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Synthetic protocol for diarylethenes through Suzuki–Miyaura coupling†

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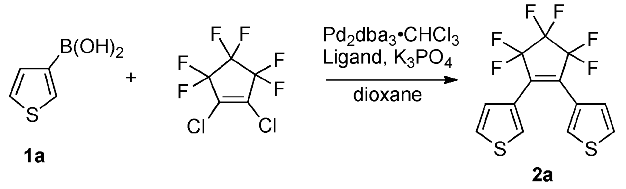
The synthesis of a variety of diarylethenes through the Suzuki–Miyaura coupling reaction of 1,2-dichlorohexafluorocyclopentene with arylboronic acids and esters has been developed. Thiophenes with various substituents such as cyano and ester functionalities can be incorporated.

In recent years, organic photochromic compounds have attracted much attention due to the potential applications for photoswitching materials.[1] Among various photochromic systems, diarylethene is one of the most prospective organic molecules owing to its advantageous properties over other photochromic compounds in terms of its thermal stability and fatigue resistance as well as its intriguing photochromic behaviour.[2] Among various platforms for diarylethenes, a perfluorocyclopentene unit exhibits the highest reversible durability and photo-responsibility.[3] However, their synthetic procedure has been limited so far to nucleophilic addition–elimination reaction of perfluorocyclopentene with unstable heteroaryllithium reagents at low temperatures.[2a,4] Although this method has been successfully applied to the synthesis of a variety of diarylethenes, the reaction requires the moisture-free and cryogenic conditions and often results in low yields. Furthermore, the use of highly reactive organolithium species does not tolerate the presence of a functionality such as carbonyl and cyano groups. In addition, perfluorocyclopentene is rather volatile (bp 27 °C) and not easy to handle. On the other hand, 1,2-dichlorohexafluorocyclopentene is less volatile (bp 90 °C). Here we report the novel synthetic method for diarylethenes through Suzuki–Miyaura cross-coupling.

We anticipated that cross-coupling of 1,2-dichlorohexafluorocyclopentene would be facilitated by a proper choice of phosphine ligands. Optimization of the cross-coupling conditions was conducted with 3-thienylboronic acid as a model substrate. The use of triphenylphosphine as a ligand provided none of the desired diarylethenes **2a**. After several trials, we found that the employment of Buchwald's ligands, S-Phos and X-Phos, worked nicely.[5] The reaction of 3-thienylboronic acid in the presence of X-Phos and $Pd_2dba_3{\cdot}CHCl_3$ furnishes **2a** in 86% yield (Table 1, entry 4, method A). We then applied this procedure of method A to 2-methylthienyl derivatives, because most of the diarylethenes have 2-methyl substituents to improve the stability of diarylethenes after photo-induced ring-closure. Unfortunately, however, the cross-coupling with 2-methyl-3-thienylboronic acid under the same reaction conditions with X-Phos resulted in low yield. Eventually, the use of tricyclohexylphosphine and CsF in toluene/H_2O (10/1) furnished the desired diarylethene **2b** in 82% yield (Table 2, entry 6, method B).

Table 1 Optimization of Suzuki–Miyaura coupling with 3-thienylboronic acid[a]



Entry	Ligand	Time/h	Yield (%)
1	PPh_3	16	0
2	S-Phos	16	70
3	X-Phos	3	67
4	X-Phos	16	86

[a] Reaction conditions: 3-thienylboronic acid (3.0 equiv.), 1,2-dichlorohexafluorocyclopentene (1.0 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (1 mol% Pd), phosphine ligand (2 mol%), K_3PO_4 (3.0 equiv.), 100 °C.

These reaction conditions can be applied to various substrates (Table 3). Other aromatic groups such as phenyl and 3-furyl can be introduced to provide **2c** and **2d** in good yields by method A (entries 1 and 2). Boronic esters, which can be prepared efficiently *via* transition-metal catalysis, can also be a coupling partner in this reaction. The reaction of 2,5-dimethyl-3-thienylboronic ester **1f** resulted in poor yield under the same conditions as those with boronic acids, but the yield of **2e** was improved up to 56% by the use of 9.0 equiv. of CsF and 10 mol% of the palladium catalyst. Under these conditions, various arylboronic esters can be converted into the corresponding diarylethenes. Thienyl groups with ester and cyano functionalities can be introduced to furnish the corresponding diarylethenes **2g** and **2h** in moderate yields (entries 5 and 6). These reactive substituents cannot be tolerated in the conventional diarylethene synthesis with organolithium reagents. However, the reaction with 2-formylthienylboronic ester **1i** resulted in low yield of **2i** because of the serious side reactions (entry 7).

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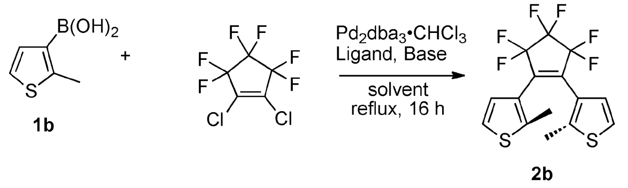
† Electronic supplementary information (ESI) available: Experimental procedures, spectral data for all new compounds, photophysical data, and crystallographic data of **4a**, CCDC 820786. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc12020d

Table 2 Optimization of Suzuki–Miyaura cross-coupling with 2-methyl-3-thienylboronic acid[a]



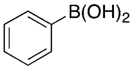
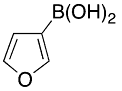
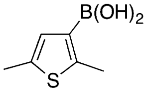
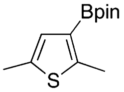
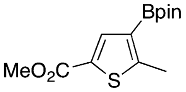
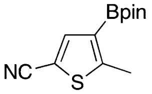
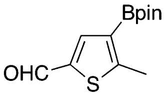
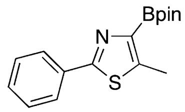
1b

2b

Entry	Base	Ligand	Solvent	Yield (%)
1	K_3PO_4	X-Phos	Dioxane	22
2	K_3PO_4	S-Phos	Dioxane	48
3	K_3PO_4	tBu$_3$P·HBF$_4$	Dioxane	20
4	K_3PO_4	S-Phos	Toluene/H_2O	63
5	K_3PO_4	PCy_3	Toluene/H_2O	70
6	CsF	PCy_3	Toluene/H_2O	82

[a] Reaction conditions: 2-methyl-3-thienylboronic acid (3.0 equiv.), 1,2-dichlorohexafluorocyclopentene (1.0 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (1 mol% Pd), phosphine ligand (2 mol%), base (3.0 equiv.).

Table 3 Synthesis of diarylethenes with various arylboronic acids and esters[a]

Entry	Substrate	Method	Product	Yield (%)
1	 **1c**	A	**2c**	91
2	 **1d**	A	**2d**	88
3	 **1e**	B	**2e**	88
4	 **1f**	B	**2e**	56[b]
5	 **1g**	B	**2g**	63[b]
6	 **1h**	B	**2h**	45[b]
7	 **1i**	B	**2i**	29[b]
8	 **1j**	B	**2j**	69[b]

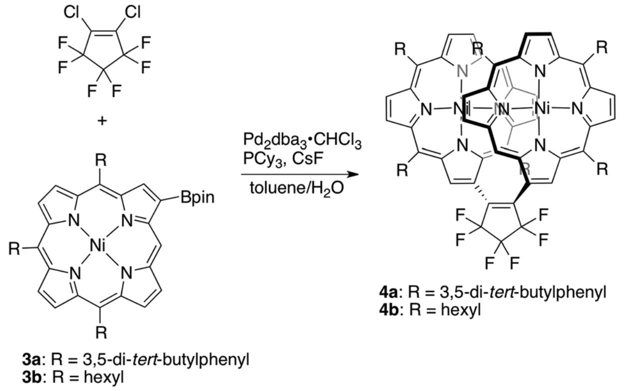
[a] Reaction conditions: method A: arylboronic acid (3.0 equiv.), 1,2-dichlorohexafluorocyclopentene (1.0 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (1 mol% Pd), X-Phos (2 mol%), K_3PO_4 (3.0 equiv.), dioxane, reflux, 16 h; method B: arylboronic acid or ester (3.0 equiv.), 1,2-dichlorohexafluorocyclopentene (1.0 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (1 mol% Pd), PCy_3 (2 mol%), CsF (3.0 equiv.), toluene/H_2O, reflux, 16 h. [b] $Pd_2dba_3{\cdot}CHCl_3$ (10 mol%) and CsF (9.0 equiv.) were used under otherwise the same conditions.

None of the monoarylated products were observed in any cases, even though an excess amount of dichlorocyclopentene was employed. The reaction with thiazolylboronic ester **1j** also afforded only diarylated product **2j** in 69% yield (entry 8). This feature is notable because the conventional organolithium method often provided monothiazolylcyclopentenes predominantly.[6]

The uniqueness of the present procedure was demonstrated by the efficient introduction of porphyrin moieties into the hexafluorocyclopentene ring, which is quite difficult by the conventional organolithium method. Lithiated porphyrin derivatives are difficult to be generated due to their electron rich characteristic and reactive feature against lithium reagents.[7] Although the reaction with *meso*-borylporphyrins resulted in only protodeborylation, 2-boryl-5,10,15-tris(3,5-di-*tert*-butylphenyl)porphyrin Ni(II) **3a** underwent smooth coupling reaction to afford disubstituted product **4a** in 45% yield under the conditions of method B (Scheme 1).[8] However, the reaction with Zn(II) and free-base porphyrins only afforded deborylated porphyrins without the formation of the desired products. The structure of product **4a** was assigned by the ^{1}H NMR spectrum, exhibiting two singlet peaks at 9.64 and 9.31 ppm and six doublet peaks in the region from 8.62 to 8.48 ppm. The reaction with 2-boryl-5,10,15-trihexylporphyrin Ni(II) **3b** also furnished the diarylethene **4b** in 54% yield. The ^{1}H NMR spectrum of **4b** displayed relatively downfield-shifted signals for five β-protons from 9.08 to 8.91 ppm and upfield-shifted signals for two β-protons at 8.37 and 7.98 ppm. These upfield-shifts can be accounted for by the aromatic ring current effect due to the adjacent porphyrin ring, implying a strongly packed structure of **4b**. The exact structure of **4a** was unambiguously elucidated by X-ray diffraction analysis (Fig. 1). The two porphyrin rings adopted a slipped conformation with the dihedral angle of 61° between two adjacent pyrrole planes. The bond length between C2A–C1C is 1.45 Å and the bond length between C1C–C5C is 1.35 Å, that is a typical bond length for non-conjugated C–C double bonds. This fact suggests that each porphyrin unit does not have significant π-conjugation to the perfluorocyclopentene moiety. As a diarylethene, diporphyrin **4a** takes the photoreactive antiparallel conformation. Furthermore, the intramolecular distance between C1A–C1B is 3.69 Å, which is within the distance capable of photocyclization.[2d] Unfortunately, however, both products **4a** and **4b** did not exhibit any photochromic behaviour by photo-irradiation, probably due to steric repulsion by *meso*-substituents on the porphyrin rings as well as rapid quenching of the excited state by the nickel centre.

Fig. 2 shows UV/vis absorption spectra of **4a** and **4b** in CH_2Cl_2. Both compounds showed typical spectra of porphyrins, showing Soret bands at 409 and 410 nm and Q-bands at 532 and 574 nm and 541 and 584 nm, respectively. The broadening of Soret bands of **4a** and **4b** can be explained by exciton coupling between two porphyrin units. Compared to the corresponding porphyrin monomer, red-shift of the Q-band was observed for both **4a** and **4b**, indicating a slight electronic conjugation of porphyrin rings and the perfluorocyclopentene moiety.[9]

In conclusion, we have demonstrated novel and versatile synthesis of diarylethenes through a Suzuki–Miyaura cross-coupling reaction. The present protocol is applicable for various substrates bearing reactive functionalities such as cyano and ester moieties, which cannot be compatible under the conventional diarylethene synthesis using organolithium reagents. This procedure



Scheme 1 Suzuki–Miyaura cross-coupling of dichlorocyclopentene with β-borylporphyrins.

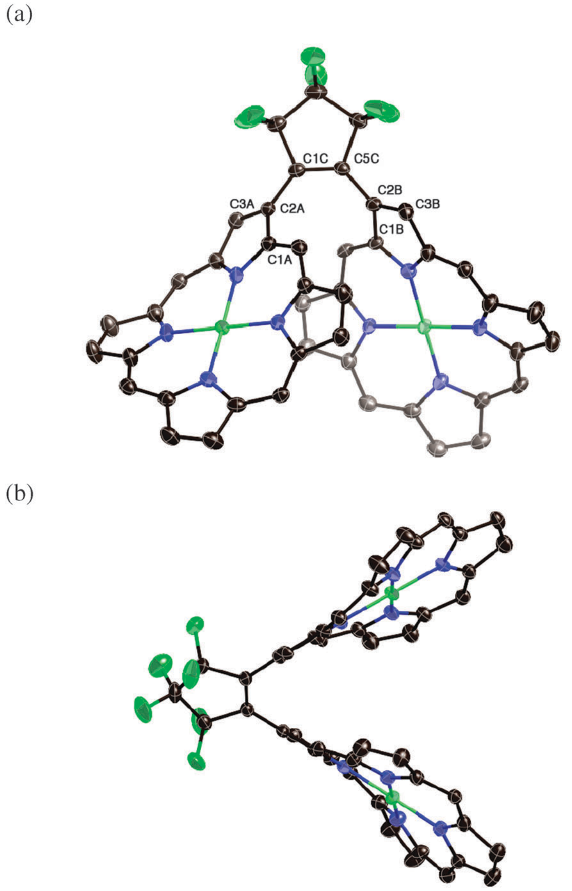


Fig. 1 X-Ray crystal structure of **4a**. (a) Top view and (b) side view. *meso*-Aryl substituents and hydrogen atoms are omitted for clarity. Thermal ellipsoids are at 50% probability level.

also allows us to synthesize novel and exotic diarylethenes, as exemplified by the efficient construction of 1,2-diporphyrinyl-cyclopentenes.

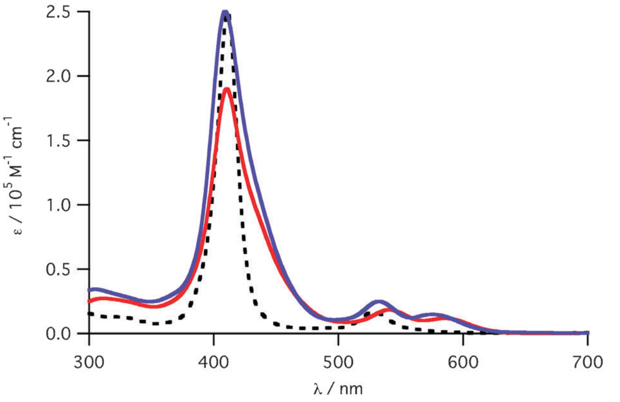


Fig. 2 UV/vis absorption spectra of **4a** (red solid line), **4b** (blue solid line) and 5,10,15-trihexylporphyrin Ni(II) (black dotted line) in CH_2Cl_2.

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