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Optical Properties and Sequence Information of Tin-Centered Conjugated Microporous Polymers

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Dedication ((optional))

Abstract: We synthesized conjugated microporous polymers (CMPs) based on tetrakis(4-ethynylphenyl)stannane and diiodobenzene as tectons, employing Sonogashira couplings under different conditions. Through variation of the reaction conditions (catalysts, bases and solvents), appearance, surface area and emission properties of the formed CMPs were significantly altered. Wet-chemical, acid-mediated digestion and analysis of the resulting struts of these otherwise insoluble networks give insight into the molecular setup.

Introduction

Conjugated microporous polymers (CMPs) containing tetrahedral building blocks are a class of materials with attractive applications, including gas separation, catalyst scaffolding or energy storage.^[1] The stability of these materials in combination with their ease of preparation and functionalization make them enticing, though it comes at the cost of *absolute* insolubility and therefore relies on - in most cases - indirect methods to assign their internal structure. Useful techniques as IR-, solid-state NMR-spectroscopy, but also microscopy and gas sorption measurements, assess only bulk materials' properties - they do not probe fine details such as defect structures that must be present in such materials.

Yet, CMPs have been investigated fairly thoroughly and Thomas *et al.* have recently emphasized the importance of monomer purity and reaction conditions, both influencing surface area as well as appearance of the formed CMPs.^[2] Nevertheless, important questions remain, including the characterization and rationalization of optical properties of these partially conjugated

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materials as a direct consequence of the network-forming organic connectors. An aspect virtually not understood is the fluorescence of such CMPs. A seminal paper was published by Scherf *et al.* who prepared microemulsions of a tetraphenylmethane-diethynylbenzene-based network and demonstrated emission of the emulsions in water (Scheme 1).^[3]



Scheme 1. Scherf's fluorescent CMP microparticles.

They reported that CMP 3 displays green fluorescence $(\lambda_{em,max} = 485-510 \text{ nm})$ as dispersion in water. This is surprising, as the main chromophore in this system is bis(phenylethynyl)benzene, with $\lambda_{\text{em,max}}$ of around 311 nm and shoulders around 360 nm.^[4] The authors speculate about the dramatic red shift in emission and invoke a mix of aggregate formation, but also that bis(phenylethynyl)benzenes are prone towards red-shifted emission upon attachment of polar substituents to the chromophore. Yet, the cause for this dramatic red shift is not fully understood. Other structures, similar to CMP 3, have been prepared but their fluorescence was either not mentioned or not investigated.^[5] CMPs with a bis(phenylethynyl)benzene "strut" connecting tetrahedral carbon, silicon or tin centers should be colorless and deep-blue emissive. However, most of the reported materials are yellow, deep beige brown, dark brown or orange or their color is simply not mentioned. Most are described as nonfluorescent.[6-7]

We work on poly(*para*-phenyleneethynylene)s (PPEs), having investigated their optical and structural properties in depth.^[8] From our experience, the appearance of the PPEs (color, brilliancy) gives a qualitative idea of the purity of the materials, which appear either as lemon yellow or bright orange-**yellow** solids. Colors such as brown, violet, grey, purplish etc. always indicated the presence of defects in PPEs. This is probably also the case for the CMPs with phenyleneethynylene (PE) trimers as their chromophore.

CMPs containing PE units as struts connected by tetrahedral centers can be digested by chloroacetic acid if a tin atom is the central unit.^[9] Insoluble and infusible CMPs are digested into their building blocks, which then are analyzed by conventional solution phase NMR and GC-MS to detect defect structures and end groups. In this contribution, we investigate the effect of different

FULL PAPER

reaction conditions for network formation on composition and optical properties of digestible tin-centered CMPs 6.

Results and Discussion

We prepared the porous polymers **6a-k** *via* Sonogashira coupling of the tin-based tetrahedral monomer **4** with diiodobenzene **5** (Scheme 2). Table 1 lists the different reaction conditions and catalyst systems employed. Synthesis was either based on the procedure for CMPs by Thomas *et al.* (Table 1, **CMP 6a**)^[2] or on

a protocol developed by our group for the synthesis of PPEs (Table 1, **CMP 6h**).^[9]



Scheme 2. Synthetic procedure to tin-centered CMPs 6.

Table 1: Synthetic conditions, optical properties, nitrogen content, BET surface areas and GCMS yield after wet-chemical digestion of CMPs 6a-k.

Synthesis					Emission Maxima ^a		Elemental Analysis	BET⁵	Digestion ^c
CMP	Catalyst	Solvent	Base	Reaction temperature and time	Solid state λ _{max, em} [nm]	Suspension in THF (c = 1 mg/mL) λ _{max, em} [nm]	Nitrogen content [%]	m²/g	Ratio organic linker 11:12
6a	Pd(PPh ₃) ₄ (2 mol%)	DMF	NEt ₃	21 h, 100 °C	524	522 (shoulder 460)	-	426	only 11
6b	Pd(PPh ₃) ₄ (0.2 mol%)	DMF	NEt ₃	21 h, 100 °C	524	520 (shoulder 460)	-	32	6:1
6c	Pd(PPh ₃) ₄ (2 mol%)	Toluene/ DMF 1:1	NEt ₃	21 h, 100 °C	532	522, 478	-	7	384:1
6d	Pd(PPh ₃) ₄ (2 mol%)	Toluene	NEt ₃	21 h, 100 °C	539	533	-	10	62:1
6e	Pd(PPh ₃) ₂ Cl ₂ (2 mol%)	Toluene	NEt ₃	21 h, 100 °C	541	540	-	753	4:1
6f	Pd(PPh ₃) ₂ Cl ₂ (2 mol%)	Toluene	Piperidine	21 h, 100 °C	529 (shoulder 480)	518, 477	-	116	6:1
6g	$Pd(PPh_3)_2Cl_2 \text{ (0.2 mol\%)}$	Toluene	Piperidine	3 d, 75 °C	512, 477	469, 510	0.23	27	9:1
6h	Pd(PPh ₃) ₂ Cl ₂ (0.2 mol%), Cul (0.4 mol%)	Toluene	Piperidine	3 d, 75 °C	470, 503	462, 503	0.55	25	11:1
6i	Pd(PPh ₃) ₂ Cl ₂ (0.1 mol%), Cul (0.4 mol%)	Toluene	Piperidine	3 d, 75 °C	511, 473	461, 503	0.10	6	11:1
6j	Pd(PPh ₃) ₂ Cl ₂ (0.2 mol%), Cul (0.4 mol%)	THF	Piperidine	3 d, 75 °C	522 (shoulder 480)	466, 509	0.23	2	10: 1
6k	Pd(PPh ₃) ₂ Cl ₂ (0.2 mol%), Cul (0.4 mol%)	DMF	Piperidine	3 d, 75 °C	522, 471	464, 511	0.73	6	9:1

[a]: Excitation wavelength: λ_{exc} = 376 nm. [b] Determined through nitrogen sorption experiments at 77 K. [c] After treatment with chloroacetic acid (20 eq) in toluene at 90 °C for 20 h.



Both synthetic procedures were systematically varied to yield CMPs **6b-e** and **6f,g,i-k**, which were purified by Soxhlet extraction from methanol and dried under vacuum. The yields ranged from 93% to "112%" which we attribute to encapsulated palladium/ligand residues rather than unreacted halides (*vide supra*). The color of the resulting powders ranges from pale yellow to dark orange under daylight (Figure 1, top). In general, CMPs prepared employing PPE conditions (or slightly varied, **6f-k**) were pale yellow in the solid state, whereas the polymers prepared after Thomas' protocol were dark orange. All of the CMPs are fluorescent in the solid state and in suspension of the finely ground powders in THF. Whereas polymers **6g-k** appear similar, the emission color of **6a-f** ranges from greenish to bright yellow in the solid state, and from blue to yellowish-green in their suspensions.

Emission spectra reveal two groups of emission types in dependence of the base employed, reaction time and temperature (Figure 2). CMPs from triethylamine and/or high catalyst loading (top) show red shifted emission maxima compared to those prepared in piperidine (bottom). Catalyst and solvent choice do not have a great influence on emission properties but catalyst loading has. The emission maxima for **6ae** in the solid state do not differ notably, as they are between 524 nm and 541 nm. Noticeably, there are shoulders in the blue shifted area which are even more distinct when the emission spectra are recorded in suspensions of THF. If compared to polymers **6f-k**, the shoulders become apparently well-resolved peaks. There are now two maxima present in the emission spectra of the solid state - between 503 nm and 529 nm (503 nm

and 518 nm in suspensions) and another maximum between 471 nm and 480 nm (461 nm and 477 nm in suspensions).

To compare the structure of the polymers and set it into relation to the emission properties we synthesized a model compound consisting of the PE strut that should also be present in the polymers (Scheme 3). 10 shows an intense blue fluorescence in the solid state and in solution (see supporting information). While 10 exhibits a well-resolved vibronic finestructure in THF $(\lambda_{em,max} = 407 \text{ nm})$, its emission spectrum is bathochromically shifted in the solid state ($\lambda_{em,max} = 452 \text{ nm}$) and less well-resolved. Although its maximum is close to those of the CMPs synthesized from piperidine, fluorescence from the networks is slightly redshifted. Comparing spectral features with those received from the polymers from triethylamine, the red shift becomes even more apparent (Figure 2). These differences between the emission properties of the polymers 6a-k and also the model compound 10 can be explained by additional effects arising from the deviant spatial orientation of the optically active bis(phenylethynyl)benzene units within the polymeric structure compared to an arrangement of single molecules as formed in 10. The formation of CMPs from tetrahedral monomers could lead to a variety of possible alignments of the chromophores to each other. Current investigations in this field confirm this assumption and hint at the existence of further coupled excitonic states and different decay channels arising from changes in packing, orientation and distances concerning the chromophores.^[10] Fluorescence lifetime measurements were conducted for 10, 6b and 6f in the solid state at their emission maxima (see Supporting Information). In general, multi-exponential decays were observed, common in thin-films due to different orientations. However, lifetime depends on the

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Figure 2: Emission spectra of polymers 6a-e (top) and 6f-k (bottom) in the solid state (left) and in suspensions of THF (right, c = 1 mg/mL) in comparison with the model compound 10.



emission maximum for **6b** and **6f** and is longer for the red-shifted maximum. Thus, aggregation and rigidification of the electronically independent struts of the microporous polymers cannot solely account for the emission but further effects, e.g. excimers, or defects influence spectral features of the networks. Porosity was determined by nitrogen sorption measurements at 77K and calculation of the Brunauer-Emmet-Teller (BET) surface areas of the CMPs. Noticeably, some of the polymers exhibit a high surface area while others are non-porous (Table 1). The highest surface areas were achieved for CMPs **6a** and **6e** (426 m²/g and 753 m²/g) - both synthesized according to the protocol

of Thomas et al. utilizing a relatively high amount of palladium catalyst (2 mol%) and triethylamine as base. Pore size distribution analysis revealed pores of 1.6 nm and 2.8 nm in size, showing a small mesoporous distribution (see Supporting Information). We observed a strong solvent effect concerning the surface area when changing from DMF to toluene (6a to 6d, 426 m²/g to 10 m²/g). Although there are no other literature known tincentered CMPs, our results correspond to earlier reports where solvent choice influences morphology and porosity of similar materials.^[11,12] Surprisingly, a catalyst change from Pd(PPh₃)₄ to Pd(PPh₃)₂Cl₂ leads to the highest observed surface area (6d to 6e, 10 m²/g to 753 m²/g). When piperidine as a base is employed, the surface area decreases (6e to 6f, 753 m^2/g to 116 m^2/g). Reducing the catalyst loading to PPE-based conditions produces materials with very low surface areas (CMP 6g-k). Even though different solvents were tested, the low catalyst loading (0.2 mol%) always resulted in a non-porous network (CMP 6b, 6g-k). One explanation could be that in some cases the pores within the polymers are too small for interdiffusion of nitrogen. SEM images were taken exemplarily of 6e, 6f and 6g to reveal differences in the morphology of the materials (see Supporting Information for SEM data). For the reasonably porous CMP 6f and non-porous 6g (surface areas: 116 m²/g (6f); 27 m²/g (6g)) the sharp-edged particles severely vary in size whereas for 6e (753 m²/g) the material forms well-defined spherical conglomerates of similar size and shape as observed for nanoparticular CMPs previously

FULL PAPER





Figure 3: SEM images of CMP 6e. Top: overview. Bottom: Detail of the highly porous preparations of 6e. Clearly visible are the roundish clumped together spherical species sized around 500 nm.

synthesized (Figure 3).^[3,5b,13] The structures are fairly uniform and interestingly enough very dependent upon the synthetic conditions. To further elucidate the inner structure of the CMPs and to investigate a correlation between porosity/morphology and reactivity we cleaved their tin-carbon-bonds by heating suspensions with chloroacetic acid in toluene overnight (Scheme 4). After neutralization with sodium bicarbonate and washing with water to remove the acid residues or even simple stirring over solid K₂CO₃, we performed GC-MS analyses. Spectra show prominent signals of the expected organic linker 11 and mono-reacted 12 (see Supporting Information for GCMS data). In some cases, unreacted phenylacetylene was detected in negligible amounts. The recorded IR-spectra of the polymers support a low residue of phenylacetylene as they show only very weak signals at 3300 cm⁻¹, the typical band for alkyne C-H vibration, compared to the monomer 4 (see Supporting Information). For linker 11 and 12, the GC-MS intensity ratios are listed in table 1. Our digestion experiments show that from 6a only organic linker 11 is formed. For 6b, a much smaller catalyst loading is employed resulting in incomplete polymerization, evident from the detection of compound 12. Conditions optimized for the coupling of aromatic iodides with alkynes 6g-k for PPEs do give higher amounts of the expected trimeric PE-strut 11, but also some corresponding iodinated dimer is left in the polymeric structure. In contrast, conditions for preparation of 6c and 6d resulted in less mono-reacted compound **12** and thus a higher degree of polymerization.



Scheme 4: Conditions for digestion of the polymers 6a-k.

Except for linkers **11**, **12** and phenylacetylene no other organic compounds were detected in the GC-MS traces or during purification of the digest *via* column chromatography (see Supporting Information for all spectra). If one looks into PPEs, the use of a high catalyst loading is discouraged, as it leads invariably to the formation of butadiyne defects.^[8] This is apparently different for **CMP**s, where the growing polymer support suppresses diyne formation, as no diphenylbutadiyne was detected in the chromatograms.

Elemental analyses of the networks indicate incorporation of nitrogen defect structures employing piperidine as a base (PPE conditions). Nitrogen content ranges from 0.10% to 0.73% for CMPs 6g-k. Whereas nitrogen is absent using tertiary triethylamine (bathochromically shifted emission), prolonged reaction times might lead to Buchwald-Hartwig amination with secondary amines,^[14] resulting in CMPs with blue-shifted emission features. Nitrogen containing moieties blocking the pores within the CMPs could also be the reason for the nonporosity of the materials. However, our GC-MS analyses of the digests did not reveal the presence of nitrogen containing organic compounds, despite neutralization of the formerly acidic reaction mixtures. The explanation for the observed optical properties and behavior concerning the porosity remains difficult, but our approach led to an insight into the inner structure of completely insoluble networks.

Conclusions

The CMPs **6a-k** with tin as the central connecting atom were systematically synthesized *via* Sonogashira-Hagihara coupling, employing different reaction conditions, catalyst loadings, solvents etc. The habitus i.e. the color and the emission characteristics of the CMP **6** is dependent upon the reaction conditions and selected solvents. All of the - in a formal sense identical - materials are fluorescent, yet show emission colors and porosities that are dependent upon the use of the base, the solvent and the catalyst loading. Typically, triethylamine gives more red-emitting CMPs, while piperidine leads to bright yellow or greenish emitting solids. As a consequence, an important and still unsolved question is the nature of the active chromophore and fluorophore in the CMPs, as the synthesized model compound **10** with the two triphenylstannyl substituents has a very intense blue-shifted emission as against any of the investigated CMPs (for

FULL PAPER

detailed information see Supporting Information). The reason for the difference could be a weak but persistent 3D conjugation through the tin centers or the fact that the fluorophores in the CMP show increased excimeric or aggregative behavior compared to that of the model compound.

Piperidine-made materials exhibit lower BET surface areas than their triethylamine analogues. Digestion of the polymers with chloroacetic acid reveals the fine structure of the CMPs yielding subtle differences. When using triethylamine as base and high catalyst loadings, we find higher crosslinking densities as expressed by the presence of a high amount of PE-trimer strut **11** compared to mono-reacted compound **12** in the digests of our CMPs; however, it is not clear if there is still Pd and/or solvent encapsulated – a reasonable assumption, as our materials are in some cases not porous and the formal yield can exceed 100%.

While even the digestion of the CMPs is not able to solve the whole puzzle of the structure-property correlation we can identify the connecting linker within the polymeric network and exclude the formation of diynes or other defect structures - which gives us a significant insight into the inner workings of insoluble CMPs assembled from tetrahedral building blocks.

Experimental Section

Syntheses of the polymers

CMP 6a: Tetrakis(4-ethynylphenyl)stannane (99.0 mg, 189 µmol, 1.00 eq) and 1,4-diiodobenzene (125 mg, 379 µmol, 2.00 eq) were dissolved in a degassed mixture of DMF (900 µL) and NEt₃ (600 µL). Pd(PPh₃)₄ (4.38 mg, 3.79 µmol, 2 mol%) was added and the reaction mixture was stirred at 100 °C for 21 h. The precipitate was filtered and washed with methanol. After pestling, the crude product was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as dark brown powder (124 mg, 97%). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 71.94, H 4.29. Decomposition: > 370 °C. IR: \tilde{v} = 3285, 3053, 2960, 1913, 1674, 1584, 1536, 1508, 1438, 1387, 1306, 1259, 1188, 1090, 1065, 02, 861, 831, 809, 754, 735, 712, 689, 658, 638, 591, 521, 466, 456, 425 cm⁻¹.

CMP 6b: Tetrakis(4-ethynylphenyl)stannane (150 mg, 287 µmol, 1.00 eq) and 1,4-diiodobenzene (189 mg, 573 µmol, 2.00 eq) were dissolved in a degassed mixture of DMF (1.36 mL) and NEt₃ (910 µL). Pd(PPh₃)₄ (663 µg, 0.2 mol%) was added after prepartation of a stock solution of 6.63 mg catalyst in 5.00 mL degassed NEt₃ and adding 500 µL of it to the reaction mixture. After stirring for 21 h at 100 °C the crude product was collected via filtration and washed with methanol and pestled. Soxhlet extraction with methanol over 1 d yielded the product as a dark yellow powder (198 mg, "103%"). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 69.79, H 3.70. Thermal decomposition: > 370 °C. IR: \tilde{v} = 3289, 3061, 6007, 2958, 2363, 2341, 2160, 1901, 1582, 1536, 1507, 1494, 1388, 1305, 1258, 1189, 1099, 1064, 1013, 1006, 948, 831, 811, 712, 657, 637, 590, 533, 523, 514, 462, 449 cm⁻¹.

CMP 6c: Tetrakis(4-ethynylphenyl)stannane (139 mg, 265 µmol, 1.00 eq) and 1,4-diiodobenzene (175 mg, 530 µmol, 2.00 eq) were dissolved in a mixture of degassed toluene/DMF (1.25 mL, 1:1 v:v) and NEt₃ (830 µL). Then Pd(PPh₃)₄ (6.13 mg, 5.30 µmol, 2 mol%) was added and the reaction

mixture was stirred at 100 °C for 21 h. After collection of the crude product via filtration, washing with methanol and prestling it was purified via Soxhlet extraction with methanol over 1 d. The polymer was obtained as a dark orange powder (200 mg, "112%"). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 68.22, H 4.73. Thermal decomposition: > 370 °C. IR: $\tilde{v} = 3060, 3010, 2960, 1655, 1583, 1536, 1508, 1439, 1387, 1306, 1258, 1189, 1099, 1064, 1012, 830, 810, 759, 712, 658, 642, 589, 522, 457 cm⁻¹.$

CMP 6d: Tetrakis(4-ethynylphenyl)stannane (99.0 mg, 189 µmol, 1.00 eq) and 1,4-diiodobenzene (125 mg, 379 µmol, 2.00 eq) were dissolved in a degassed mixture of toluene (900 µL) and NEt₃ (600 µL). Pd(PPh₃)₄ (4.38 mg, 3.79 µmol, 2 mol%) was added and the reaction mixture was stirred at 100 °C for 21 h. The crude product was collected via filtration and washed with methanol. After pestling the crude product was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as dark brown powder (119 mg, 93%). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 72.88, H 4.26. Decomposition: > 370 °C. IR: \tilde{v} = 3285, 3059, 2959, 1909, 1658, 1584, 1536, 1508, 1438, 1388, 1306, 1259, 1190, 1100, 1065, 1013, 949, 832, 812, 754, 719, 693, 659, 638, 592, 524, 466, 456, 426 cm⁻¹.

CMP 6e: Tetrakis(4-ethynylphenyl)stannane (200 mg, 382 µmol, 1.00 eq) and 1,4-diiodobenzene (252 mg, 764 µmol, 2.00 eq) were dissolved in a degassed mixture of toluene (1.80 mL) and NEt₃ (1.20 mL). Pd(PPh₃)₂Cl₂ (5.37 mg, 7.64 µmol, 2 mol%) was added and the reaction mixture was stirred at 100 °C for 21 h. The crude product was collected via filtration and washed with methanol. After pestling, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as bright yellow powder (248 mg, 97%). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 65.07, H 4.73. Decomposition: > 370 °C. IR: $\tilde{v} = 3734$, 3671, 3629, 3061, 2960, 2898, 2360, 2340, 2164, 1735, 1653, 1585, 1539, 1508, 1438, 1389, 1372, 1306, 1258, 1190, 1065, 1043, 1007, 863, 809, 692, 659, 637, 607, 524, 467 cm⁻¹.

CMP 6f: Tetrakis(4-ethynylphenyl)stannane (200 mg, 382 µmol, 1.00 eq) and 1,4-diiodobenzene (252 mg, 764 µmol, 2.00 eq) were dissolved in a degassed mixture of toluene (1.30 mL) and piperidine (1.12 mL). Pd(PPh₃)₂Cl₂ (5.37 mg, 7.64 µmol, 2 mol%) was added and the reaction mixture was stirred at 100 °C for 21 h. The crude product was collected via filtration and washed with methanol. After pestling, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as dark yellow powder (258 mg, "101%"). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 71.06, H 3.80. Decomposition: > 370 °C. IR: $\tilde{\nu}$ = 3059, 2320, 1905, 1792, 1631, 1582, 1536, 1502, 1389, 1301, 1257, 1099, 1062, 1005, 948, 829, 807, 750, 715, 696, 659, 639, 598, 518, 461, 453 cm⁻¹.

CMP 6g: Tetrakis(4-ethynylphenyl)stannane (150 mg, 287 µmol, 1.00 eq) and 1,4-diiodobenzene (189 mg, 537 µmol, 2.00 eq) were dissolved in a degassed mixture of toluene (950 µL) and piperidine (340 µL). Pd(PPh₃)₂Cl₂ (402 µg, 0.574 µmol, 0.2 mol%) was added by preparing a stock solution of 5 mL degassed piperidine, 4.02 mg palladium catalyst and adding 500 µL *via* syringe into the reaction vessel. The reaction mixture was stirred at 75 °C for 3 d. The crude product was collected via filtration and washed with methanol. After pestling, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as yellow powder (195 mg, "102%"). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 70.87, H 3.73, N 0.23. Thermal decomposition: > 370 °C. IR: $\tilde{v} = 3298$, 3059, 3010, 2961, 1907, 1629, 1582, 1536, 1508, 1387, 1305, 1258, 1185, 1095, 1064, 1006, 948, 831, 810, 712, 657, 637, 593, 521, 459 cm⁻¹.

CMP 6h: Tetrakis(4-ethynylphenyl)stannane (200 mg, 382 µmol, 1.00 eq) and 1,4-diiodobenzene (252 mg, 764 µmol, 2.00 eq) were dissolved in a degassed mixture of toluene (1.30 mL) and piperidine (620 µL). Pd(PPh₃)₂Cl₂ (537 µg, 764 nmol, 0.2 mol%) and Cul (291 µg, 1.53 µmol, 0.4 mol%) were added by preparing a stock solution of 5 mL degassed piperidine, 5.37 mg palladium catalyst and 2.91 mg Cul and adding 500 µL *via* syringe into the reaction vessel. The reaction mixture was stirred at 75 °C for 3 d. The crude product was collected via filtration and washed with methanol. After pestling, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as pale yellow powder (250 mg, 97%). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 71.81, H 3.97, N 0.55. Thermal decomposition: > 370 °C. IR: \tilde{v} = 3289, 3059, 2932, 2853, 1911, 1700, 1665, 1629, 1583, 1535, 1508, 1495, 1441, 1387, 1305, 1258, 1207, 1187, 1099, 1064, 1013, 1006, 948, 831, 811, 754, 712, 688, 658, 637, 592, 522, 466, 455 cm⁻¹.

CMP 6i: Tetrakis(4-ethynylphenyl)stannane (150 mg, 287 µmol, 1.00 eq) and 1,4-diiodobenzene (189 mg, 537 µmol, 2.00 eq) were dissolved in a degassed mixture of toluene (950 µL) and piperidine (340 µL). Pd(PPh₃)₂Cl₂ (201 µg, 287 nmol, 0.1 mol%) and Cul (218 µg, 1.15 µmol, 0.4 mol%) were added by preparing a stock solution of 5 mL degassed piperidine and 2.01 mg palladium catalyst, 2.18 mg Cul and adding 500 µL *via* syringe into the reaction vessel. The reaction mixture was stirred at 75 °C for 3 d. The crude product was collected via filtration and washed with methanol. After pestling, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as pale yellow powder (191 mg, 99%). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 70.83, H 4.05, N 0.10. Thermal decomposition: > 370 °C. IR: $\tilde{v} = 3302$, 3286, 059, 3006, 2961, 2931, 1907, 1629, 1583, 1536, 1508, 1387, 1305, 1259, 1186, 1098, 1064, 1006, 944, 831, 810, 759, 713, 657, 637, 593, 522, 465 cm⁻¹.

CMP 6j: Tetrakis(4-ethynylphenyl)stannane (150 mg, 287 µmol, 1.00 eq) and 1,4-diiodobenzene (189 mg, 537 µmol, 2.00 eq) were dissolved in a degassed mixture of THF (960 µL) and piperidine (340 µL). Pd(PPh₃)₂Cl₂ (402 µg, 574 nmol, 0.2 mol%) and Cul (218 µg, 1.13 µmol, 0.4 mol%) were added by preparing a stock solution of 5 mL degassed piperidine, 4.02 mg palladium catalyst and 2.18 mg Cul and adding 500 µL *via* syringe into the reaction vessel. The reaction mixture was stirred at 75 °C for 3 d. The crude product was collected via filtration and washed with methanol. After pestling, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as yellow powder (204 mg, "106%"). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 72.23, H 4.18, N 0.23. Thermal decomposition: > 370 °C. IR: $\tilde{v} = 3290$, 3056, 2960, 1903, 1629, 1583, 1536, 1508, 1442, 1387, 1305, 1258, 1186, 1064, 1006, 863, 831, 809, 712, 658, 637, 592, 522, 466 cm⁻¹.

CMP 6k: Tetrakis(4-ethynylphenyl)stannane (150 mg, 287 µmol, 1.00 eq) and 1,4-diiodobenzene (189 mg, 537 µmol, 2.00 eq) were dissolved in a degassed mixture of DMF (960 µL) and piperidine (340 µL). Pd(PPh₃)₂Cl₂ (402 µg, 574 nmol, 0.2 mol%) and CuI (218 µg, 1.13 µmol, 0.4 mol%) were added by preparing a stock solution of 5 mL degassed piperidine, 4.02 mg palladium catalyst and 2.18 mg CuI and adding 500 µL *via* syringe into the reaction vessel. The reaction mixture was stirred at 75 °C for 3 d. The crude product was collected via filtration and washed methanol. After grinding, it was purified by Soxhlet extraction with methanol over 1 d. The polymer was obtained as yellow powder (193 mg, 100%). Elemental Analysis (%): calculated C 78.72, H 3.60, Sn 17.68. Found C 68.98, H 4.14, N 0.73. Thermal decomposition: > 370 °C. IR: $\tilde{\nu}$ = 3060, 2956, 1905, 1632, 1583, 1508, 1495, 1387, 1305, 1258, 1188, 1092, 1064, 1013, 1006, 949, 831, 810, 754, 712, 689, 657, 638, 592, 532, 522, 464, 454, 534, 428, 418, 409 cm⁻¹.

General procedure for the cleavage reaction

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The polymer CMP **6** (30.0 mg, 1.00 eq) was suspended in 3 mL of anhydrous toluene and chloroacetic acid (84.5 mg, 894 µmol, 20.0 eq) was added. The reaction mixture was stirred overnight at 90 °C. Afterwards, it was diluted with dichloromethane (50 mL) and the organic layer was washed with deionized water (4 x 50 mL). After drying over MgSO₄ the solvents were evaporated under reduced pressure and the crude product purified via column chromatography (PE/DCM 20:1) to yield organic linker **11** and **12**.

For further analytical data see supplementary information.

Keywords: conjugated microporous polymers • structure elucidation • fluorescence • network analysis • defects

- a) T. Hasell, A. I. Cooper, *Nat. Rev. Mater.* 2016, *1*, 16053. b) J. R. Holst, A. I. Cooper, *Adv. Mater.* 2010, *22*, 5212-5216. b) J.-X. Jiang, A. I. Cooper, in Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis (Eds: M. Schröder), Springer-Verlag Berlin-Heidelberg 2009, Chapter 5, pp. 1-33. c) Y. Xu, S. Jin, H. Xu, A. Nagai, D. Jiang, *Chem. Soc. Rev.* 2013, *42*, 8012-8031. d) A. Thomas, P. Kuhn, J. Weber, M.-M. Titirici, M. Antonietti, *Macromol. Rapid Commun.* 2009, *30*, 221–236.
- [2] M. Trunk, A. Herrmann, H. Bildirir, A. Yassin, J. Schmidt, A. Thomas, *Chem. Eur. J.* 2016, 22, 7179-7183.
- [3] A. Patra, J.-M. Koenen, U. Scherf, *Chem. Commun.* 2011, 47, 9612-9614.
 [4] a) L. Zhao, I. F. Perepichka, F. Türksoy, A. S. Batsanov, A. Beeby, K. S., Findlay, M. R. Bryce, *New J. Chem.* 2004, 28, 912-918. b) Q. Chu, Y. Pang, *Spectrochimica Acta Part A* 2004, *50*, 7, 1459–1467.
- [5] a) B. Kim, N. Park, S. M. Lee, H. J. Kim, S. U. Son, *Polym. Chem.* 2015, 6, 7363-7367. b) H. Ma, H. Ren, X. Zou, S. Meng, F. Sun, G. Zhu, *Polym. Chem.* 2014, 5, 144-152.
- [6] a) E. Stöckel, X. Wu, A. Trewin, C. D. Wood, R. Clowes, N. L. Campbell, J. T. A. Jones, Y. Z. Khimyak, D. J. Adams, A. I. Cooper, *Chem. Commun.* 2009, 212-214. b) Z. Xiang, C. Dapeng, W. Wang, W. Yang, B. Han, J. Lu, , *Phys. Chem. C*, 2012, 116, 9, 5974–5980.
- [7] R. Dawson, A. Laybourn, Y. Z. Khimyak, D.J. Adams, A. I. Cooper, *Macromolecules* **2010**, *43*, 8524-8530.
- [8] a) U. H. F. Bunz, *Chem. Rev.* 2000, 100, 1605-1644. b) U. H. F. Bunz, *Acc. Chem. Res.* 2001, 34, 998-1010. c) T. Miteva, L. Palmer, L. Kloppenburg, D. Neher, U. H. F. Bunz, *Macromolecules* 2000, 33, 652-654. d) J. M. Imhof, R. K, Bly, C. G. Bangcuyo, L. Rozanski, D. A. Vanden Bout, U. H. F. Bunz, *Macromolecules* 2005, 38, 5892-5896. e) J. N. Wilson, P. M. Windscheif, U. Evans, M. L. Myrick, U. H. F. Bunz, *Macromolecules* 2002, 35, 8681-8683.
- [9] A. C. Uptmoor, J. Freudenberg, S. Schwäbel, F. Paulus, F. Rominger, F. Hinkel, U. H. F. Bunz, Angew. Chem. Int. Ed. 2015, 54, 14673-14676.
- [10] a) R. Haldar, A. Mazel, R. Joseph, M. Adams, I. A. Howard, B. S. Richards, M. Tsotsalas, E. Redel, S. Diring, F. Odobel, C. Wöll, *Chem Eur. J.* 2017, 23, 14316-14322. b) Z. Hu, T. Adachi, R. Haws, B. Shuang, R. J. Ono, C. B. Bielawski, C. F. Landes, P. J. Rossky, D. A. Vanden Bout, *J. Am. Chem. Soc.* 2014, *136*, 16023-16031.
- [11] a) F. Markl, I. Braun, E. Smarsly, U. Lemmer, N. Mechau, G. Hernandez-Sosa, U. H. F. Bunz, ACS Macro Lett. 2014, 3, 788-790. b) U. H. F. Bunz, in Conjugated Polymers, A Practical Guide to Synthesis; (Eds: K. Müllen, J. R. Reynolds, T. Masuda) RSC: Cambridge, 2014, pp. 156–179.
- [12] D. C. Sherrington, Chem. Commun. 1998, 2275.
- [13] J. Jiang, F. Su, A. Trewin, C. D. Wood, N. L. Campbell, H. Niu, C. Dickinson, A. Y. Ganin, M. J. Rosseinsky, Y. Z. Khimyak, A. I. Cooper, Angew. Chem. Int. Ed. 2007, 46, 8574-8578.

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[14] a) F. Paul, J. Patt, J. F. Hartwig, *J. Am. Chem. Soc.* **1994**, *116*, 5969-5970. b) A. S. Guram, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 7901-7902.

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Layout 2:

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