 1715, 1605 cm^{-1}. M_n = 9235. PD = 2.06.

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Supporting Information Available: Experimental procedures and analytical and spectroscopic data of all compounds prepared in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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