Supporting Information:

Isoreticular Two-Dimensional Covalent Organic Frameworks Synthesized by On-Surface Condensation of Diboronic Acids

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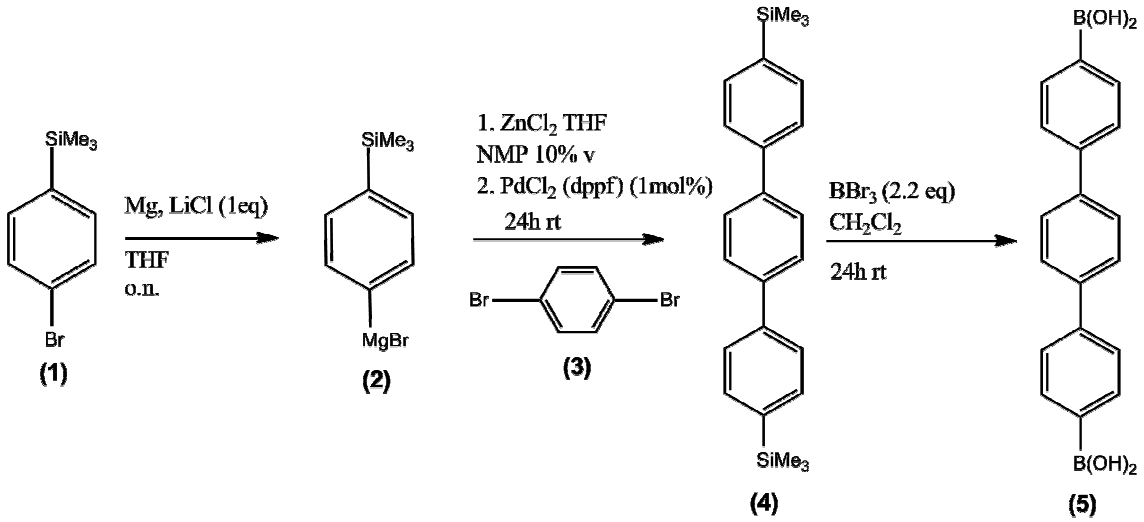
(1) Synthesis of terphenyldiboronic acid ([1,1':4',1''-terphenyl]-4,4''-diyldiboronic acid)

(2) Synthesis of quaterphenyldiboronic acid ([1,1':4',1'':4'',1'''-quaterphenyl]-4,4'''-diyldiboronic acid)

1. Synthesis of terphenyldiboronic acid ([1,1':4',1''-terphenyl]-4,4''-diyldiboronic acid)



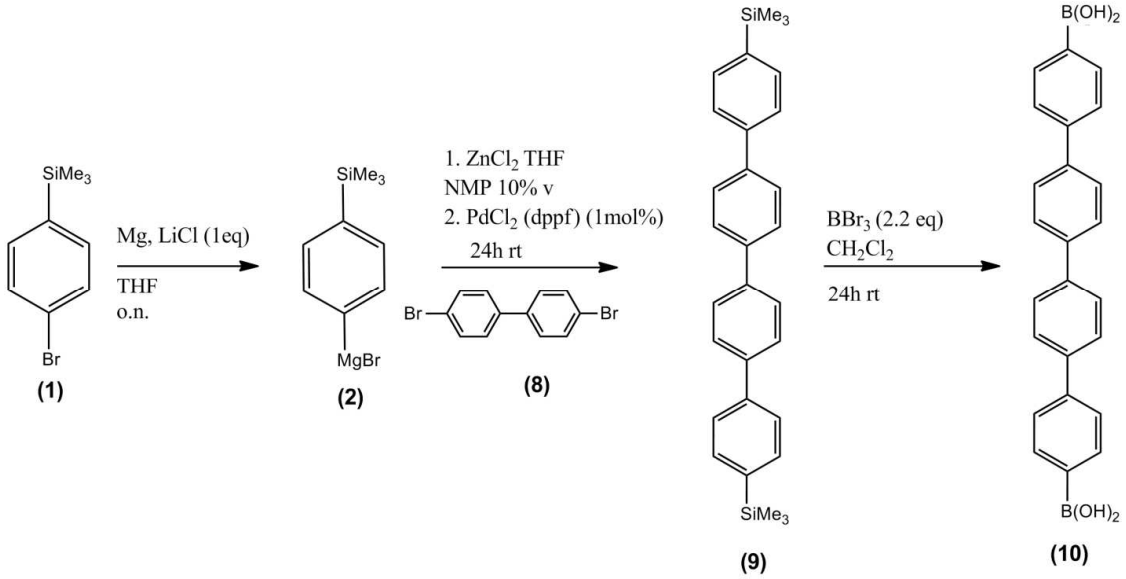
A round-bottom flask equipped with a magnetic stirring bar was charged with magnesium turnings (2.15 g, 88.20 mmol, 1.4 equiv.) and lithium chloride (3.00 g, 63.35 mmol, 90 %, 1.0 equiv). The reactants were dried under vacuum at 250 °C, the mixture was then allow to cool under argon atmosphere. Subsequently 50 ml of anhydrous tetrahydrofuran was added. Activation of the magnesium turnings was achieved by stirring for ca. one hour. Afterwards (4-bromophenyl)trimethylsilane **(1)** (15.21 g, 63.35 mmol, 1.0 equiv) was added dropwise. After 5 minutes, an exothermic reaction set in. The solution was stirred for another hour, and subsequently added dropwise to an ice bath-cooled mixture of zinc (II) chloride (4.36 g, 32.00 mmol, 0.5 equiv.) in 32 ml THF and 3.2 ml (10 %) *N*-Methyl-2-pyrrolidone (NMP).

In a 250 ml round-bottom flask palladium (II) acetate (28.10 mg, 1.13 mmol, 0.50 mol%), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (102.60 mg, 0.25 mmol, 1.0 mol%) and 1, 4-dibromobenzene **(3)** (5.90 g, 25.00 mmol, 0.4 equiv) were dissolved in tetrahydrofuran (20 ml). This mixture was added dropwise to the zinc compound, after a short time the color of the exothermic reaction turned brown and a solid precipitated. The suspension was quenched with a saturated ammonium chloride solution. The mixture was extracted four times with diethylether. Successively the grey solid was filtered and dried at 80 °C in an oven for 16 h. Recrystallization in n-heptane yielded the product as a grey solid (5.68 g, 15.5 mmol, 60 %).

[1,1';4',1'']terphenyl-4,4''-di-trimethylsilane **(4)** (5.68 g, 15.5 mmol, 1.0 equiv) was dissolved in 140 ml dichloromethane. Subsequently boron tribromide (9.5 g, 37.9 mmol, 2.2 equiv) was added and the reaction mixture was stirred at room temperature for 24 h. The white suspension was poured on ice (250 g) and stirred

until the ice was completely molten. Dichloromethane was removed on the rotary evaporator and the product was filtered. Recrystallization in water yielded a white powder **(5)** (2.83 g, 8.9 mmol, 57 %).

2. Synthesis of quaterphenyldiboronic acid ([1,1':4',1":4",1"'-quaterphenyl]-4,4"'-diyldiboronic acid)



In a round-bottomed flask bis(di-*tert*-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II) (5 mg, 0.007 mmol) and 4,4'-dibromo-1,1'-biphenyl **(8)** (0.624 g, 2.0 mmol, 0.4 equiv.) were dissolved in tetrahydrofuran (20 ml). This mixture was added dropwise to the zinc compound. The suspension was quenched with 50 ml of a saturated ammonium chloride solution. The mixture was extracted four times with 30 ml of diethylether. Subsequently the white solid was filtered and dried *in vacuo* (0.56 g, 1.3 mmol, 65 %).

4,4"'-bis(trimethylsilyl)-1,1':4',1":4",1"'-quaterphenyl **(9)** (0.56 g, 1.3 mmol, 1.0 equiv) was dissolved in 25 ml dichloromethane. Subsequently boron tribromide (0.715 g, 2.86 mmol, 2.2 equiv) was added and the reaction mixture was stirred at room temperature for 24 h. The white suspension was poured on ice (250 g) and stirred until the ice was completely molten. Dichloromethane was removed on the rotary evaporator and the product was filtered. Recrystallization in water yielded a white powder **(10)** (0.38 g, 0.96 mmol, 74 %).