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# Discrete Triptycene-based Hexakis(metalsalphenes) – Extrinsic Soluble Porous Molecules of Isostructural Constitution

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**Abstract:** In 2013 the concept of OMIMs (organic molecules of intrinsic microporosity) has been introduced by McKeown et al. These OMIMs are constructed on the basis of rigid molecular cores such as triptycene, spirobifluorenes and others. Like shape-persistent organic cages, these are soluble discrete molecules and therefore an interesting alternative to 3D, insoluble porous materials, such as metal-organic frameworks, covalent-organic frameworks or zeolites. OMIMs are chemically and thermally robust because the formation of strong covalent bonds has been used for their synthesis. Till date a few OMIMs have been reported, most of them did not contain any functional unit to enhance gas sorption properties. Here we introduce an isostructural series of metal-salphene based OMIMs with different metal ions ( $Zn^{2+}$ , Ni<sup>2+</sup>, Cu<sup>2+</sup>, Pd<sup>2+</sup>, and Pt<sup>2+</sup>) integrated into the backbone. The influence of the metal centers on interaction with gas molecules has been investigated by gas sorption experiments.

#### Introduction

Porous materials with high specific surface areas are interesting compounds for many potential applications, such as gas sorption, separation of mixtures, catalysis, sensor applications and many more.<sup>[1]</sup> There are a number of possibilities to classify porous materials; one is to distinguish into soluble and insoluble materials. Soluble porous organic materials are either based on polymers with a certain degree of stiffness based on kinked units, the so-called PIMs (polymers of intrinsic microporosity),<sup>[2]</sup> or on structurally defined discrete molecules.<sup>[3]</sup> These can further be sub-classified into intrinsic porous molecules (such as shape-persistent organic cages)<sup>[16, 4]</sup> or extrinsically porous (e.g. porous molecular crystals based on hydrogen-bonding).<sup>[5]</sup>

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In 2013, Neil B. McKeown introduced the concepts of OMIMs (organic molecules of intrinsic microporosity):[6] stiff molecules with large intrinsic molecular free volumes (IMFV).<sup>[7]</sup> OMIMs consist of rigid building blocks, as for instance triptycene, spirobifluorene or centrohexaindane as central units, which are connected e.g. to the same bulky molecular construction units or larger π-planes. In contrast to most cages, which are based on relatively weak covalent bonds formed by dynamic covalent chemistry (DCC),<sup>[8]</sup> OMIMs are built on much stronger covalent bonds and are therefore predominantly chemically and thermally significantly more robust. Till date, a few examples of OMIMs have been published, showing that materials with high specific surface areas of up to 754 m<sup>2</sup>/g can be achieved.<sup>[9]</sup> Although it was not named as such, OMIMs have been described before. In 2005, McKeown presented а rigid phthalocyaninetetrakisporphyrine hybrid molecule that cannot pack properly with a measured specific Brunauer-Emmett-Teller (BET) surface area of 110 m<sup>2</sup>/g.<sup>[9g]</sup>

In 2009 MacLachlan et al. introduced the first triptycene-based OMIMs with specific BET surface areas of up to 499 m<sup>2</sup>/g.<sup>[9e]</sup> These triptycene-based OMIMs were synthesized by the formation of nickel-salphen pockets. Besides characterization of the pores of the materials by nitrogen sorption, the uptake of hydrogen gas at 77K was measured. However, in this study neither other metals have been incorporated into the salphen pockets nor detailed adsorption studies have been discussed.<sup>[10]</sup> Metal-salphens as well as salens are known to be catalytically active at the metal centers due to free ligation sites.<sup>[11]</sup> The interaction with other small molecules strongly depends on the nature of the metal ion as well as on the ligand. Metal salphens and salens have been integrated into MOFs<sup>[12]</sup> and porous organic polymers.<sup>[13]</sup> In this respect, our group recently presented the formation of a metal-assisted salphene organic framework (MaSOF) based on triptycenehexakissalicylaldehyde 1.<sup>[14]</sup> A clear dependency of gas-sorption properties related to the incorporated metal ions was detected. Despite the trend found and the seemingly isostructural nature of the material, some degree of uncertainty about defects, polymer-size etc. still remains,<sup>[15]</sup> which influences gas-sorption properties. To avoid or at least minimize structural uncertainties, we decided to synthesize and study isostructural metal-salphen based OMIMs, containing the same substructures as has been assumed for the triptycene-based MaSOFs,<sup>[14]</sup> which will be discussed herein.

#### **Results and Discussion**

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Scheme 1. Synthesis of triptycene-based hexakis metal-salphens M<sub>6</sub>-3.

The whole synthesis is based on hexakissalicylaldehyde 1, which originally was synthesized in a three-step approach from hexabromotriptycene in 32% overall yield.<sup>[9c, 14]</sup> We were able to improve the synthesis (overall yields of 82%) and slightly shortened it by direct cross-coupling with the p-boronic ester of salicylaldehyde (for details, see Supporting Information). With the exception of the platinum-based salphen Pt<sub>6</sub>-3, all other metalsalphens (M<sub>6</sub>-3; M = Zn, Ni, Cu, Pd)) were synthesized in one step by condensing aldehyde 1 and imine 2<sup>[16]</sup> in the presence of the metal(II) acetate or the corresponding hydrate in dry DMF at slightly elevated temperature (see Scheme 1), giving the metalsalphens in yields between 84% and 98%. It is worth mentioning that all final compounds, except the zinc salphen Zn<sub>6</sub>-3 were purified by silica column chromatography. For the Pt-salphen Pt<sub>6</sub>-3 Pt(dmso)<sub>2</sub>Cl<sub>2</sub><sup>[17]</sup> in combination with Et<sub>3</sub>N had to be used to give the product in 30% yield. All compounds were characterized by NMR, IR, UV/vis, MS and purity approved by elemental analysis (see Supporting Information).

From Ni<sub>6</sub>-3, Cu<sub>6</sub>-3 and Pd<sub>6</sub>-3 single crystals of decent quality were obtained for structure analysis by X-ray diffraction (Figure 1). Ni<sub>6</sub>-3 and Cu<sub>6</sub>-3 are isomorphic and crystallize in the trigonal space group *R*-3 with six salphen molecules in the unit cell.



Figure 1. Single-crystal X-ray structures of Ni<sub>6</sub>-3 (a and b) and Pd<sub>6</sub>-3 (c and d). a) and c) represent stick models of the molecules with the metal ions highlighted as colored balls. b) and d) packing in the unit cell depicted as wire frame models with the metal ions as colored balls. The insets show photographs of light microscopic images of the crystals. Solvate molecules are ommitted for clarity.

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For the crystals of Ni6-3 DMSO solvate molecules could be found and refined, whereas for the Cu6-3 electron-density of disordered solvate molecules needed to be removed by the SQUEEZE routine function to solve the structure. The cell parameters of Cu6-**3** (a = b = 39.879(3) Å and c = 25.5429(18) Å) are slightly larger than those of Ni<sub>6</sub>-3 (a = b = 39.2557(9) Å and c = 26.1996(7) Å). For Ni<sub>6</sub>-3 and Cu<sub>6</sub>-3 the molecular structures are D<sub>3</sub>-symmetric, with both enantiomers in the unit cell. The shortest metal to metal distance for Ni<sub>6</sub>-3 is 11.3 Å between two adjacent salphen blades connected ortho to the triptycene core, followed by 14.9 Å of two salphen units attached at the same side of two triptycene phenylene rings and 17.8 Å, if they are oriented trans to each other. In the corresponding Cu<sub>6</sub>-3 the distances are 11.1 Å, 15.2 Å and 17.5 Å. **Pd<sub>6</sub>-3** is crystallizing in the triclinic space group *P*-1 with two molecules in the unit cell. The Pd6-3 molecule crystallized in  $C_1$ -symmetry. Here, the metal to metal distances are with 10.9 Å, 15.3 Å and 17.2 Å comparable to the two other metal salphens.



Figure 2. Comparison of N2-sorption data of all M6-3 at 77 K.

All compounds have been investigated by gas sorption analysis. We started with Pd6-3, which was initially investigated in its assynthesized state, as received directly as a solid after column chromatographic workup and removing of the solvent by rotary evaporation. The film-like compound gave a negligible measured BET surface area of 3 m<sup>2</sup>/g after activation at 180 °C in fine vacuum. Therefore, we changed the protocol to generate the solid material, simply by precipitation of the compound by pouring the DCM solution into methanol, getting a voluminous precipitate. After thermal activation (180 °C, overnight) in fine vacuum, the compound showed a typical type-I isotherm<sup>[18]</sup> for the sorption of N<sub>2</sub> at 77 K with a specific BET surface area of 427 m<sup>2</sup>/g (Figure 2). Therefore, all other salphens M6-3 have been activated in the same way, giving all comparable BET surface areas in the range of 356 to 435 m<sup>2</sup>/g (Fig. 2). These values are a bit lower than for the corresponding MaSOFs,<sup>[14]</sup> but in the typical range of other OMIMs<sup>[9a, 9d-f]</sup> or a number of porous organic cages.<sup>[4b, 19]</sup> Pore analysis by NLDFT (non-local density functional theory) as well as QSDFT (quench solid density functional theory) methods gave similar broad peaks between 5.7 and 30 Å for all compounds (see Supporting Information), which suggests that the pores are less structured and less unique than found in the MASOFs. By powder X-ray diffraction investigations, for all salphens  $M_{6}$ -3 except  $Ni_{6}$ -3 a distinct although broad peak in the range of 6.26° to 6.29° is detected. By light microscopy as well as scanning electron microscopy some degree of crystallinity of the samples has been confirmed (see Supporting Information). In case of Zn<sub>6</sub>-3 two types of crystallites are found. One type are agglomerates of very small thin crystals and the other are crystals of hexagonal shape of about 100 nm in size. The sample of Ni<sub>6</sub>-3 shows much larger crystalline domains of a few micrometers, whereas the isostructural Cu<sub>6</sub>-3 has formed smaller spherical crystals, in size comparable to Zn<sub>6</sub>-3. Pd<sub>6</sub>-3 is forming hexagonal rods embedded in smaller particles and Pt<sub>6</sub>-3 is in shape similar as Cu<sub>6</sub>-3.

The sorption of other gases has been investigated too (see Supporting Information). The salphens adsorb at 77 K and 1 bar between 0.6-0.7 wt% H<sub>2</sub>, which is reasonable lower than found for the MaSOFs (0.9-1.3 wt%).<sup>[14]</sup> At 273 K and 1 bar the compounds adsorb between 0.4 and 0.5 mmol/g CH<sub>4</sub>, which correspond to 0.7 to 1.0 wt%. The amount of adsorbed CO<sub>2</sub> at 273 K and 1 bar is between 5.0 and 5.8 wt%. Again this is substantially lower than reported for the corresponding MaSOFs (10.2-15.6 wt%).



Figure 3. Comparison of heat of adsorption of all M6-3 for CO2 at 273 K.

Although the overall numbers are per se lower than for the corresponding MASOFs, the big advantage of the molecular materials is the unity of chemical constitution without having defects. This is in contrast to the MaSOFs, which are threedimensional polymers that contain probably a certain degree of defect sites such as metal free salphen units, non-reacted amine or aldehyde functions or benzimidazole or imidazoline units<sup>[20]</sup> which are generated by competing reactions. Therefore, the impact of the metal salphen units on the heat of adsorption  $(Q_{st})$ should be more reliable than it is for MaSOFs. The heat of adsorption for CO<sub>2</sub> follows the trend Zn<sub>6</sub>-3 ( $Q_{st} = 29.1 \text{ kJ/mol}$ ) >  $Pt_{6}-3 (Q_{st} = 27.9 \text{ kJ/mol}) > Ni_{6}-3 (Q_{st} = 26.9 \text{ kJ/mol}) > Cu_{6}-3 (Q_{st} = 26.9 \text{ kJ/$ = 25.0 kJ/mol) > Pd<sub>6</sub>-3 (Q<sub>st</sub> = 24.4 kJ/mol); see Figure 3. This order is different from the one found in the corresponding MaSOFseries (Pt-MaSOF100 (32.2 kJ/mol) ~ Cu-MaSOF100 (32.1 kJ/mol) > Zn-MaSOF100 (30.3 kJ/mol) > Ni-MaSOF100 (27.8 kJ/mol) > Pd-MaSOF 100 (27.3 kJ/mol),<sup>[14]</sup> but the values for the zinc- and nickelcontaining porous materials are comparable. This discrepancy in the series clearly points out the intrinsic problem with

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interpretation of the data of amorphous network materials due to their imperfectness. For instance, in the IR-spectra of the **Pt-** and **Pd-MaSOFs** substantial bands of unreacted aldehyde groups were detected revealing structural defects. Thus, the values determined for the molecular and structurally perfect **Pt<sub>6</sub>-3** and **Pd<sub>6</sub>-3** seem to be more reliable to compare the impact of the metal salphen unit on gas sorption.

The calculated selectivities of binary gas mixtures (CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub>) have been analyzed. The Henry selectivities for CO<sub>2</sub>/CH<sub>4</sub> at zero coverage is with  $S_{\rm H}$  = 15 the highest for **Zn<sub>6</sub>-3** and higher than for all the other hexasalphens **M<sub>6</sub>-3**, which are between  $S_{\rm H}$  = 8 and 10. This is expected, because Zn-salphens are known to be much better Lewis acids that can be coordinated by CO<sub>2</sub> than the other metal salphens we investigated within this series.<sup>[21]</sup> The same trend is seen for CO<sub>2</sub>/N<sub>2</sub>. Here, the  $S_{\rm H}$  = 68 for **Zn<sub>6</sub>-3** is double as high as for all other hexasalphens **M<sub>6</sub>-3** ( $S_{\rm H}$  = 35 and 38).

Table 1 Gas sorption data of all metal-salphens

The selectivities of binary mixtures of CO<sub>2</sub>/CH<sub>4</sub> (1:1) at 273 K have also been analyzed according to the ideal adsorbed solution theory (IAST).<sup>[22]</sup> The trend basically follows the one of the Henry selectivities (see Table 1), again with the zinc salphen **Zn<sub>6</sub>-3** being superior to the others. With S<sub>IAST</sub> = 7.1 these are a bit lower than in the corresponding MaSOFs.<sup>[14]</sup> We also investigated binary mixtures of CO<sub>2</sub>/N<sub>2</sub> (20/80), which is a typical ratio for a postcombusting mixture.<sup>[23]</sup>

However, values for all other **M**<sub>6</sub>-**3** are in the range between  $S_{IAST}$  = 21 and 26, which are nearly half those of the corresponding MaSOFs ( $S_{IAST}$  are between 42 and 56).<sup>[14]</sup> Unfortunately, gas sorption parameters of several samples of **Zn**<sub>6</sub>-**3** could neither accurately be fitted by a Tóth or Dual-Langmuir-Freundlich isotherm to calculate reasonable IAST curves, which could have completed the comparison of this series.

M6-3	SA <sub>BET</sub> <sup>[a]</sup>	gas uptake <sup>[b]</sup>					Q <sub>st</sub> [kJ/mol] <sup>[c]</sup>		S <sub>Henry</sub> (273 K) <sup>[d]</sup>		S <sub>IAST</sub> (273 K)	
		H <sub>2</sub> (77 K)	CH4 (273 K)	CH4 (263 K)	CO <sub>2</sub> (273 K)	CO <sub>2</sub> (263 K)	CH₄	CO <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub> <sup>[e]</sup>	$CO_2\!/N_2{}^{[f]}$
Zn	411	3.7 (0.7)	0.5 (0.8)	0.6 (0.9)	1.3 (5.8)	1.6 (6.8)	17.9	29.1	15	68	7.1	_ [g]
Ni	435	3.6 (0.7)	0.4 (0.7)	0.6 (0.9)	1.1 (5.0)	1.4 (6.0)	18.3	26.9	8	35	5.4	24
Cu	414	3.0 (0.6)	0.4 (0.7)	0.6 (0.9)	1.2 (5.2)	1.4 (6.2)	20.3	25.0	9	37	6.0	26
Pd	427	3.3 (0.7)	0.5 (0.8)	0.6 (1.0)	1.3 (5.6)	1.5 (6.6)	20.1	24.4	10	36	5.9	21
Pt	356	2.9 (0.6)	0.5 (0.8)	0.6 (1.0)	1.2 (5.2)	1.4 (6.3)	11.2 <sup>[h]</sup>	27.9	9	38	5.4	22

[a] N<sub>2</sub>, 77 K, in  $[m^2g^{-1}]$ . [b] Values in [mmol g<sup>-1</sup>] and [wt-%] in parentheses. [c] Isosteric heat of adsorption; values given for zero-coverage. [d] Henry's Law selectivity of gas A over gas B. [e] IAST selectivity for a simulated CO<sub>2</sub>/CH<sub>4</sub> mixture (0.5:0.5) at 0.1 bar. [f] IAST selectivity for a simulated CO<sub>2</sub>/N<sub>2</sub> mixture (0.2:0.8) at 0.1 bar. [g] Insufficient parameters for Tóth fit. [h] Insufficient parameters for virial fit.

### Conclusions

In summary, we have synthesized a series of isostructural metal ion containing molecular OMIMs M6-3 varying only in the nature of the metal ions embedded in the salphen pockets. These OMIMs can be seen as structural models for MaSOFs based on the same building block.<sup>[14]</sup> In contrast to the polymeric MaSOFs, the OMIMs presented here are structurally defined and do not contain any defects. Therefore, a comparison of the impact of the metal ion on gas sorption selectivity seems to be more accurate than in the corresponding MaSOFs, although one needs to keep in mind that the gas sorption data was collected for amorphous samples - so the structure-property relationsship is still not perfect. Indeed, the order of the metal salphens is different than found in the corresponding MaSOFs. Here the one with Zn<sup>2+</sup> shows the highest heat of adsorption ( $Q_{st} = 29.1 \text{ kJ/mol}$ ) for CO<sub>2</sub> where the impact of the metal is closer to the expected value than found in the MaSOFs. The Henry selectivity  $S_{\rm H}$  = 68 for CO<sub>2</sub> vs N<sub>2</sub> in combination with the high specific surface area of 411 m<sup>2</sup>/g is comparable to other molecular porous systems. Nevertheless,

getting highly crystalline (activated) porous materials of those OMIMs is the final goal, which is more challenging, due to the prevention of structural collapsing of the crystalline order upon solvate removal.<sup>[3c, 5c]</sup> Furthermore, other structurally related OMIMs will be revisited that before could not be processed to form porous materials.<sup>[24]</sup>

### **Experimental Section**

For experimental details such as synthetic procedures, characterisation of all new compounds, NMR and MALDI-TOF MS spectra, crystal structure data as well as gas sorption data, see Supporting Information.

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**Keywords:** salphens • gas-sorption • porosity • triptycene• metal coordination

- (a) A. G. Slater, A. I. Cooper, *Science* 2015, 348; (b) F. Beuerle, B. Gole, *Angew. Chem. Int. Ed.* 2018, 57, 4850-4878.
- [2] (a) P. M. Budd, B. S. Ghanem, S. Makhseed, N. B. McKeown, K. J. Msayib, C. E. Tattershall, *Chem. Commun.* **2004**, 230-231; (b) N. B. McKeown, P. M. Budd, *Macromol.* **2010**, *43*, 5163-5176.
- [3] (a) J. R. Holst, A. Trewin, A. I. Cooper, *Nat. Chem.* 2010, *2*, 915; (b) N.
  B. McKeown, *J. Mater. Chem.* 2010, *20*, 10588-10597; (c) M.
  Mastalerz, *Chem. Eur. J.* 2012, *18*, 10082-10091; (d) J. Tian, P. K.
  Thallapally, B. P. McGrail, *CrystEngComm* 2012, *14*, 1909-1919; (e) M.
  I. Hashim, C.-W. Hsu, H. T. M. Le, O. Š. Miljanić, *Synlett* 2016, *27*, 1907-1918.
- [4] (a) T. Hasell, A. I. Cooper, *Nature Reviews Materials* 2016, *1*, 16053;
  (b) T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat Mater* 2009, *8*, 973-978; (c) M. Mastalerz, M. W. Schneider, I. M. Oppel, O. Presly, *Angew. Chem. Int. Ed.* 2011, *50*, 1046-1051; (d) S. M. Elbert, F. Rominger, M. Mastalerz, *Chem. Eur. J.* 2014, *20*, 16707-16720; (e) G. Zhang, O. Presly, F. White, I. M. Oppel, M. Mastalerz, *Angew. Chem. Int. Ed.* 2014, *53*, 1516-1520; (f) M. Mastalerz. Svnlett 2013, *24*, 781-786.
- [5] (a) T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, O. Daugulis, A. J. Jacobson, O. Š. Miljanić, *Nat. Commun.* 2014, *5*, 5131; (b) S. A. Dalrymple, G. K. H. Shimizu, *J. Am. Chem. Soc.* 2007, *129*, 12114-12116; (c) M. Mastalerz, I. M. Oppel, *Angew. Chem. Int. Ed.* 2012, *51*, 5252-5255; (d) H. Wang, Z. Bao, H. Wu, R.-B. Lin, W. Zhou, T.-L. Hu, B. Li, J. C.-G. Zhao, B. Chen, *Chem. Commun.* 2017, *53*, 11150-11153; (e) Y. He, S. Xiang, B. Chen, *J. Am. Chem. Soc.* 2011, *133*, 14570-14573; (f) M. I. Hashim, H. T. M. Le, T.-H. Chen, Y.-S. Chen, O. Daugulis, C.-W. Hsu, A. J. Jacobson, W. Kaveevivitchai, X. Liang, T. Makarenko, O. Š. Miljanić, I. Popovs, H. V. Tran, X. Wang, C.-H. Wu, J. I. Wu, *J. Am. Chem. Soc.* 2018.
- [6] (a) L. J. Abbott, A. G. McDermott, A. Del Regno, R. G. D. Taylor, C. G. Bezzu, K. J. Msayib, N. B. McKeown, F. R. Siperstein, J. Runt, C. M. Colina, J. Phys. Chem. B 2013, 117, 355-364; (b) L. J. Abbott, N. B. McKeown, C. M. Colina, J. Mater. Chem. A 2013, 1, 11950-11960; (c) A. Del Regno, F. R. Siperstein, R. G. D. Taylor, N. B. McKeown, Microporous Mesoporous Mater. 2013, 179, 265.
- [7] T. M. Long, T. M. Swager, Adv. Mater. 2001, 13, 601-604.
- [8] (a) M. Mastalerz, Angew. Chem. Int. Ed. 2010, 49, 5042-5053; (b) G.
   Zhang, M. Mastalerz, Chem. Soc. Rev. 2014, 43, 1934-1947.
- [9] (a) B. Kohl, F. Rominger, M. Mastalerz, Org. Lett. 2014, 16, 704-707;
  (b) B. Kohl, F. Rominger, M. Mastalerz, Chem. Eur. J. 2015, 21, 17308-17313;
  (c) D. Reinhard, F. Rominger, M. Mastalerz, J. Org. Chem. 2015, 80, 9342-9348;
  (d) R. G. D. Taylor, M. Carta, C. G. Bezzu, J. Walker, K. J. Msayib, B. M. Kariuki, N. B. McKeown, Org. Lett. 2014, 16, 1848-1851;
  (e) J. H. Chong, S. J. Ardakani, K. J. Smith, M. J. MacLachlan, Chem. Eur. J. 2009, 15, 11824-11828;
  (f) R. G. D. Taylor, C. G. Bezzu, M. Carta, K. J. Msayib, J. Walker, R. Short, B. M. Kariuki, N. B. McKeown, Chem. Eur. J. 2016, 22, 2466-2472;
  (g) S. Makhseed, N. B. McKeown, K. Msayib, A. Bumajdad, J. Mater. Chem. 2005, 15, 1865-1870.
- [10] D. Anselmo, G. Salassa, E. C. Escudero-Adan, E. Martin, A. W. Kleij, Dalton Transactions 2013, 42, 7962-7970.
- [11] (a) P. G. Cozzi, *Chem. Soc. Rev.* 2004, 33, 410-421; (b) R. M. Haak, S. J. Wezenberg, A. W. Kleij, *Chem. Commun.* 2010, 46, 2713-2723; (c) C. J. Whiteoak, G. Salassa, A. W. Kleij, *Chem. Soc. Rev.* 2012, 41, 622-631; (d) R. M. Clarke, T. Storr, *Dalton Transactions* 2014, 43, 9380-9391.

- [12] (a) S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* 2006, 2563-2565; (b) W. Xuan, C. Ye, M. Zhang, Z. Chen, Y. Cui, *Chem. Sci.* 2013, *4*, 3154-3159; (c) F. Song, C. Wang, J. M. Falkowski, L. Ma, W. Lin, *J. Am. Chem. Soc.* 2010, *132*, 15390-15398; (d) R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-i. Noro, S. Kitagawa, *Angew. Chem. Int. Ed.* 2004, *43*, 2684-2687; (e) J. M. Falkowski, C. Wang, S. Liu, W. Lin, *Angew. Chem. Int. Ed.* 2011, *50*, 8674-8678; (f) C. Zhu, G. Yuan, X. Chen, Z. Yang, Y. Cui, *J. Am. Chem. Soc.* 2012, *134*, 8058-8061; (g) S.-C. Xiang, Z. Zhang, C.-G. Zhao, K. Hong, X. Zhao, D.-R. Ding, M.-H. Xie, C.-D. Wu, M. C. Das, R. Gill, K. M. Thomas, B. Chen, *Nat. Commun.* 2011, *2*, 204.
- (a) M. Mastalerz, H.-J. S. Hauswald, R. Stoll, Chem. Commun. 2012, [13] 48, 130-132; (b) A. K. Crane, M. J. MacLachlan, Eur. J. Inorg. Chem. 2012, 2012, 17-30; (c) J. Chun, S. Kang, N. Kang, S. M. Lee, H. J. Kim, S. U. Son, J. Mater. Chem. A 2013, 1, 5517-5523; (d) H. Li, B. Xu, X. Liu, S. A. C. He, H. Xia, Y. Mu, J. Mater. Chem. A 2013, 1, 14108-14114; (e) Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou, W.-Q. Deng, Nat. Commun. 2013, 4, 1960; (f) H. Li, Z. Li, Y. Zhang, X. Luo, H. Xia, X. Liu, Y. Mu, RSC Adv. 2014, 4, 37767-37772; (g) T.-T. Liu, Z.-J. Lin, P.-C. Shi, T. Ma, Y.-B. Huang, R. Cao, ChemCatChem 2015, 7, 2340-2345; (h) J. Wang, W. Huang, L. Pan, H. Wang, C. Zhang, X. Liu, Macromolecular Research 2015, 23, 309-312; (i) J. Chen, H. Li, M. Zhong, Q. Yang, Green Chemistry 2016, 18, 6493-6500; (j) T.-T. Liu, J. Liang, Y.-B. Huang, R. Cao, Chem. Commun. 2016, 52, 13288-13291; (k) K. S. Song, D. Kim, K. Polychronopoulou, A. Coskun, ACS Appl. Mater. Interfaces 2016, 8, 26860-26867; (I) L.-H. Li, X.-L. Feng, X.-H. Cui, Y.-X. Ma, S.-Y. Ding, W. Wang, J. Am. Chem. Soc. 2017, 139, 6042-6045; (m) R. Luo, Y. Chen, Q. He, X. Lin, Q. Xu, X. He, W. Zhang, X. Zhou, H. Ji, ChemSusChem 2017, n/a-n/a; (n) X. Han, Q. Xia, J. Huang, Y. Liu, C. Tan, Y. Cui, J. Am. Chem. Soc. 2017, 139, 8693-8697; (o) G. Yuan, H. Jiang, L. Zhang, Y. Liu, Y. Cui, Coord. Chem. Rev. 2017.
- [14] D. Reinhard, W.-S. Zhang, Y. Vaynzof, F. Rominger, R. R. Schröder, M. Mastalerz, Chem. Mater. 2018.
- [15] (a) A. C. Uptmoor, R. Ilyas, S. M. Elbert, I. Wacker, R. R. Schröder, M. Mastalerz, J. Freudenberg, U. H. F. Bunz, *Chem. Eur. J.* 2018, 24, 1674-1680; (b) A. C. Uptmoor, J. Freudenberg, S. T. Schwäbel, F. Paulus, F. Rominger, F. Hinkel, U. H. F. Bunz, *Angew. Chem. Int. Ed.* 2015, 54, 14673-14676.
- [16] M.-A. Muñoz-Hernández, T. S. Keizer, S. Parkin, B. Patrick, D. A. Atwood, Organomet. 2000, 19, 4416-4421.
- [17] J. H. Price, A. N. Williamson, R. F. Schramm, B. B. Wayland, *Inorg. Chem.* **1972**, *11*, 1280-1284.
- [18] K. S. W. Sing, in *Pure Appl. Chem., Vol.* 57, **1985**, p. 603.
- [19] (a) M. W. Schneider, I. M. Oppel, M. Mastalerz, *Chem. Eur. J.* 2012, *18*, 4156-4160; (b) J. C. Lauer, W. S. Zhang, F. Rominger, R. R. Schröder, M. Mastalerz, *Chem. Eur. J.* 2018, *24*, 1816-1820.
- [20] M. M. Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz, R. M. Haak, A. W. Kleij, *Eur. J. Org. Chem.* **2010**, 2010, 4823-4831.
- [21] (a) A. Decortes, A. W. Kleij, *ChemCatChem* **2011**, *3*, 831-834; (b) A. Decortes, M. Martinez Belmonte, J. Benet-Buchholz, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 4580-4582.
- [22] A. L. Myers, J. M. Prausnitz, AIChE J. 1965, 11, 121-127.
- [23] (a) J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown, J. Liu, *Chem. Soc. Rev.* 2012, *41*, 2308-2322; (b) L.-C. Lin, J. Kim, X. Kong, E. Scott, T. M. McDonald, J. R. Long, J. A. Reimer, B. Smit, *Angew. Chem. Int. Ed.* 2013, *52*, 4410-4413.
- [24] M. Mastalerz, I. M. Oppel, Eur. J. Org. Chem. 2011, 2011, 5971-5980.

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