Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie

DOI: 10.1002/zaac.201800197

ARTICLE

Synthesis of Some Di- and Tetraphosphonic Acids by Suzuki Cross-Coupling

Alexandra Schütrumpf,[a] Andrew Duthie,[b] Enno Lork,[a] Gündoğ Yücesan,[c] and Jens Beckmann*[a]

Abstract. Five diphosphonic acids, namely, benzene-1,4-bis-*p*-phenylphosphonic acid (**1**), anthracene-9,10-bis-*p*-phenylphosphonic acid (**2**), benzene-1,2-bis-*p*-phenylphosphonic acid (**3**), benzene-1,3-bis-*p*-phenylphosphonic acid (**4**), and biphenyl-4,4′-bis-*p*-phenylphosphonic acid (**5**) as well as three tetraphosphonic acids, namely, benzene-1,2,4,5-tetrakis-*p*-phenylphosphonic acid (**6**), tetrabiphenylsilane tetrakis-4-phosphonic acid (**7**), and pyrene-1,3,6,8-tetrakis-*p*-phenylphosphonic acid (**8**) and their dimethyl esters **1a**–**8a** were prepared via Suzuki cross-coupling reactions involving *p*-dimethylphosphonatophenylboronic acid and brominated aromatics. The Suzuki cross-coupling occurs under milder conditions than the transition metal catalyzed Arbuzov reaction usually applied for the preparation of dialkyl phosphonates. For the same starting material both reactions are complementary and yield phosphonic acids with different spacer lengths, which was exemplified for tetrakis(4-bromophenyl)silane. Suzuki cross-coupling gives rise to **7**, whereas the Arbuzov reaction produces tetraphenylsilane tetrakis-4-phosphonic acid.

Introduction

Metal organophosphonates constitute a unique class of porous materials, which recently received tremendous attention in material science.[1–4] For instance, porous metal organic frameworks (MOFs) or proton-conducting membranes (PCMs) for fuel cells based on metal organophosphonates are thermally more stable and hydrolytically less sensitive than their carboxylate counterparts.[5,6] Up to the early 2000s, most metal-organophosphonates possessed highly dense pillared-layered and lamellar structures because their syntheses relied on structurally flexible alkylphosphonate linkers.[7–9] More recently, with the introduction of the rigid tetratopic arylphosphonate linkers, such as the square planar tetra(4-phosphonophenyl) porphyrin[10] and the tetrahedral tetraphenylmethane tetrakis-4-phosphonic acid[11] precluded the formation of dense 2D metal oxide layers. Their introduction has increased the distances between the organophosphonate adhesive units and favored the formation of metal oxide clusters and stable one-dimensional inorganic building units to form one-dimensional hexagonal void channels or porous diamandoid networks. Arylphosphonates have shown to be important in void space formation as the structural rigidity of the aromatic linkers was essential to maintain the distance between the phosphonate binding units. All these studies suggested that the nature of the bridging ligand is the most important factor defining the structure of metal organophosphonates and their functions. Despite the limitless potential of the porous metal organophosphonates in material science, the number of aromatic bridging ligands in phosphonate chemistry is still too limited to conduct more comprehensive studies to create novel metal arylphosphonates and identify their basic patterns to perform the isoreticular synthesis to control the pore sizes.[2] The different geometric orientations expanding tether lengths and geometrical orientations such as V- and X-shaped ligands have not been studied yet due to the synthetic challenges in the preparation of suitable arylphosphonic acids. The vast majority of dialkyl arylphosphonates is prepared via a transition metal catalyzed variant of the Arbuzov reaction, which is often notoriously sluggish.[12] Typical synthetic protocols require temperatures above 150 °C for several hours, during which the catalysts often need to be added in small portions plus several days under reduced pressure to remove the solvents completely. Despite some improvements in recent years,[13,14] the yields are still unsatisfying particularly for target molecules with multiple phosphonate sites. The number of commercially or synthetically available brominated aromatics suitable as starting materials is also limited especially with respect to the increasing tether lengths and multiple phosphonate sites. In addition, the regioselective bromination of aromatic compounds is still an emerging field of science[15] and it would be time consuming to follow the bromination path to create brominated aryl scaffolds to synthesize the corresponding arylphosphonic acids. In this work, we describe the preparation of dimethyl arylphosphonates via Suzuki cross-coupling reactions[16] using *p*-dimethylphosphonato-phenylboronic acid, a reagent that has been reported only in the patent literature.[17] The Suzuki cross-coupling occurs under substantially milder conditions (refluxing toluene) than the metal-catalyzed Arbuzov reaction. The dimethyl arylphosphonates were subsequently converted by hydrolysis into previously known and new di- and tetraphosphonic acids, which might find applications in material science in the future.

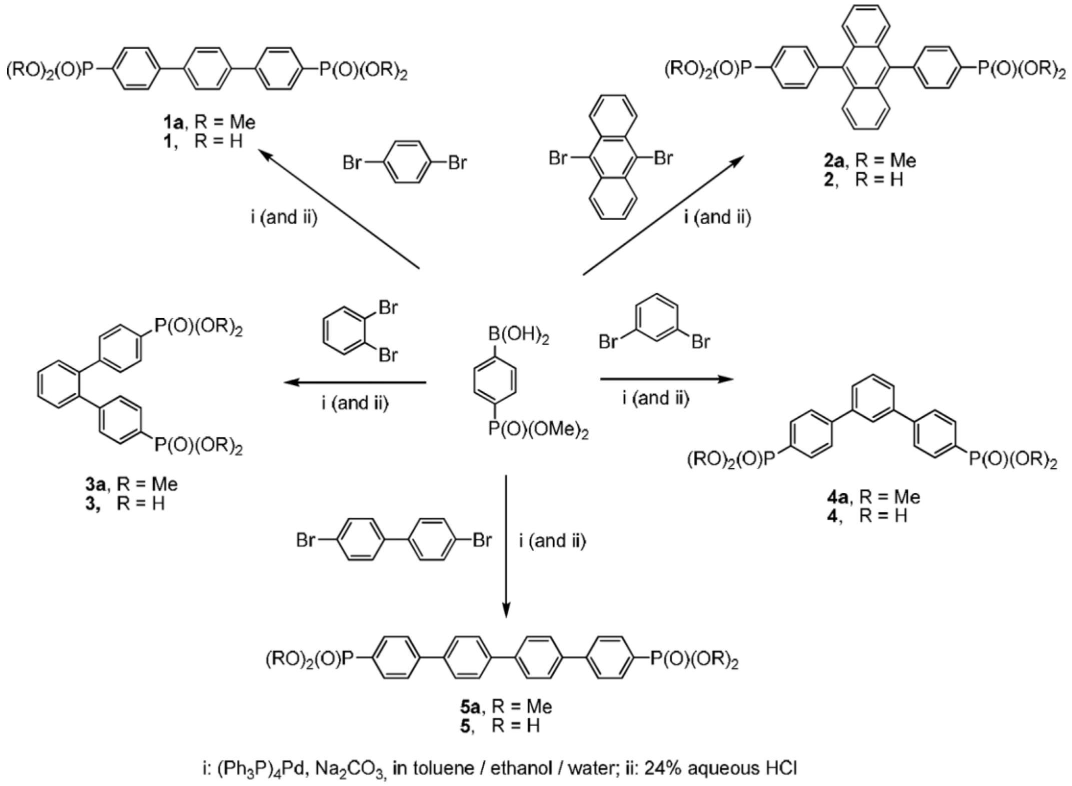
---

* Prof. Dr. J. Beckmann
E-Mail: j.beckmann@uni-bremen.de
Homepage: http://www.uni-bremen.de/de/beckmann/
[a] Institut für Anorganische Chemie und Kristallographie
Universität Bremen
Leobener Straße 7, 28359 Bremen, Germany
[b] School of Life and Environmental Sciences
Deakin University
Pigdons Road, Waurn Ponds 3217, Australia
[c] Department of Food Chemistry and Toxicology
Technische Universität Berlin
Gustav-Meyer-Allee 25, 13355 Berlin, Germany

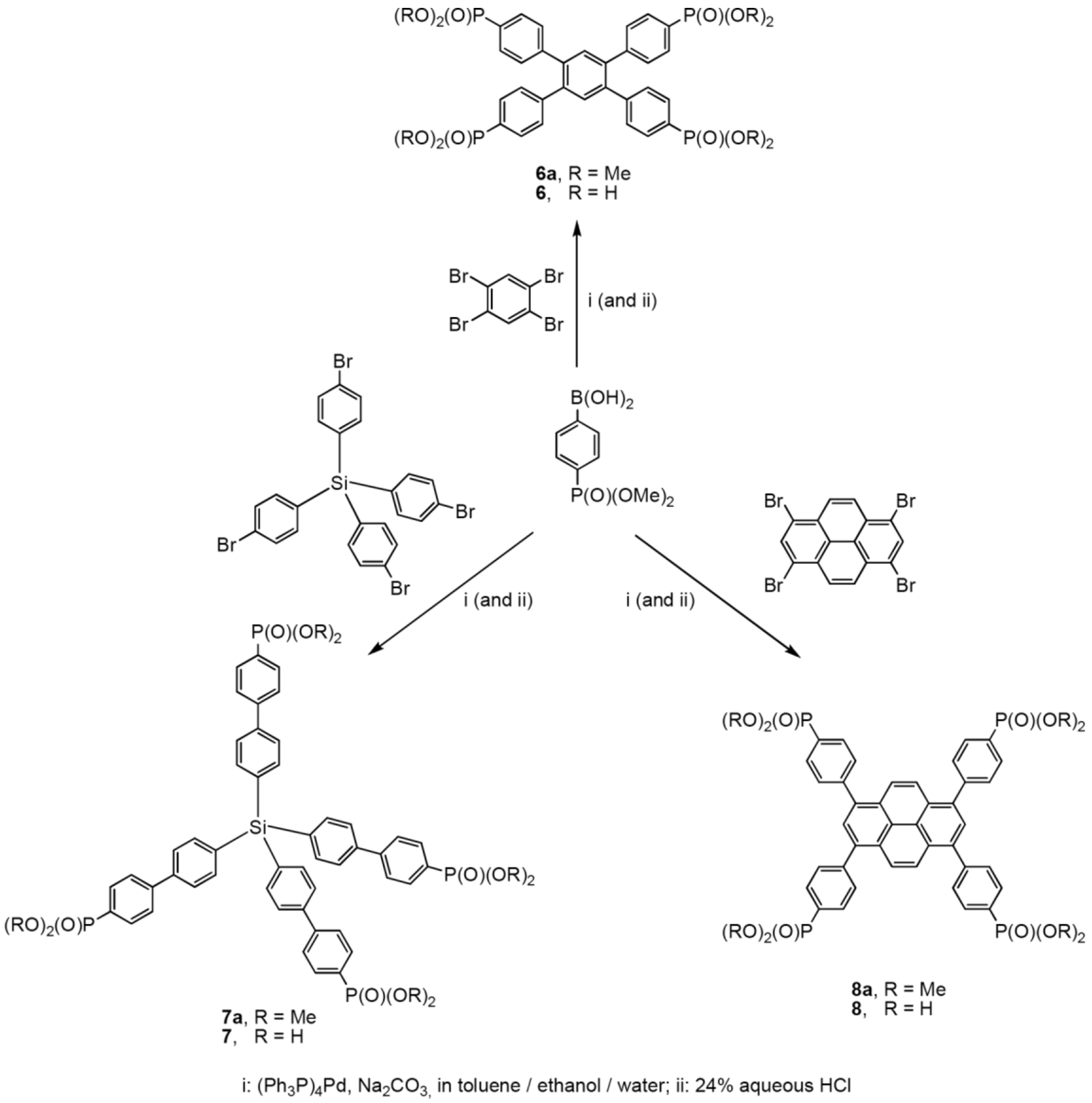
Results and Discussion

The reaction of *p*-dimethylphosphonatophenylboronic acid with di- and tetrabrominated aromatics and sodium carbonate in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium in refluxing toluene afforded five diphosphonic dimethyl esters **1a**–**5a** (Scheme 1) and three tetraphosphonic dimethyl esters **6a**–**8a** (Scheme 2), which were isolated after column chromatography in yields between 26 and 87 %.

The dimethyl phosphonates **1a**–**5a** were obtained as (micro-)crystalline solids that are well soluble in common organic solvents, such as chloroform, toluene or THF. The quantitative characterization of **1a**–**5a** was achieved by ^{1}H, ^{13}C, and ^{31}P-NMR spectroscopy, which, besides the microanalysis, confirmed the analytical purity of the bulk materials. The molecular structures of **1a**, **2a**, **4a**, and **6a** were established by single-crystal X-ray crystallography, which provided independent confirmation for the identity of these compounds (Figure 1). The hydrolysis of **1a**–**5a** with conc. hydrochloric acid gave rise to the diphosphonic acids **1**–**5** (Scheme 1) and the tetraphosphonic acids **6**–**8**, which were isolated in 72 % to nearly quantitative yields (Scheme 2). The linear diphosphonic acids, **1** and **2** were previously reported,[18,19] whereas the structural isomers of **1**, namely, **3** and **4** were unknown. The synthesis of the V-shaped arylphosphonate linkers **3** and **4** is especially useful with respect to the formation of molecular cage structures in conjunction with the corner forming auxiliary ligands. The concurrent use of **1**, **3**, **4**, and **5** for the preparation of MOFs would be significant to form expanding macrocycle or cage molecules following up the mechanism previously reported.[20–23] Likewise, the anthracene core in **2** has significant potential to form void spaces due to the T-shape of the central aryl core and difficulty of such linker arrangements to form dense pillared layered networks. The number of metal complexes synthesized using **1** is very limited.[24–26] The linear diphosphonic acid **5**, a structural analogue of **1** with longer tether length, was claimed in the literature, however, no details about its preparation, use and characterization have been disclosed.[26] From the tetraphosphonic acids, **6** was described previously,[27] whereas **7** and **8** are new compounds. The tetrabiphenylsilane tetrakis-4-phosphonic acid (**7**) is a topological analog of tetraphenylmethane tetrakis-4-phosphonic acid and tetraphenylsilane tetrakis-4-phosphonic acid,[28] which was recently used for the preparation of Cu and Zn-based MOFs showing very high surface areas.[11,29] Notably, both tetraphosphonic acids were prepared from the same starting material, namely tetrakis(4-bromophenyl)silane. In this notion, the common transition metal-catalyzed Arbuzov reaction[28] and the Suzuki cross-coupling reaction applied herein are complementary methods giving rise to different space lengths, e.g. phenyl vs. biphenyl. The number of reported tetratopic planar arylphosphonate linkers are limited to porphyrin and pyrene scaffolds and there are two articles, in which the porous networks are reported using the porphyrin tetrakis-*p*-phenylphosphonic acid[10] and tetraethyl-1,3,6,8-pyrenetetraphosphonate monoester.[30] Both ligands formed void channels via coordination of tetratopic tetragonal planar arrangements with one-dimen-



Scheme 1. Synthesis of diphosphonic acids **1**–**5** and their dimethyl esters **1a**–**5a**.

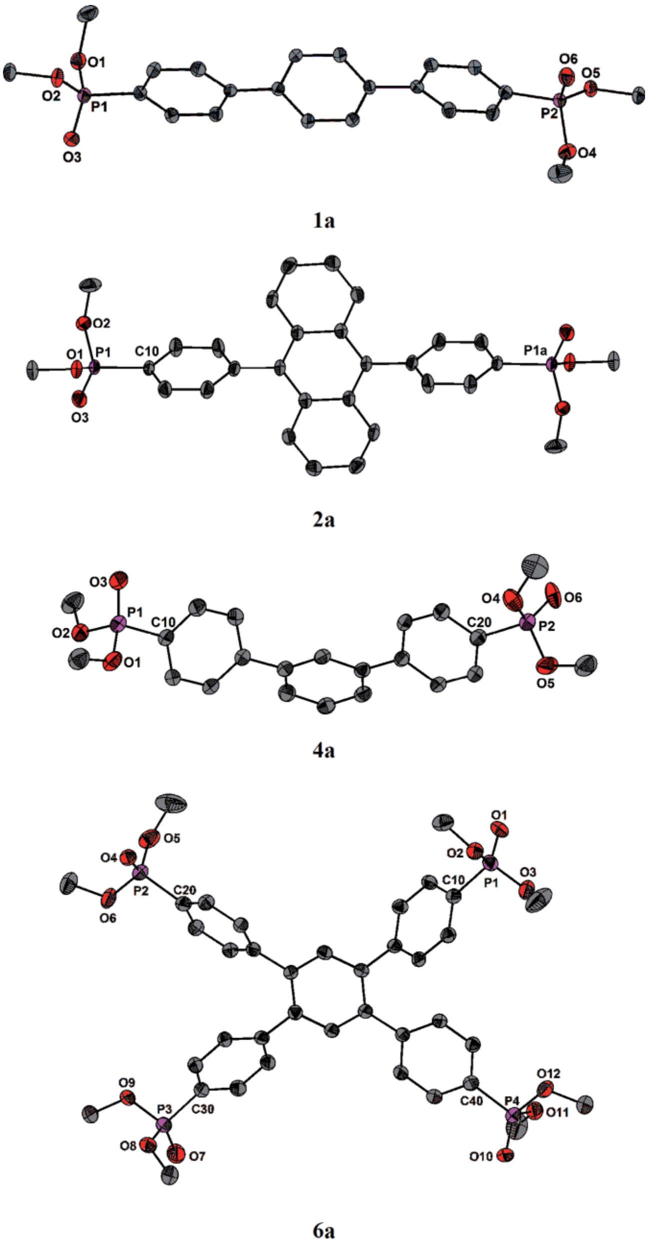


Scheme 2. Synthesis of tetraphosphonic acids **6–8** and their dimethyl esters **6a–8a**.

sional inorganic building units. The phosphonic acid **8** was constructed on the same pyrene core with expanding phenyl arms at the same 1,3,6,8 positions forming a platform potentially leading to larger void spaces. All phosphonic acids **1–8** are virtually insoluble in chloroform, toluene, or THF, which might be attributed to extensive intermolecular hydrogen bonding of the phosphonate groups and π stacking of the aromatic rings.[28] The solubility of **1**, **3**, **4**, and **7** in methanol or DMSO was sufficiently high for their NMR characterization. However, all phosphonic acids are soluble in 1 M sodium hydroxide solution, which effects deprotonation. In this way, the phosphonates derived from **1–8** were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. From acetonitrile solutions of **1–8** ESI-MS spectra, recorded in the negative detection mode, also showed indicative mass clusters related to the phosphonate ions. For selected phosphonic acids, ^{31}P MAS NMR spectra were recorded, which showed single resonances for **2**, **4**, and **7** at δ = 18.6, 16.2, and 18.7 ppm, respectively.

Conclusions

In this paper we report a new strategy utilizing the Suzuki cross-coupling reactions to synthesize arylphosphonate linkers with expanding tether lengths that could be employed in the synthesis of isoreticular MOFs exhibiting larger pore diameters. Using this strategy, we have created a large library of longer branched arylphosphonates and dimethyl arylphosphonates starting with simple *p*-dimethylphosphonatophenylboronic acid and brominated aromatics. We are currently performing more comprehensive and systematic studies to establish the structural patterns of metal-arylphosphonates to engineer the void channels using the reported new linker arrangements.



1a

2a

4a

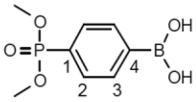
6a

Figure 1. Molecular structures of **1a**, **2a**, **4a**, and **6a** showing 30 % probability ellipsoids and essential atomic numbering.

Experimental Section

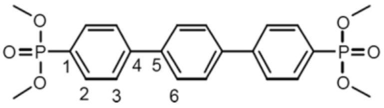
General: 9,10-Dibromoanthracene[31] and tetrakis(4-bromophenyl)-silane[32] were prepared according to the literature. All other reagents were obtained commercially and used as received. Dry Solvents were collected from a SPS800 mBraun solvent system. The ^{1}H-, ^{13}C-, ^{19}F-^{29}Si-, and ^{31}P-NMR spectra were recorded at room temperature with a Bruker Avance-360 spectrometer and are referenced to $SiMe_4$ (^{1}H, ^{13}C, ^{29}Si,), CCl_3F (^{19}F), and H_3PO_4 (^{31}P). IR spectra were measured with a Perkin-Elmer Paragon 500 FT-IR spectrometer. Electron impact mass spectrometry (EI MS) was carried out with a Finnigan MAT 95. The ESI MS spectra were obtained with a Bruker Esquire-LC ion trap MS. Acetonitrile solutions ($c = 1 \times 10^{-6}$ mol·L^{-1}) were injected directly into the spectrometer at a flow rate of 3 µL·min^{-1}. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 5 L·min^{-1} and a pressure of 5 psi, respectively. Pressure in the mass analyzer region was usually about 1×10^{-5} mbar. Spectra were collected for 1 min and averaged. Microanalyses were carried out by the Analytische Laboratorien GmbH (Lindlar, Germany).

Synthesis of *p*-Dimethylphosphonatophenylboronic Acid:[17] A mixture of *p*-bromophenylboronic acid (10.0 g, 49.8 mmol) and trimethyl phosphit (92.6 g, 746 mmol) in toluene (400 mL) was heated under reflux. During 6 h, a solution of tri-*n*-butyltin hydride (17.4 g, 59.7 mmol) and azo-bis(isobutyronitrile) (1.22 g, 1.47 mmol) in toluene (300 mL) was added. Subsequently, the reaction mixture was heated under reflux for 12 h. The solvent was removed under reduced pressure and the crude product purified by column chromatography (silica gel, ethyl acetate). The product was obtained as colorless solid (9.41 g, 40.9 mmol, 82 %; Mp. 108 °C).



^{1}H NMR (200 MHz, CD_3OD): δ = 7.95–7.81 (m, 2 H, H-3), 7.73 [dd, 2 H, $^3J(^1H-^1H)$ = 8.1, $^3J(^1H-^{31}P)$ = 13.1 Hz, H-2], 3.76 [d, 6 H, $^3J(^1H-^{31}P)$ = 11.1 Hz, C*H*$_3$] ppm. **^{11}B-{^{1}H} NMR** (115 MHz, CD_3OD): δ = 29.7 ppm. **^{13}C{^{1}H} NMR** (50 MHz, CD_3OD): δ = 134.9 [d, $^2J(^{13}C-^{31}P)$ = 14.8 Hz, C-2], 131.6 [d, $^3J(^{13}C-^{31}P)$ = 9.7 Hz, C-3], 131.2 [d, $^4J(^{13}C-^{31}P)$ = 9.1 Hz, C-4], 128.5 [d, $^1J(^{13}C-^{31}P)$ = 188.8 Hz, C-1], 53.5 [d, $^2J(^{13}C-^{31}P)$ = 5.8 Hz, *C*H$_3$] ppm. **^{31}P{^{1}H} NMR** (81 MHz, CD_3OD): δ = 23.5 [$^1J(^{31}P-^{13}C)$ = 188.8 Hz] ppm. **ESI MS**: *m*/*z* = 253.0 [M + Na]$^+$, calcd. for $C_8H_{12}BNaO_5P$ = 253.0 g·mol^{-1}.

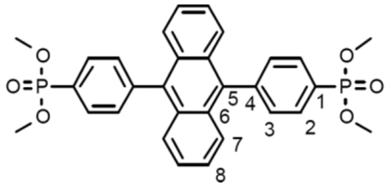
Synthesis of 1,4-Bis(*p*-dimethylphosphonatophenyl)benzene (1a): A mixture of 1,4-dibromobenzene (1.00 g, 4.23 mmol), *p*-dimethylphosphonatophenylboronic acid (3.89 g, 17.2 mmol), sodium carbonate (1.79 g, 17.3 mmol) and tetrakis(triphenylphosphine)palladium (0.24 g, 0.21 mmol) in toluene (50 mL), ethanol (25 mL) and water (25 mL) was heated under reflux for 24 h. To the reaction mixture, water (50 mL) was added and the aqueous layer extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with saturated brine (50 mL) and dried with sodium sulfate. Removal of volatiles under reduced pressure and purification by column chromatography (silica; dichloromethane / methanol = 20:1) afforded the product as a colorless solid. Recrystallization from dichloromethane / hexane furnished colorless crystals of **1a** (1.26 g, 2.82 mmol, 67 %; Mp. 161 °C).



^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98–7.81 (m, 4 H, arom.-H), 7.80–7.65 (m, 8 H, arom.-H), 3.80 [d, 12 H, $^3J(^1H-^{31}P)$ = 11.1 Hz, C*H*$_3$] ppm. **^{13}C{^{1}H} NMR** (50 MHz, $CDCl_3$): δ = 144.5 [d, $^4J(^{13}C-^{31}P)$ = 3.0 Hz, C-4], 139.6 (C-5), 132.4 [d, $^3J(^{13}C-^{31}P)$ = 10.1 Hz, C-3], 127.8 (C-6), 127.1 [d, $^2J(^{13}C-^{31}P)$ = 15.3 Hz, C-2], 125.7 [d, $^1J(^{13}C-^{31}P)$ = 190.7 Hz, C-1], 52.7 [d, $^2J(^{13}C-^{31}P)$ = 5.5 Hz, *C*H$_3$] ppm. **^{31}P{^{1}H} NMR** (81 MHz, $CDCl_3$): δ = 22.9 ppm. $C_{22}H_{24}O_6P_2$ (446.37): calcd. C 59.20; H 5.42 %; found: C 59.11; H 5.35 %. **EI MS**: *m*/*z* = 446.37 [M]$^+$, calcd. for $C_{22}H_{24}O_6P_2$ = 446.36 g·mol^{-1}.

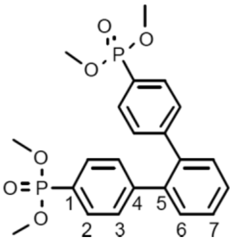
Synthesis of 9,10-Bis(*p*-dimethylphosphonatophenyl)anthracene (2a): A mixture of 9,10-dibromoanthracene (1.00 g, 2.97 mmol), *p*-

dimethylphosphonatophenylboronic acid (2.73 g, 11.9 mmol), sodium carbonate (1.26 g, 11.9 mol), and tetrakis(triphenylphosphine)palladium (0.17 g, 0.15 mmol) was treated as described for **1a**. Purification by column chromatography (silica; ethyl acetate / methanol = 20:1) and recrystallization from dichloromethane / hexane afforded yellow crystals of **2a** (1.26 g, 2.23 mmol, 77 %; Mp. > 230 °C).



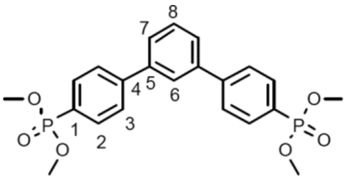
^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.0 [dd, 4 H, $^3J(^1H-^1H)$ = 8.2 Hz, arom.-H], 7.67–7.53 (m, 8 H, arom.-H), 7.43–7.29 (m, 4 H, arom.-H), 3.92 [d, 12 H, $^3J(^1H-^{31}P)$ = 11.1 Hz, CH_3] ppm. **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ = 143.7 [d, $^4J(^{13}C-^{31}P)$ = 3.0 Hz, C-4], 136.1 (C-5), 131.9 [d, $^3J(^{13}C-^{31}P)$ = 10.2 Hz, C-3], 131.5 [d, $^2J(^{13}C-^{31}P)$ = 15.2 Hz, C-2], 129.4, 126.4 [d, $^1J(^{13}C-^{31}P)$ = 190.8 Hz, C-1], 126.5, 125.5, 52.9 [d, $^2J(^{13}C-^{31}P)$ = 5.6 Hz, CH_3] ppm. **$^{31}P\{^1H\}$ NMR** (81 MHz, $CDCl_3$): δ = 22.8 ppm. **UV** (CH_2Cl_2): λ_{max} = 261, 355, 375, 395 nm. $C_{30}H_{28}O_6P_2$ (546.49): calcd. C 65.93; H 5.16 %; found: C 66.07; H 5.24 %. **EI MS**: m/z = 546.49 $[M]^+$, calcd. for $C_{30}H_{28}O_6P_2$ = 546.49 g·mol^{-1}.

Synthesis of 1,2-Bis(p-dimethylphosphonatophenyl)benzene (3a). A mixture of 1,2-dibromobenzene (0.50 g, 2.12 mmol), *p*-dimethylphosphonatophenylboronic acid (0.89 g, 8.47 mmol), sodium carbonate (0.89 g, 8.47 mol), and tetrakis(triphenylphosphine)palladium (0.12 g, 0.10 mmol) was treated as described for **1a**. Purification by column chromatography (silica; dichloromethane / methanol = 20:1) afforded a colorless solid of **3a** (0.38 g, 0.85 mmol, 40 %; Mp. 91 °C).



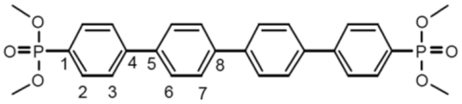
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.72–7.55 (m, 4 H, arom.-H), 7.51–7.37 (m, 4 H, arom.-H), 7.27–7.16 (m, 4 H, arom.-H), 3.75 [d, 12 H, $^3J(^1H-^{31}P)$ = 11.1 Hz, CH_3] ppm. **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ = 145.5 [d, $^4J(^{13}C-^{31}P)$ = 3.1 Hz, C-4], 139.3 (C-5), 131.5 [d, $^3J(^{13}C-^{31}P)$ = 10.2 Hz, C-3], 130.6, 129.6 [d, $^2J(^{13}C-^{31}P)$ = 15.4 Hz, C-2],126.9, 125.0 [d, $^1J(^{13}C-^{31}P)$ = 190.7 Hz, C-1], 52.7 [d, $^2J(^{13}C-^{31}P)$ = 5.5 Hz, CH_3] ppm. **$^{31}P\{^1H\}$ NMR** (81 MHz, $CDCl_3$): δ = 22.8 [$^1J(^{31}P-^{13}C)$ = 190.7 Hz] ppm. $C_{22}H_{24}O_6P_2$ (446.37): calcd. C 59.20; H 5.42 %; found: C 59.21; H 5.27 %. **EI MS**: m/z = 446.37 $[M]^+$, calcd. for $C_{22}H_{24}O_6P_2$ = 446.37 g·mol^{-1}.

Synthesis of 1,3-Bis(*p*-dimethylphosphonatophenyl)benzene (4a): A mixture of 1,3-dibromobenzene (1.00 g, 4.23 mmol), *p*-dimethylphosphonatophenylboronic acid (3.89 g, 17.2 mmol), sodium carbonate (1.79 g, 17.3 mol), and tetrakis(triphenylphosphine)palladium (0.24 g, 0.21 mmol) was treated as described for **1a**. Purification by column chromatography (silica; dichloromethane / methanol = 20:1) and recrystallization from dichloromethane / hexane afforded colorless crystals of **4a** (1.65 g, 3.69 mmol, 87 %; Mp. 107 °C).



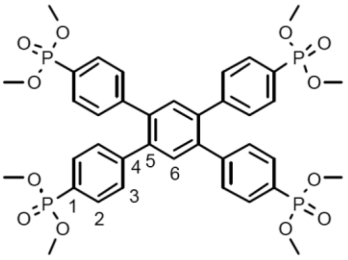
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98–7.51 (m, 12 H, arom.-H), 3.79 [d, 12 H, $^3J(^1H-^{31}P)$ = 11.1 Hz, CH_3] ppm. **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ = 145.0 [d, $^4J(^{13}C-^{31}P)$ = 3.0 Hz, C-4], 140.7 (C-5), 132.4 [d, $^3J(^{13}C-^{31}P)$ = 10.2 Hz, C-3], 129.6, 127.3 [d, $^2J(^{13}C-^{31}P)$ = 15.4 Hz, C-2], 127.1, 126.3, 125.8 [d, $^1J(^{13}C-^{31}P)$ = 190.2 Hz, C-1], 52.7 [d, $^2J(^{13}C-^{31}P)$ = 5.5 Hz, CH_3] ppm. **$^{31}P\{^1H\}$ NMR** (81 MHz, $CDCl_3$): δ = 22.8 [$^1J(^{31}P-^{13}C)$ = 190.7 Hz] ppm. $C_{22}H_{24}O_6P_2$ (446.37): calcd. C 59.20; H 5.42 %; found: C 59.05; H 5.32 %. **ESI MS**: m/z = 469.36 $[M + Na]^+$, Calcd. for $C_{22}H_{24}NaO_6P_2$ = 469.36 g·mol^{-1}.

Synthesis of 4,4′-Bis(*p*-dimethylphosphonatophenyl)biphenyl (5a): A mixture of 4,4′-dibromobiphenyl (0.50 g, 1.60 mmol), *p*-dimethylphosphonatophenylboronic acid (1.47 g, 6.41 mmol), sodium carbonate (0.68 g, 6.41 mmol) and tetrakis(triphenylphosphine)palladium (0.09 g, 0.08 mmol) was treated as described for **1a**. Purification by column chromatography (silica, dichloromethane / methanol = 20:1) afforded a colorless solid of **5a** [0.58 g, 1.11 mmol, 69 %; Mp. 210 °C (decomposition)].



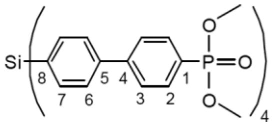
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.98–7.82 (4H, m, arom.-H), 7.88–7.69 (12H, m, arom.-H), 3.81 [d, 12 H, $^3J(^1H-^{31}P)$ = 11.1 Hz, CH_3] ppm. **$^{13}C\{^1H\}$ NMR** (50 MHz, $CDCl_3$): δ = 144.8 [d, $^4J(^{13}C-^{31}P)$ = 3.4 Hz, C-4], 140.2 (C-8), 139.0 [d, $^5J(^{13}C-^{31}P)$ = 1.13 Hz, C-5], 132.5 [d, $^3J(^{13}C-^{31}P)$ = 10.2 Hz, C-3], 127.7, 127.5, 127.1 [d, $^2J(^{13}C-^{31}P)$ = 15.3 Hz, C-2], 125.5 [d, $^1J(^{13}C-^{31}P)$ = 190.7 Hz, C-1], 52.7 [d, $^2J(^{13}C-^{31}P)$ = 5.5 Hz, CH_3] ppm. **$^{31}P\{^1H\}$ NMR** (81 MHz, $CDCl_3$): δ = 23.0 [$^1J(^{31}P-^{13}C)$ = 190.5 Hz] ppm. $C_{28}H_{28}O_6P_2$ (522.46): calcd. C 64.37; H 5.40 %; found: C 64.43; H 5.44 %. **EI MS**: m/z = 522.46 $[M]^+$, calcd. for $C_{28}H_{28}O_6P_2$ = 522.46 g·mol^{-1}.

Synthesis of 1,2,4,5-Tetrakis(*p*-dimethylphosphonatophenyl)benzene (6a): A mixture of 1,2,4,5-tetrabromobenzene (0.90 g, 2.28 mmol), *p*-dimethylphosphonatophenylboronic acid (3.15 g, 13.7 mmol), sodium carbonate (0.96 g, 9.14 mol) and tetrakis(triphenylphosphine)palladium (0.13 g, 0.11 mmol) was treated as described for **1a**. Purification by column chromatography (silica; dichloromethane / methanol = 20:1) and recrystallization from dichloromethane / hexane afforded colorless crystals of **6a** (0.50 g, 0.61 mmol, 27 %; Mp. > 230 °C).



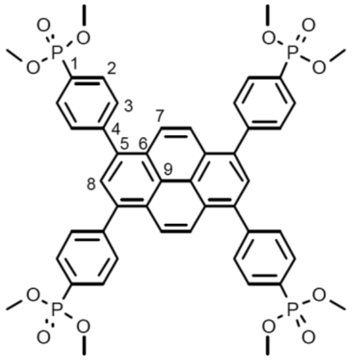
^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.68 [dd, 8 H, $^{3}J(^{1}\text{H-}^{1}\text{H})$ = 8.2 Hz, arom.-H], 7.50 (s, 2 H, H-6), 7.35–7.23 (m, 8 H, arom.-H), 3.76 [d, 24 H, $^{3}J(^{1}\text{H-}^{31}\text{P})$ = 11.1 Hz, CH_3] ppm. **^{13}C{^{1}H} NMR** (50 MHz, CDCl$_3$): δ = 144.3 [d, $^{4}J(^{13}\text{C-}^{31}\text{P})$ = 3.0 Hz, C-4], 139.3, 132.9, 131.7 [d, $^{3}J(^{13}\text{C-}^{31}\text{P})$ = 10.2 Hz, C-3], 129.8 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 15.3 Hz, C-2], 125.7 [d, $^{1}J(^{13}\text{C-}^{31}\text{P})$ = 190.8 Hz, C-1], 52.7 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 5.6 Hz, CH_3] ppm. **^{31}P{^{1}H} NMR** (81 MHz, CDCl$_3$): δ = 22.5 [$^{1}J(^{31}\text{P-}^{13}\text{C})$ = 190.7 Hz] ppm. $C_{38}H_{42}O_{12}P_4$ (814.63): calcd. C 56.03; H 5.20 %; found: C 55.92; H 5.22 %. **EI MS**: *m/z* = 814.63 [M]$^+$, calcd. for $C_{38}H_{42}O_{12}P_4$ = 814.63 g·mol^{-1}.

Synthesis of Dimethyltetrabiphenylsilane Tetrakis-4-phosphonate (7a): A mixture of tetrakis(4-bromophenyl)silane (1.00 g, 1.54 mmol), *p*-dimethylphosphonatophenylboronic acid (0.65 g, 9.26 mmol), sodium carbonate (0.65 g, 6.17 mmol), and tetrakis(triphenylphosphine) palladium (0.09 g, 0.07 mmol) was treated as described for **1a**. Purification by column chromatography (silica; ethyl acetate / methanol = 10:1) afforded a colorless solid of **7a** (1.42 g, 1.32 mmol, 86 %; Mp. > 230 °C).



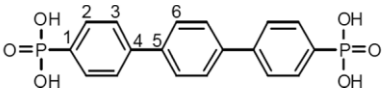
^{1}H NMR (200 MHz, CDCl$_3$): δ = 7.97–7.81 (m, 8 H, arom.-H), 7.80–7.60 (m, 24 H, arom.-H), 3.79 [d, 24 H, $^{3}J(^{1}\text{H-}^{31}\text{P})$ = 11.1 Hz, CH_3] ppm. **^{13}C{^{1}H} NMR** (50 MHz, CDCl$_3$): δ = 144.9 [d, $^{4}J(^{13}\text{C-}^{31}\text{P})$ = 3.0 Hz, C-4], 141.2 (C-5), 136.9, 133.5, 132.4 [d, $^{3}J(^{13}\text{C-}^{31}\text{P})$ = 10.2 Hz, C-3], 127.2 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 15.4 Hz, C-2], 126.9, 125.8 [d, $^{1}J(^{13}\text{C-}^{31}\text{P})$ = 190.7 Hz, C-1], 52.7 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 5.5 Hz, CH_3] ppm. **^{29}Si-{^{1}H} NMR** (71 MHz, CDCl$_3$): δ = –14.3 ppm. **^{31}P{^{1}H} NMR** (81 MHz, CDCl$_3$): δ = 22.8 [$^{1}J(^{31}\text{P-}^{13}\text{C})$ = 190.6 Hz] ppm. $C_{56}H_{56}O_{12}P_4Si$ (1073.02): calcd. C 62.68; H 5.26 %; found: C 62.58; H 5.18 %. **ESI MS**: *m/z* = 1096.00 [M + Na]$^+$, calcd. for $C_{56}H_{56}O_{12}P_4SiNa$ = 1096.00 g·mol^{-1}.

Synthesis of 1,3,6,8-Tetrakis(*p*-dimethylphosphonatophenyl)pyrene (8a): A mixture of 2,3,6,7-tetrabromopyrene (1.00 g, 1.93 mmol), *p*-dimethylphosphonatophenylboronic acid (2.66 g, 11.5 mmol), sodium carbonate (0.81 g, 7.72 mol) and tetrakis(triphenylphosphine)palladium (0.11 g, 0.09 mmol) was treated as described for **1a**. Purification by column chromatography (silica, dichloromethane / methanol = 20:1) and recrystallization from dichloromethane / hexane afforded yellow crystals of **8a** (0.47 g, 0.50 mmol, 26 %; Mp. > 230 °C).



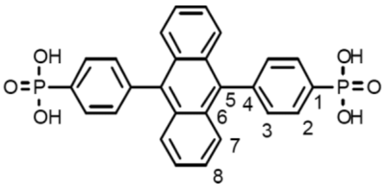
^{1}H NMR (200 MHz, CDCl$_3$): δ = 8.15 (s, 4 H, arom.-H), 8.06–7.91 (m, 12 H, arom.-H), 7.84–7.72 (m, 6 H, arom.-H), 3.85 [d, 24 H, $^{3}J(^{1}\text{H-}^{31}\text{P})$ = 11.1 Hz, CH_3] ppm. **^{13}C{^{1}H} NMR** (50 MHz, CDCl$_3$): δ = 145.0 [d, $^{4}J(^{13}\text{C-}^{31}\text{P})$ = 3.1 Hz, C-4], 136.4 (C-5), 132.0 [d, $^{3}J(^{13}\text{C-}^{31}\text{P})$ = 10.1 Hz, C-3], 130.7 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 15.3 Hz, C-2], 129.2, 128.3, 126.1 [d, $^{1}J(^{13}\text{C-}^{31}\text{P})$ = 190.3 Hz, C-1], 125.7, 125.5, 52.8 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 5.6 Hz, CH_3] ppm. **^{31}P{^{1}H} NMR** (81 MHz, CDCl$_3$): δ = 22.7 [$^{1}J(^{31}\text{P-}^{13}\text{C})$ = 190.3 Hz] ppm. **UV** (DCM): λ_{max} = 230, 250, 301, 388 nm. $C_{48}H_{46}O_{12}P_4$ (938.77): calcd. C 61.41; H 4.94 %; found: C 61.39; H 4.79 %. **EI MS**: *m/z* = 938.77 [M]$^+$, calcd. for $C_{48}H_{46}O_{12}P_4$ = 938.77 g·mol^{-1}.

Synthesis of Benzene-1,4-bis-*p*-phenylphosphonic Acid (1): A suspension of **1a** (0.95 g, 2.13 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2 d. The solvent was removed to give a colorless solid of **1** (0.73 g, 1.87 mmol, 92 %; Mp. 161 °C).



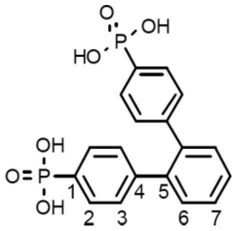
^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.38–7.15 (m, 12 H, arom.-H), 1.96 (s, 4 H, OH) ppm. **^{13}C{^{1}H} NMR** (50 MHz, [D$_6$]DMSO): δ = 141.9 [d, $^{4}J(^{13}\text{C-}^{31}\text{P})$ = 3.0 Hz, C-4] 139.0 [d, $^{5}J(^{13}\text{C-}^{31}\text{P})$ = 0.9 Hz, C-5], 133.1 [d, $^{1}J(^{13}\text{C-}^{31}\text{P})$ = 182.7 Hz, C-1], 131.3 [d, $^{3}J(^{13}\text{C-}^{31}\text{P})$ = 10.2 Hz, C-3], 127.6 (C-6), 126.4 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 14.3 Hz, C-2] ppm. **^{31}P{^{1}H} NMR** (81 MHz, [D$_6$]DMSO): δ = 13.9 [$^{1}J(^{31}\text{P-}^{13}\text{C})$ = 182.7 Hz] ppm. **IR** (KBr):ṽ = 2884 (OH), 1144 (PO) cm^{-1}. $C_{18}H_{16}O_6P_2$ (390.26): calcd. C 55.40; H 4.13 %; found: C 55.43; H 4.23 %. **ESI MS**: *m/z* = 457.22 [M-2H+3Na]$^+$, calcd. for $C_{18}H_{14}Na_3O_6P_2$ = 457.22 g·mol^{-1}.

Synthesis of Anthracene-9,10-bis-*p*-phenylphosphonic Acid (2): A suspension of **2a** (1.26 g, 2.30 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2d. The solvent was removed to give a yellow solid of **2** (1.01 g, 2.06 mmol, 90 %; Mp. > 230 °C).



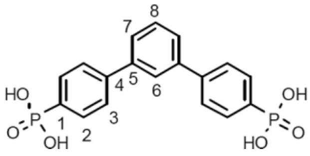
^{1}H NMR (200 MHz, 1 M NaOH in D$_2$O): δ = 7.79–7.60 (m, 4 H, arom.-H), 7.43–7.32 (m, 4 H, arom.-H), 7.19–7.05 (m, 4 H, arom.-H), 7.00–6.97 ,(m, 4 H, arom.-H) ppm. **^{13}C{^{1}H} NMR** (50 MHz, 1 M NaOH in D$_2$O): δ = 141.4 [d, $^{1}J(^{13}\text{C-}^{31}\text{P})$ = 168.0 Hz, C-1], 139.7 [d, $^{2}J(^{13}\text{C-}^{31}\text{P})$ = 17. 4 Hz, C-2], 137.9, 131.5, 131.4 [d, $^{3}J(^{13}\text{C-}^{31}\text{P})$ = 10.0 Hz, C-3], 130.0, 127.6, 126.6 ppm. **^{31}P{^{1}H} NMR** (81 MHz, 1 M NaOH in D$_2$O): δ = 12.6 [$^{1}J(^{31}\text{P-}^{13}\text{C})$ = 167.9 Hz] ppm. **IR** (KBr):ṽ = 2812 (OH), 1171 (PO) cm^{-1}. **UV** (DMSO): λ_{max} = 262, 358, 376, 398 nm. **UV** (NaOH): λ_{max} = 258, 356, 374, 395 nm. $C_{26}H_{20}O_6P_2$ (490.38): calcd. C 63.68; H 4.11 %; found: C 63.50; H 4.08 %. **ESI MS**: *m/z* = 489.37 [M – H]$^-$, calcd. for $C_{26}H_{19}O_6P_2$ = 489.37 g·mol^{-1}.

Synthesis of Benzene-1,2-bis-*p*-phenylphosphonic Acid (3): A suspension of **3a** (0.38 g, 0.85 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2 d. The solvent was removed to give a colorless solid of **3** (0.32 g, 0.82 mmol, 96 %; Mp. > 305 °C).



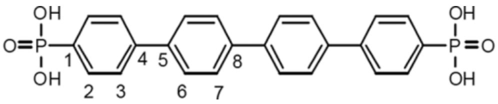
^{1}H NMR (200 MHz, $CDOD_3$): δ = 7.62–7.47 (m, 4 H, arom.-H), 7.43–7.30 (m, 4 H, arom.-H), 7.20–7.09 (m, 4 H, arom.-H), ppm. **^{13}C{^{1}H} NMR** (50 MHz, $CDOD_3$): δ = 145.2 [d, $^4J(^{13}C\text{-}^{31}P)$ = 2.9 Hz, C-4], 140.0 (C-5), 130.7, 130.7 [d, $^3J(^{13}C\text{-}^{31}P)$ = 10.3 Hz, C-3], 130.3 [d, $^1J(^{13}C\text{-}^{31}P)$ = 186.7 Hz, C-1]129.9 [d, $^2J(^{13}C\text{-}^{31}P)$ = 15.1 Hz, C-2],128.3 ppm. **^{31}P{^{1}H} NMR** (81 MHz, $CDOD_3$): δ = 17.3 [$^1J(^{31}P\text{-}^{13}C)$ = 186.0 Hz] ppm. **IR** (KBr):ṽ = 2923 (OH), 1183 (PO) cm^{-1}. $C_{18}H_{16}O_6P_2$ (390.26): calcd. C 55.40; H 4.13 %; found: C 55.51; H 4.01 %. **ESI MS**: *m/z* = 389.26 [M – H]$^-$, calcd. for $C_{18}H_{15}O_6P_2$ = 389.26 g·mol^{-1}.

Synthesis of Benzene-1,3-bis-*p*-phenylphosphonic Acid (4): A suspension of **4a** (1.60 g, 3.69 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2 d. The solvent was removed to give a colorless solid of **4** (1.21 g, 3.10 mmol, 84 %; Mp. > 230 °C).



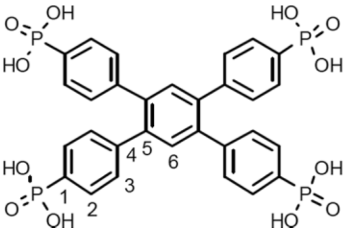
^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 7.99–7.55 (m, 12 H, arom.-H), 4.91 (s, 4 H, O*H*) ppm. **^{13}C{^{1}H} NMR** (50 MHz, [D$_6$]DMSO): δ = 142.3 [d, $^4J(^{13}C\text{-}^{31}P)$ = 3.0 Hz, C-4], 140.26, 134.9, 131.2 [d, $^3J(^{13}C\text{-}^{31}P)$ = 10.4 Hz, C-3], 129.8, 126.7 [d, $^2J(^{13}C\text{-}^{31}P)$ = 14.3 Hz, C-2], 126.6, 125.5 ppm. **^{31}P{^{1}H} NMR** (81 MHz, [D$_6$]DMSO): δ = 13.9 [$^1J(^{31}P\text{-}^{13}C)$ = 182.7 Hz] ppm. **IR** (KBr):ṽ = 2851 (OH), 1142 (PO) cm^{-1}. $C_{18}H_{16}O_6P_2$ (390.26): calcd. C 55.40; H 4.13 %; found: C 55.26; H 4.13 %. **ESI MS**: *m/z* = 389.26 [M – H]$^-$, calcd. for $C_{18}H_{15}O_6P_2$ = 389.26 g·mol^{-1}

Synthesis of Biphenyl-4,4′-bis-*p*-phenylphosphonic Acid (5): A suspension of **5a** (0.40 g, 0.86 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2 d. The solvent was removed to give a colorless solid of **5** (0.29 g, 0.62 mmol, 72 %; Mp. > 230 °C).



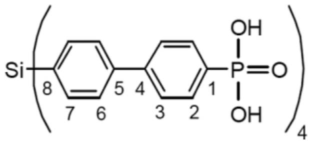
^{1}H NMR (200 MHz, 1 M NaOH in D_2O): δ = 7.84–7.65 (m, 4 H, arom.-H), 7.62–7.35 (m, 8 H, arom.-H), 7.33–7.19 (m, 4 H, arom.-H) ppm. **^{13}C{^{1}H} NMR** (50 MHz, 1 M NaOH in D_2O): δ = 140.3 [d, $^4J(^{13}C\text{-}^{31}P)$ = 2.9 Hz, C-4], 140.2 [d, $^1J(^{13}C\text{-}^{31}P)$ = 168.2 Hz, C-1], 139.5, 139.0, 131,2 [d, $^3J(^{13}C\text{-}^{31}P)$ = 9.0 Hz, C-3], 127.5,127.4, 126.3 [d, $^2J(^{13}C\text{-}^{31}P)$ = 12.9 Hz, C-2] ppm. **^{31}P{^{1}H} NMR** (81 MHz, 1 M NaOH in D_2O): δ = 12.4 [$^1J(^{31}P\text{-}^{13}C)$ = 168.0 Hz] ppm. **IR** (KBr):ṽ = 2923 (OH), 1145 (PO) cm^{-1}. $C_{24}H_{20}O_6P_2$ (466.36): calcd. C 61.81; H 4.32 %; found: C 61.66; H 4.22 %. **ESI MS**: *m/z* = 509.31 [M-3H+2Na] $^-$, calcd. for $C_{24}H_{17}Na_2O_6P_2$ = 509.31 g·mol^{-1}.

Synthesis of Benzene-1,2,4,5-tetrakis-*p*-phenylphosphonic Acid (6): A suspension of **6a** (0.40 g, 0.49 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2 d. The solvent was removed to give a colorless solid of **6** (0.25 g, 0.36 mmol, 73 %; Mp. > 230 °C).



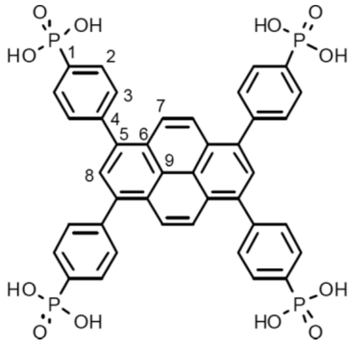
^{1}H NMR (200 MHz, 1 M NaOH in D_2O): δ = 7.63–7.36 (m, 10 H, arom.-H), 7.29–7.12 (m, 8 H, arom.-H) ppm. **^{13}C{^{1}H} NMR** (50 MHz, 1 M NaOH in D_2O): δ = 141.1 [d, $^4J(^{13}C\text{-}^{31}P)$ = 2.8 Hz, C-4], 139.7, 139.5 [d, $^1J(^{13}C\text{-}^{31}P)$ = 167.4 Hz, C-1], 133.4, 130.3 [d, $^3J(^{13}C\text{-}^{31}P)$ = 8.9 Hz, C-3], 129.3 [d, $^2J(^{13}C\text{-}^{31}P)$ = 12.8 Hz, C-2] ppm. **^{31}P{^{1}H} NMR** (81 MHz, 1 M NaOH in D_2O): δ = 12.4 [$^1J(^{31}P\text{-}^{13}C)$ = 167.8 Hz] ppm. **IR** (KBr):ṽ = 2924 (OH), 1144 (PO) cm^{-1}. $C_{30}H_{26}O_{12}P_4$ (702.41): calcd. C 51.30; H 3.73 %; found: C 51.32; H 3.69 %. **ESI MS**: *m/z* = 371.8 [M-4H+2Na]$^{2-}$, calcd. for $C_{30}H_{22}Na_2O_{12}P_4$ = 744.36 g mol^{-1} (for *z* = 2: 372.18 g·mol^{-1}).

Synthesis of Tetrabiphenylsilane Tetrakis-4-phosphonic Acid (7): A suspension of **7a** (1.08 g, 1.00 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2d. The solvent was removed to give a colorless solid of **7** (0.88 g, 0.91 mmol, 91 %; Mp. > 230 °C).



^{1}H NMR (200 MHz, $CDOD_3$): δ = 8.41–8.14 (32H, m, arom.-H) ppm. **^{13}C{^{1}H} NMR** (50 MHz, $CDOD_3$): δ = 144.3 [d, $^4J(^{13}C\text{-}^{31}P)$ = 2.9 Hz, C-4], 142.5, 138.1, 134.6, 133.4 [d, $^1J(^{13}C\text{-}^{31}P)$ = 1984.9 Hz, C-1], 132.7 [d, $^3J(^{13}C\text{-}^{31}P)$ = 10.3 Hz, C-3], 128.1, 128.0 [d, $^2J(^{13}C\text{-}^{31}P)$ = 14.6 Hz, C-2] ppm. **^{29}Si-{^{1}H} NMR** (71 MHz, $CDOD_3$): δ = –14.9 ppm. **^{31}P{^{1}H} NMR** (81 MHz, $CDOD_3$): δ = 15.3 [$^1J(^{31}P\text{-}^{13}C)$ = 184.9 Hz] ppm. **IR** (KBr):ṽ = 2867 (OH), 1142 (PO) cm^{-1}. $C_{48}H_{40}O_{12}P_4Si$ (960.80): calcd. C 60.00; H 4.20 %; found: C 59.97; H 4.26 %. **ESI MS**: *m/z* = 959.80 [M – H]$^-$, calcd. for $C_{48}H_{39}O_{12}P_4Si$ = 959.80 g·mol^{-1}.

Synthesis of Pyrene-1,3,6,8-tetrakis-*p*-phenylphosphonic Acid (8): A suspension of **8a** (0.42 g, 0.45 mmol) in a 24 % solution of HCl in water (50 mL) was heated under reflux for 2d. The solvent was removed to give a colorless solid of **8** (0.30 g, 0.36 mmol, 81 %; Mp. > 230 °C).



^{1}H NMR (200 MHz, 1 M NaOH in D_2O): δ = 8.02 (s, 4 H, arom.-H), 7.91(s, 2 H, arom.-H), 7.83–7.68 (m, 8 H, arom.-H), 7.55–7.43 (m, 8 H, arom.-H) ppm. **^{13}C{^{1}H} NMR** (50 MHz, 1 M NaOH in D_2O): δ = 141.6 [d, $^4J(^{13}C\text{-}^{31}P)$ = 2.7 Hz, C-4], 141.0 [d, $^1J(^{13}C\text{-}^{31}P)$ = 167.5 Hz, C-1],138.0, 131.4 [d, $^3J(^{13}C\text{-}^{31}P)$ = 8.9 Hz, C-3], 130.8 [d, $^2J(^{13}C\text{-}^{31}P)$ = 12.8 Hz, C-2], 130.6, 128.5.0, 126.2 ppm. **^{31}P{^{1}H} NMR** (81 MHz, 1 M NaOH in D_2O): δ = 12.5 [$^1J(^{31}P\text{-}^{13}C)$ = 169.2 Hz] ppm. **IR** (KBr):$\tilde{\nu}$ = 2923 (OH), 1141 (PO) cm^{-1}. **UV** (NaOH): λ_{max} = 260, 300, 388 nm. **UV** (DMSO): λ_{max} = 261, 303, 395 nm. $C_{40}H_{30}O_{12}P_4$ (826.55): calcd. C 58.12; H 3.66 %; found: C 58.01; H 3.55 %. **ESI MS**: *m/z* = 825.55 [M – H]$^-$, calcd. for $C_{40}H_{29}O_{12}P_4$ = 825.55 g·mol^{-1}.

Single Crystal X-ray Crystallography: Intensity data were collected with a STOE IPDS 2T area detector (**1a**·H_2O, **4a**, **6a**) and a Siemens P4 diffractometer (**2a**) fitted at 173 K with graphite-monochromated Mo-K_α (0.7107 Å) radiation. All structures were solved by direct methods and refined based on F^2 by use of the SHELX program package.[33] All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND.[34]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1842627 (**1a**·H_2O), CCDC-1842628 (**2a**), CCDC-1842629 (**4a**), and CCDC-1842630 (**6a**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Keywords: Suzuki cross-coupling; Phosphonic acids; Metall-organic frameworks (MOFs); Linker

References

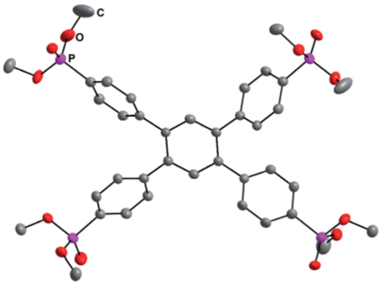
[1] G. K. Shimizu, R. Vaidhyanathan, J. M. Taylor, *Chem. Soc. Rev.* **2009**, *38*, 1430–1449.
[2] K. J. Gagnon, H. P. Perry, A. Clearfield, *Chem. Rev.* **2011**, *112*, 1034–1054.
[3] M. Taddei, F. Costantino, R. Vivani, *Eur. J. Inorg. Chem.* **2016**, 4300–4309.

Table 1. Crystal data and structure refinement of **1a**, **2a**, **4a**, and **6a**.

	1a·H_2O	**2a**	**4a**	**6a**
Formula	$C_{22}H_{26}O_7P_2$	$C_{30}H_{28}O_6P_2$	$C_{22}H_{24}O_6P_2$	$C_{38}H_{42}O_{12}P_4$
Formula weight /g·mol^{-1}	464.37	546.46	446.35	814.60
Crystal system	triclinic	triclinic	monoclinic	triclinic
Crystal size /mm	0.5 × 0.3 × 0.05	0.31 × 0.25 × 0.18	0.5 × 0.2 × 0.05	0.5 × 0.1 × 0.05
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a /Å	12.340(3)	6.544(3)	36.269(7)	11.939(2)
b /Å	12.693(3)	7.534(5)	6.317(1)	12.779(3)
c /Å	15.522(3)	13.219(6)	22.368(5)	13.002(3)
α /°	89.91(3)	92.01(4)	90	89.38(3)
β /°	71.37(3)	95.75(2)	121.27(3)	85.89(3)
γ /°	77.44(3)	96.75(4)	90	83.14(3)
V /Å^3	2242.5(8)	643.2(6)	4381(2)	1964.4(7)
Z	4	1	8	2
ρ_{calcd} /Mg·m^{-3}	1.375	1.411	1.354	1.377
μ (Mo-K_α) /mm^{-1}	0.235	0.214	0.234	0.254
F(000)	976	286	1872	852
θ range /°	1.87 to 25.89	6.32 to 32.71	2.13 to 26.04	2.49 to 26.11
Index ranges	$-15 \le h \le 15$ $-15 \le k \le 15$ $-18 \le l \le 18$	$-8 \le h \le 2$ $-9 \le k \le 9$ $-17 \le l \le 17$	$-44 \le h \le 44$ $-7 \le k \le 7$ $-27 \le l \le 24$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-15 \le l \le 15$
No. of reflns collected	17203	3796	14310	13784
Completeness to θ_{max}	91.8 %	99.9 %	98.4 %	91.3 %
No. indep. reflections	8004	2964	4260	7140
No. obsd reflections with [$I > 2\sigma(I)$]	4243	2100	1884	3574
No. refined parameters	588	290	317	525
GooF (F^2)	0.993	1.022	0.847	0.913
R_1 (F) [$I > 2\sigma(I)$]	0.0696	0.0691	0.0583	0.0628
wR_2 (F^2) (all data)	0.2077	0.1941	0.1497	0.1876
Largest diff peak/hole /e·Å^{-3}	0.583 / –0.367	0.780 / –0.472	0.417 / –0.237	0.781/ –0.558

[4] G. Yücesan, Y. Zorlu, M. Sticker, J. Beckmann, *Coord. Chem. Rev.* **2018**, *369*, 105–122.
[5] C.-Y. Gao, J. Ai, H.-R. Tian, D. Wu, Z.-M. Sun, *Chem. Commun.* **2017**, *53*, 1293–1296.
[6] T. Zheng, Z. Yang, D. Gui, Z. Liu, X. Wang, X. Dai, S. Liu, L. Zhang, Y. Gao, L. Chen, *Nature Commun.* **2017**, *8*, 15369.
[7] G. Cao, H. Lee, V. M. Lynch, T. E. Mallouk, *Inorg. Chem.* **1988**, *27*, 2781–2785.
[8] G. Cao, H. G. Hong, T. E. Mallouk, *Acc. Chem. Res.* **1992**, *25*, 420–427.
[9] G. Yucesan, V. Golub, C. O'Connor, J. Zubieta, *Dalton Trans.* **2005**, 2241–2251.
[10] T. Rhauderwiek, K. Wolkersdörfer, S. Øien-Ødegaard, K.-P. Lillerud, M. Wark, N. Stock, *Chem. Commun.* **2018**, *54*, 389–392.
[11] A. Schütrumpf, A. Bulut, N. Hermer, Y. Zorlu, E. Kirpi, N. Stock, A. Ö. Yazaydın, G. Yücesan, J. Beckmann, *ChemistrySelect* **2017**, *2*, 3035–3038.
[12] P. Tavs, *Chem. Ber.* **1970**, *103*, 2428–2436.
[13] Y. Belabassi, S. Alzghari, J.-L. Montchamp, *J. Organomet. Chem.* **2008**, *693*, 3171–3178.
[14] M. C. Kohler, J. G. Sokol, R. A. Stockland, *Tetrahedron Lett.* **2009**, *50*, 457–459.
[15] K. S. Unikela, T. L. Roemmele, V. Houska, K. E. McGrath, D. M. Tobin, L. N. Dawe, R. T. Boeré, G. J. Bodwell, *Angew. Chem. Int. Ed.* **2018**, *57*, 1707–1711.
[16] A. Suzuki, *Chem. Commun.* **2005**, 4759–4763.
[17] D. Zimmer, J. J. Talley, PCT patent application WO2006/122117 A2 for Microbia, Inc. Cambridge, Massachusetts, USA, **2006**.
[18] Z. Wang, J. M. Heising, A. Clearfield, *J. Am. Chem. Soc.* **2003**, *125*, 10375–10383.
[19] S. P. Hill, T. Banerjee, T. Dilbeck, K. Hanson, *J. Phys. Chem. Lett.* **2015**, *6*, 4510–4517.
[20] J. M. Breen, W. Schmitt, *Angew. Chem.* **2008**, *120*, 7010–7014.
[21] J. M. Breen, R. Clérac, L. Zhang, S. M. Cloonan, E. Kennedy, M. Feeney, T. McCabe, D. C. Williams, W. Schmitt, *Dalton Trans.* **2012**, *41*, 2918–2926.
[22] M. B. Mahimaidoss, S. A. Krasnikov, L. Reck, C. I. Onet, J. M. Breen, N. Zhu, B. Marzec, I. V. Shvets, W. Schmitt, *Chem. Commun.* **2014**, *50*, 2265–2267.
[23] A. Bulut, M. Maares, K. Atak, Y. Zorlu, B. Cosut, J. Zubieta, J. Beckmann, H. Haase, G. Yücesan, *CrystEngComm* **2018**, *20*, 2152–2158.
[24] M. B. Dines, P. C. Griffith, *Polyhedron* **1983**, *2*, 607–611.
[25] Z. Wang, J. M. Heising, A. Clearfield, *J. Am. Chem. Soc.* **2003**, *125*, 10375–10383.
[26] S. Stockhause, P. Neumann, S. Schrader, M. Kant, L. Brehmer, *Synth. Met.* **2002**, *127*, 295–298.
[27] L. Jiménez-García, A. Kaltbeizel, V. Enkelmann, J. S. Gutmann, M. Klapper, K. Müllen, *Adv. Funct. Mater.* **2011**, *21*, 2216–2224.
[28] A. Schütrumpf, E. Kirpi, A. Bulut, F. L. Morel, M. Ranocchiari, E. Lork, Y. Zorlu, S. Grabowsky, G. Yücesan, J. Beckmann, *Cryst. Growth Des.* **2015**, *15*, 4925–4931.
[29] J. K. Zaręba, *Inorg. Chem. Commun.* **2017**, *86*, 172–186.
[30] J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, G. K. Shimizu, *J. Am. Chem. Soc.* **2012**, *134*, 14338–14340.
[31] O. Cakmak, R. Erenler, A. Tutar, N. Celik, *J. Org. Chem.* **2006**, *71*, 1795–1801.
[32] J.-H. Fournier, X. Wang, J. D. Wuest, *Can. J. Chem.* **2003**, *81*, 376–380.
[33] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
[34] K. Brandenburg, Diamond, version 4.0.4, Crystal Impact GbR: Bonn, Germany, **2012**.

Received: May 11, 2018


C
O
P