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Journal article | Accepted manuscript (Postprint)
This version is available at <https://doi.org/10.14279/depositonce-8302>

This is the peer-reviewed version of the following article:

Trunk, M., Herrmann, A., Bildirir, H., Yassin, A., Schmidt, J., & Thomas, A. (2016). Copper-Free Sonogashira Coupling for High-Surface-Area Conjugated Microporous Poly(aryleneethynylene) Networks. *Chemistry - A European Journal*, 22(21), 7179–7183. <https://doi.org/10.1002/chem.201600783>,

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Copper-Free Sonogashira Coupling for High-Surface-Area Conjugated Microporous Poly(aryleneethynylene) Networks

Matthias Trunk, Anna Herrmann, Hakan Bildirir, Ali Yassin, Johannes Schmidt, and Arne Thomas^[a]

Abstract: A modified one-pot Sonogashira cross-coupling reaction based on a copper-free methodology has been applied for the synthesis of conjugated microporous poly(aryleneethynylene) networks (CMPs) from readily available iodoarylenes and 1,3,5-triethynylbenzene. The polymerization reactions were carried out by using equimolar amounts of halogen and terminal alkyne moieties with extremely small

loadings of palladium catalyst as low as 0.65 mol%. For the first time, CMPs with rigorously controlled structures were obtained without any indications of side reactions, as proven by FTIR and solid-state NMR spectroscopy, while showing Brunauer–Emmett–Teller (BET) surface areas higher than any poly(aryleneethynylene) network reported before, reaching up to 2552 m²g⁻¹.

Introduction

Over the last two decades, microporous organic materials have seen remarkable development due to their potential applications in gas storage, separation, sensing, and catalysis.^[1,2] This development has been accelerated by the general trend towards sustainability and a call for less energy-intensive alternatives for industrial procedures, such as cryogenic distillation. Aside from ordered materials, such as metal–organic frameworks (MOFs)^[3] and covalent organic frameworks (COFs),^[4,5] microporous polymer networks (MPNs) have emerged as a family of amorphous yet highly promising materials for a range of applications.^[6–10] Apart from polymeric materials, porous organic molecules have gained an increasing amount of attention recently.^[11–16] Extensive studies have produced unique combinations of high accessible surface areas and chemical robustness, as well as thermal stability, often surpassing MOFs and COFs in those respects, although in exchange for ordered structures.^[1,2,17] A plethora of porous polymers has been obtained through a variety of polymerization methods. Especially the palladium-catalyzed procedure following the Sonogashira-type protocol published by Cooper et al.^[6] to produce conjugated microporous poly(aryleneethynylene) networks (CMPs) is a commonly employed method to incorporate functional groups into porous polymer backbones.^[18] Further functional groups can be grafted onto the polymer backbones postsynthetical-

ly.^[19–21] The importance of these materials is emphasized by the recent commercialization of CMP-1 by Sigma–Aldrich.^[22]

Since 2007, different protocols for CMP syntheses with varying solvents, temperature, starting materials, and stoichiometry have been reported.^[23–26] Initially, ethynyl-functionalized aromatic compounds were reacted with aryl iodides, which were later often succeeded by more readily available bromides, whereby lower degrees of condensation accompanied by slightly lower surface areas were observed.^[18,27] Surprisingly and solely based on empirical findings, the highest surface area for a given CMP was obtained by use of a 50% excess of alkyne functions, which should actually give unreacted alkyne end groups within the resulting network structures,^[23] and be detrimental for reaching high surface areas in a MPN. A recent article addresses the issue of this counterintuitive stoichiometry in depth, focusing on the network formation with special attention paid to open end groups within the network.^[28] Herein, the empirically found necessity for an excess of ethynyl groups for the formation of high-surface-area materials is rationalized by an ongoing reaction of ethynyl end groups, which are trapped within the precipitated material. These ethynyl groups cross-link during elongated reaction times, whereas halide end groups would remain unreactive after gelation, giving dead ends within the polymer. The steady decrease in terminal ethynyl functions was shown to be accompanied by a rise in nitrogen-accessible surface area. Nevertheless, the use of equimolar monomer ratios can also be found in the literature.^[10,24,29,30] Recently, Son and co-workers used the correct stoichiometry to create impressive surface areas of almost 1800 m²g⁻¹ by systematic variation of the phosphine ligand accompanying the palladium catalyst.^[26]

To elucidate the exact formation mechanism and the nature of the homocoupling product, Bunz and co-workers created a homocoupled CMP from a tetrahedral tin-based monomer, which was digested after polymerization. The fragments were

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analyzed to shed light on the structure of the struts linking the former nodes, and thereby on the mechanism of internal cross-linking. The struts were found to consist of isomeric enynes originating from dimers, trimers, and tetramers of alkyne groups.^[31]

To make the conventional homogeneous Sonogashira coupling less susceptible to oxygen and to prevent the formation of side-products, copper-free variants have been developed, although the copper-free mechanism is yet unknown.^[32,33] Motivated by these routes and to avoid the aforementioned side-reactions during CMP formation, we developed a copper-free polymerization method employing the exact stoichiometry of alkyne and halide functions.

From a practical point of view, the addition of the catalyst into the hot reaction mixture in the form of a slurry, as it was reported before, seemed to us unfeasible.^[6] Residues of insoluble catalyst remaining inside the syringe, cannula, or the vessel used for the preparation of the slurry can prove detrimental to reproducibility and rinsing aforementioned vessel with solvent makes the reaction prone to oxygen contamination. Thus, the herein presented route was originally developed to provide a facile and robust one-pot procedure, using equimolar amounts of ethynyl and halide groups, thus avoiding side-reactions while keeping the conversion efficiency of functional groups as high as possible.

Results and Discussion

To understand and perhaps eliminate the empirically found necessity for a large excess of alkyne functionalities, the reaction parameters were optimized for commercial starting materials, 1,4-diiodobenzene and 1,3,5-triethynylbenzene (TEB). However, the first problem for a controlled polymer synthesis was posed by the varying states in which TEB arrives after purchase (Figure 1a). Purification of the as-purchased monomer by column chromatography gave a yellow, crystalline powder (Figure 1b). Further investigation showed that the monomer can be purified by a simple sublimation procedure ($40^{\circ}\text{C}/10^{-3}\text{ mbar}$) to give pristine, colorless crystals, which correspond to the expected appearance (Figure 1c).

Storage of the alkyne at 8°C showed no evidence of decomposition over several months, whereas elongated exposure to ambient temperature caused the material to turn brown, even when stored under inert conditions. We attribute this behavior to a high inherent reactivity of multi-alkyne compounds, which could in part account for the need of an excess of these compounds when non-purified monomers are applied, because parts of the ethynyl groups have already reacted and thus are not available for further polymerization.

It is a known fact that the use of aryl iodides over bromides facilitates a smoother reaction, which lowers the probability of unreacted end groups. Therefore, iodoarylenes were exclusively used in this study. Upon testing different conditions, it was found

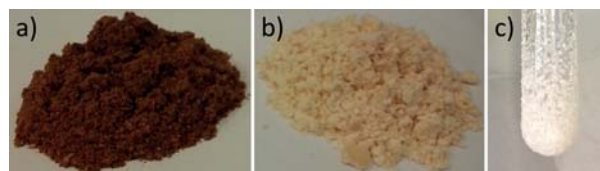
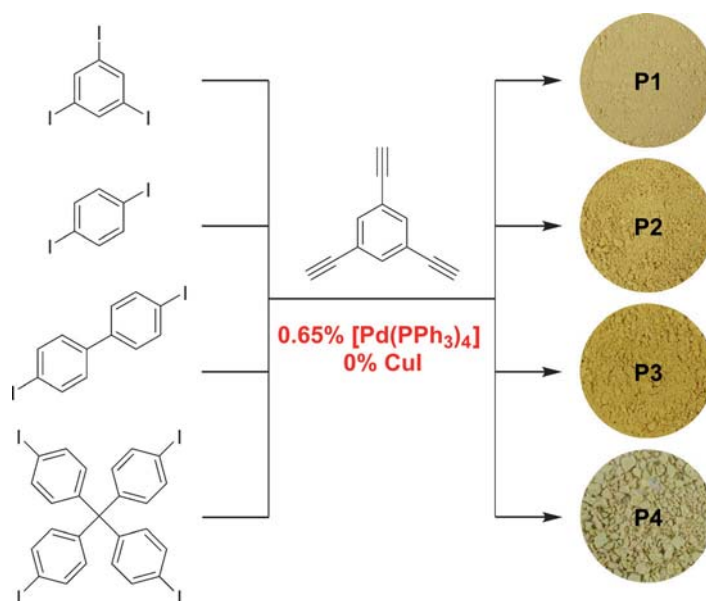


Figure 1. Varying states of 1,3,5-triethynylbenzene: a) as-purchased; b) after column chromatography from dichloromethane; and c) after sublimation.

that for aryl iodides and polyalkynes, high surface areas could be obtained when the amount of palladium catalyst [$\text{Pd}(\text{PPh}_3)_4$] was reduced to 0.65 mol% per iodide/alkyne moiety, whereas the co-catalyst, copper(I) iodide, was omitted completely.^[34] Reaction of TEB with 1,3,5-triiodobenzene, 1,4-diiodobenzene, 4,4'-diiodobiphenyl, and tetrakis(4-iodophenyl)methane in a mixture of DMF/ NEt_3 (2:1) gave highly electrostatic, spongy materials **P1–P4** (Scheme 1). The resultant powders range from off-white to yellow, according to the length and geometry of the conjugated system. Materials **P1** and **P4**, consisting only of weakly electronically conjugated 1,3-connected aromatics, were obtained as beige and off-white, respectively. In contrast, polymers emerging from 1,4-functionalised aryls form longer conjugated aromatic systems, giving rise to different hues of yellow (**P2** and **P3**). It should be noted that materials with structures similar to these materials are described in literature—**P1** corresponds to CMP-X,^[24] **P2** and **P3** correspond to CMP-1 and -2,^[6] respectively, and a structure similar to **P4** was also reported.^[35]

However, not only are the materials reported herein much closer to their ideal structures, but they also exhibit significantly enhanced BET surface areas. Furthermore, **P1–P4** are fluorescent under UV light ($\lambda = 254\text{ nm}$, light fluorescence; 366 nm,



Scheme 1. Copper-free synthetic procedure towards CMPs based on 1,3,5-triethynylbenzene. All reactions were carried out in a mixture of dimethylformamide/triethylamine (2:1) at 100°C for 20 h.

strong fluorescence), whereas reproduced CMP-1 was found to be non-fluorescent.

Compound **P1** was synthesized by reaction of TEB with 1,3,5-triiodobenzene. According to its highly symmetrical (ideal) structure, **P1** exhibits three major peaks at $\delta = 131$, 121, and 86 ppm in the ^{13}C CP/MAS NMR spectrum (Figure 2).

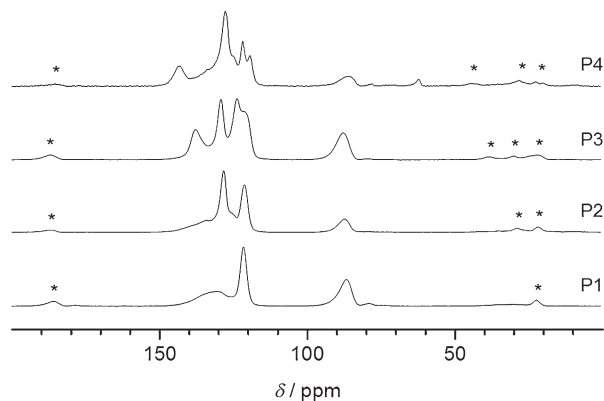


Figure 2. ^{13}C NMR spectra of **P1**–**P4**; asterisks (*) denote spinning sidebands.

These peaks can be unambiguously assigned to $\text{C}_{\text{Ar}}\text{--H}$ (130–133 ppm, very broad), the quaternary carbon atom $\text{C}_{\text{Ar}}\text{--C}\equiv\text{C}$ (121 ppm), and the acetylenic carbon atoms $\text{C}\equiv\text{C}$ (86 ppm). Compounds **P2**, **P3**, and **P4** were synthesized by reaction of TEB with 1,4-diiodobenzene, 4,4'-diiodobiphenyl, and tetrakis(4-iodophenyl)methane, respectively. As can be seen, the peak positions of the triethynylbenzene motif in **P2**, **P3**, and **P4** are largely unchanged from that in **P1** (Figure 2, dashed lines). All remaining peaks of **P2**, **P3**, and **P4** can be assigned accordingly (see the Supporting Information). Additionally, for **P1** and **P4**, small amounts of unreacted alkyne groups were found at $\delta = 78$ ppm.

The high conversion efficiency of this method was confirmed by FTIR measurements (Figure 3). Comparison of the

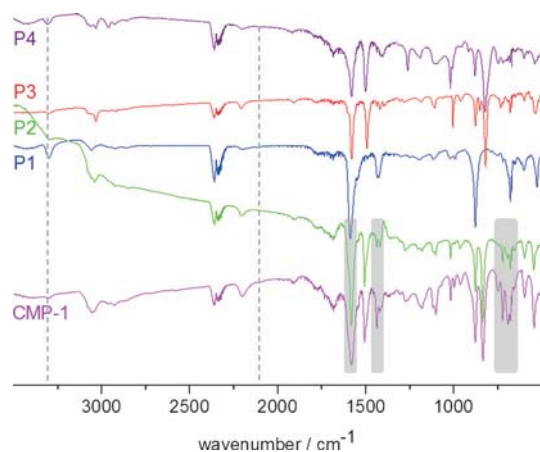


Figure 3. FTIR spectra of **P1** (blue), **P2** (green), **P3** (red), and **P4** (purple) exhibiting very low concentrations of terminal alkyne moieties (2100 and 3300 cm^{-1} , dashed lines), and conventional CMP-1 (pink). Structural differences between CMP-1 and **P2** are highlighted (shaded insets).

peak intensities for internal alkynes (2200 cm^{-1}) and terminal alkynes (2100 and 3300 cm^{-1} , dashed lines) showed low concentrations of terminal alkyne moieties for **P1** and **P4**, and traces for **P2** and **P3**, which is in good agreement with the NMR data. Furthermore, structural differences between **P2** and CMP-1, prepared by the conventional method by hot injection under excess of TEB, can be observed (Figure 3, shaded insets). The occurrence of a shoulder at 1600 cm^{-1} and the additional band at 1440 cm^{-1} in the CMP-1 spectrum resulted from the formation of enyne moieties, which is in agreement with IR data reported before^[36] and the NMR data acquired by Bunz and co-workers.^[31]

These enyne groups are the product of coupling of the remaining terminal alkyne groups, which can therefore no longer be observed for CMP-1, despite the huge excess of TEB employed in the synthesis. Further differences can be observed in the fingerprint region around 700 cm^{-1} .

As was pointed out previously, the same network structure as **P1** has been reported before.^[24] However, the previous solid-state ^{13}C NMR spectrum exhibited an additional sharp peak at $\delta = 131$ ppm, which we attribute to only partially consumed starting material due to non-optimal reaction conditions and less reactive 1,3,5-tribromobenzene. Consequently, the resulting network would exhibit a lower degree of conversion. Testament to this assumption are the comparatively low reported surface areas, which lie in the range of 370 to 400 m^2g^{-1} , whereas for **P1** a surface area of 914 m^2g^{-1} was detected. For **P2** and **P3**, 1720 and 873 m^2g^{-1} were obtained (Figure 4). These values surpass the surface areas of structurally

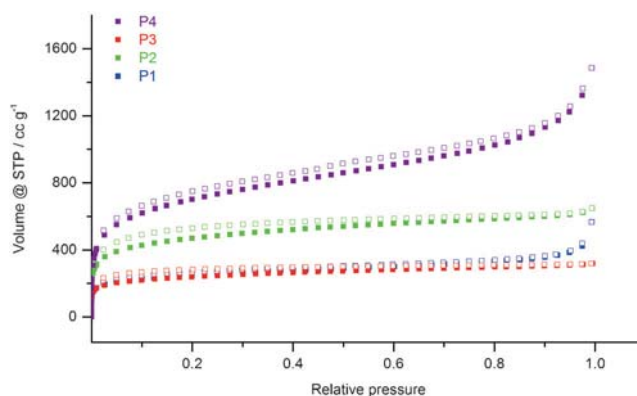


Figure 4. N_2 uptake at 77 K for **P1** (blue), **P2** (green), **P3** (red), and **P4** (purple).

related materials obtained by the conventional method of 834 m^2g^{-1} for CMP-1 and 634 m^2g^{-1} for CMP-2 (Table 1). The most significant surface-area enhancement was found for **P4**, which exhibited an impressive surface area of 2552 m^2g^{-1} . This equals more than five times the accessible surface area of the structurally related material published previously,^[35] and is the highest BET surface area of any poly(aryleneethynylene) network reported to date, surpassing even those formed by dynamic alkyne metathesis.^[10]

	S_{BET} (reported) [m^2g^{-1}]	S_{BET} (this work) [m^2g^{-1}]	CO_2 uptake [mmol g^{-1}] ^[a]	H_2 uptake [wt%] ^[b]
P1/CMP-X ^[24]	397	914	3.01	1.32
P2/CMP-1 ^[6]	834	1720	2.53	1.36
P3/CMP-2 ^[6]	634	873	2.12	1.00
P4/E2 ^[35]	488	2552	3.36	1.59

[a] CO_2 sorption experiments were performed at 273 K and 1 bar. [b] H_2 sorption experiments were carried out at 77 K and 1 bar.

The high accessible surface area of **P4** also gives rise to considerable sorption capacity towards other gases; the total uptake values for H_2 at 77 K and 1 bar, as well as for CO_2 at 273 K and 1 bar are among the highest reported for as-synthesized MPNs.^[2,37] Especially the almost linear shape of the CO_2 adsorption curve suggests remarkable uptake under high pressure (see the Supporting Information).

In compounds **P1–P3**, two dominant pore sizes around 0.6 and 0.9 nm were found according to non-local (NL) DFT calculations derived from the nitrogen-sorption measurements (Figure 5). A decrease in the relative intensity of the smaller pores is accompanied by an increase in surface area. The same tendency was reported previously^[26] and culminates in **P4** for which pores at 1.10 nm were observed exclusively, and which has the highest BET surface area.

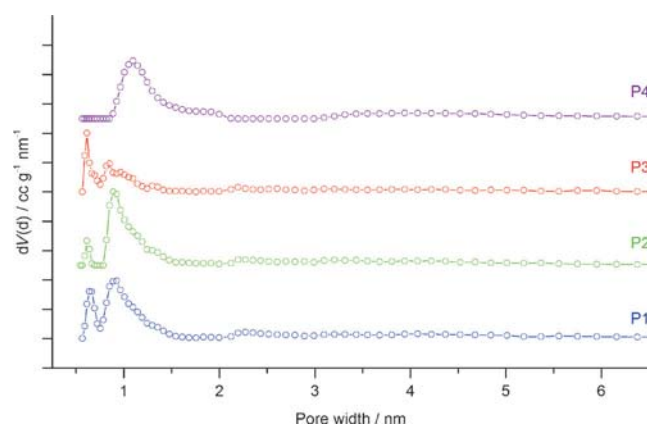


Figure 5. Pore-size distributions of **P1** (blue), **P2** (green), **P3** (red), and **P4** (purple).

Conclusion

We herein present an improved protocol for the synthesis of conjugated microporous polymers based on the Sonogashira cross-coupling reaction. Experiments were carried out in a facile one-pot procedure, and the amounts of halide and alkyne groups were adjusted to 1:1. By reduction of the amount of palladium catalyst to 0.65 mol% and removal of the co-catalyst, copper(I) iodide, for the first time, CMPs with rigorously controlled chemical structure and high BET surface areas of up to $2552\text{ m}^2\text{g}^{-1}$ were obtained. We will continue to gain

further mechanistic insights into the polymerization reaction and widen the applicability of this facile and highly efficient synthesis protocol.

Experimental Section

Materials: All chemicals were used as received unless otherwise noted. Tetrakis(4-iodophenyl)methane and 1,3,5-triiodobenzene were synthesized according to a literature procedure with slight modifications (see the Supporting Information). 1,3,5-Triethynylbenzene was purchased from TCI and sublimated before use ($40^\circ\text{C } 10^{-3}$ mbar). Tetrakis(triphenylphosphine)palladium(0) (99.9%), 1,4-diiodobenzene (99%), 1,3,5-tribromobenzene (98%), anhydrous tetrachloromethane ($\geq 99.5\%$), anhydrous dimethylformamide (99.8%), and triethylamine ($\geq 99.5\%$) were purchased from Sigma-Aldrich. 4,4'-Diiodobiphenyl (99%) was purchased from Alfa Aesar. Bis(trifluoroacetoxy)iodobenzene (98%) and iodine (99.5%) were purchased from Acros Organics. Tetraphenylmethane (96%) was purchased from Manchester Organics.

Synthetic procedure for P1: Inside the glovebox, a 50 mL glass vial was charged with 1,3,5-triethynylbenzene (100.6 mg, 670 μmol), 1,3,5-triiodobenzene (305.4 mg, 670 μmol), $[\text{Pd}(\text{PPh}_3)_4]$ (15.1 mg, 13 μmol), dimethylformamide (12 mL), and triethylamine (6 mL). The vessel was closed with a silicone septum, extracted from the glovebox, and immersed in an oil bath preheated to 100°C . The colorless solution turned increasingly yellow, and a voluminous pale yellow precipitate formed after several minutes. The mixture was kept at 100°C for 20 h, quenched by addition of methanol, and filtered. The resulting beige solid was purified by Soxhlet extraction from methanol overnight and dried in the vacuum oven at 80°C overnight.

Synthetic procedure for P2: Inside the glovebox, a 5 mL glass vial was charged with 1,3,5-triethynylbenzene (100.1 mg, 667 μmol), 1,4-diiodobenzene (329.9 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (7.5 mg, 6.5 μmol), dimethylformamide (3 mL), and triethylamine (1.5 mL). The vessel was closed with a silicone septum, extracted from the glovebox, and immersed in an oil bath preheated to 100°C . The colorless solution turned increasingly yellow, and a voluminous yellow precipitate formed after several minutes. The mixture was kept at 100°C for 20 h, quenched by addition of methanol, and filtered. The resulting yellow solid was purified by Soxhlet extraction from methanol overnight and dried in the vacuum oven at 80°C overnight.

Synthetic procedure for P3: Inside the glovebox, a 50 mL glass vial was charged with 1,3,5-triethynylbenzene (100.3 mg, 668 μmol), 4,4'-diiodobiphenyl (406.7 mg, 1.00 mmol), $[\text{Pd}(\text{PPh}_3)_4]$ (15.1 mg, 13 μmol), dimethylformamide (12 mL), and triethylamine (6 mL). The vessel was closed with a silicone septum, extracted from the glovebox, and immersed in an oil bath preheated to 100°C . The colorless solution turned increasingly yellow, and a voluminous yellow precipitate formed after several minutes. The mixture was kept at 100°C for 20 h, quenched by addition of methanol, and filtered. The resulting yellow solid was purified by Soxhlet extraction from methanol overnight and dried in the vacuum oven at 80°C overnight.

Synthetic procedure for P4: Inside the glovebox, a 50 mL glass vial was charged with 1,3,5-triethynylbenzene (20.1 mg, 134 μmol), tetrakis(4-iodophenyl)methane (82.8 mg, 101 μmol), $[\text{Pd}(\text{PPh}_3)_4]$ (3.1 mg, 2.7 μmol), dimethylformamide (24 mL), and triethylamine (12 mL). The vessel was closed with a silicone septum, extracted from the glovebox, and immersed in an oil bath preheated to 100°C . The colorless solution turned increasingly yellow, and a volu-

minous pale yellow precipitate formed after several minutes. The mixture was kept at 100 °C for 20 h, quenched by addition of methanol, and filtered off. The resulting off-white solid was purified by Soxhlet extraction from methanol overnight and dried in the vacuum oven at 80 °C overnight.

Synthetic procedure for reproduced CMP-1: Inside the glovebox, [Pd(PPh₃)₄] (50.1 mg, 43 μmol) and CuI (15.0 mg, 79 μmol) were suspended in dimethylformamide (1.5 mL) and taken up into a syringe. A 5 mL glass vial was charged with 1,3,5-triethynylbenzene (150.2 mg, 1.00 mmol), 1,4-diiodobenzene (330.0 mg, 1.00 mmol), dimethylformamide (1.5 mL), and triethylamine (1.5 mL). The vessel was equipped with a silicone septum and a balloon, the vial and syringe were extracted from the glovebox, and the vial was immersed in an oil bath preheated to 100 °C. After 5 min, the catalyst mixture was added into to the vial through the septum. The colorless solution turned yellow instantly, and a brown precipitate formed after a few seconds. The mixture was kept at 100 °C for 20 h, quenched by addition of methanol, and filtered. The resulting brown solid was purified by Soxhlet extraction from methanol overnight and dried in the vacuum oven at 80 °C overnight.

Further experimental and analytical data are given in the Supporting Information.

Acknowledgements

This work was funded by the ERC Project ORGZEO (Grant-Nr.: 278593) and the DFG (Cluster of Excellence UniCat). We thank Christina Eichenauer, Maria Unterweger, and Caren Göbel for the sorption experiments, XRD measurements, and TEM and EDX measurements, respectively.

Keywords: CO₂ sorption · conjugated microporous polymers · copper-free Sonogashira · covalent organic frameworks · hydrogen storage

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