Salen-Based Amphiphiles: Directing Self-Assembly in Water by Metal Complexation

Filippo Tosi, Marc C. A. Stuart, Sander J. Wezenberg,* and Ben L. Feringa*

Abstract: Tuning morphologies of self-assembled structures in water is a major challenge. Herein we present a salen-based amphiphile which, using complexation with distinct transition metal ions, allows to control effectively the self-assembly morphology in water, as observed by Cryo-TEM and confirmed by DLS measurements. Applying this strategy with various metal ions gives a broad spectrum of self-assembled structures starting from the same amphiphilic ligand (from cubic structures to vesicles and micelles). Thermogravimetric analysis and electric conductivity measurements reveal a key role for water coordination apparently being responsible for the distinct assembly behavior.

*I*n recent years, there has been a growing interest in the study of novel amphiphiles owing to their potential application in various fields,[1] including drug and gene delivery,[2–7] responsive materials[8–10] as well as catalysis.[11–21] Specific self-assembled structures are formed, depending on the characteristics of the amphiphile, ranging from micelles,[22] vesicles,[23] and inverted structures[24] to more complex architectures (for example nanotubes,[25] sheets,[26] or ribbons[27]). A major challenge is to control the morphology of the self-assembled structure in water in an effective and simple manner. In this regard, accessing more than one morphology with only minor modification of the parent amphiphile is a difficult task;[28] it generally requires significant structural modification and extensive chemical synthesis. We envisioned that transition metal complexation to a readily accessible ligand, forming the core of the amphiphile, would present a unique opportunity to access a broad range of aggregates.

As the ligand, salen was our first choice since these ligands and their metal complexes are known for their remarkable self-assembly properties.[29–32] Because of their modular structure, they have been successfully employed as supramolecular building blocks,[33,34] for example, in the formation

[*] F. Tosi, Dr. M. C. A. Stuart, Dr. S. J. Wezenberg, Prof. Dr. B. L. Feringa
Stratingh Institute for Chemistry, University of Groningen
Nijenborgh 4, 9747 AG, Groningen (The Netherlands)
E-mail: s.j.wezenberg@lic.leidenuniv.nl
b.l.feringa@rug.nl

Dr. M. C. A. Stuart
Groningen Biomolecular Sciences and Biotechnology Institute
University of Groningen
Nijenborgh 7, 9747 AG, Groningen (The Netherlands)

Dr. S. J. Wezenberg
Leiden Institute of Chemistry, Leiden University
Einsteinweg 55, 2333 CC, Leiden (The Netherlands)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
https://doi.org/10.1002/anie.201908010.

of Langmuir films,[35] boxes,[36–39] helical structures,[40,41] gels,[42–44] fibers,[45,46] metal-organic frameworks,[47,48] covalent organic frameworks,[49–51] and nano-rings[52] or for surface functionalization.[53] They are also easily synthesized by an imine condensation and the metalation step is usually straightforward and high yielding. Herein we report the synthesis and self-assembly in water of an amphiphilic salen ligand and its metal complexes of the late first row transition metals. In the design of our target molecule we took advantage of the modular synthesis of salen ligands by separately preparing the hydrophilic diamine and hydrophobic salicylic aldehyde components. The amphiphilic salen ligand that we envisioned (Figure 1), is then obtained in a final condensation step. In the present study, it is shown that this salen framework allows for remarkable diversification in self-assembly behavior by making different complexes (Cu, Ni, Co, Fe, Mn).
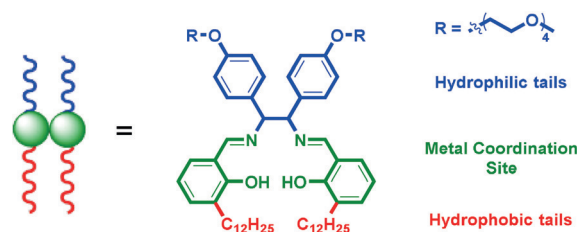

Figure 1. Design of amphiphilic metallo-salen complexes.

The synthesis of the salen ligand (Scheme 1) started from the known MOM-protected phenol **1**,[54] which was first deprotected by acidic hydrolysis and then formylated in the *ortho*-position using paraformaldehyde to afford salicylaldehyde **3**. The chiral diamine precursor **6** with pendant tetraethylene glycol chains was synthesized starting from the previously reported N-Boc protected compound **4**,[55] which was doubly functionalized with glycol chains to obtain compound **5**. After Boc deprotection, the TFA salt **6** was treated with base and subsequent condensation with aldehyde **3** in a 1:2 ratio gave the amphiphilic salen ligand **L1**.
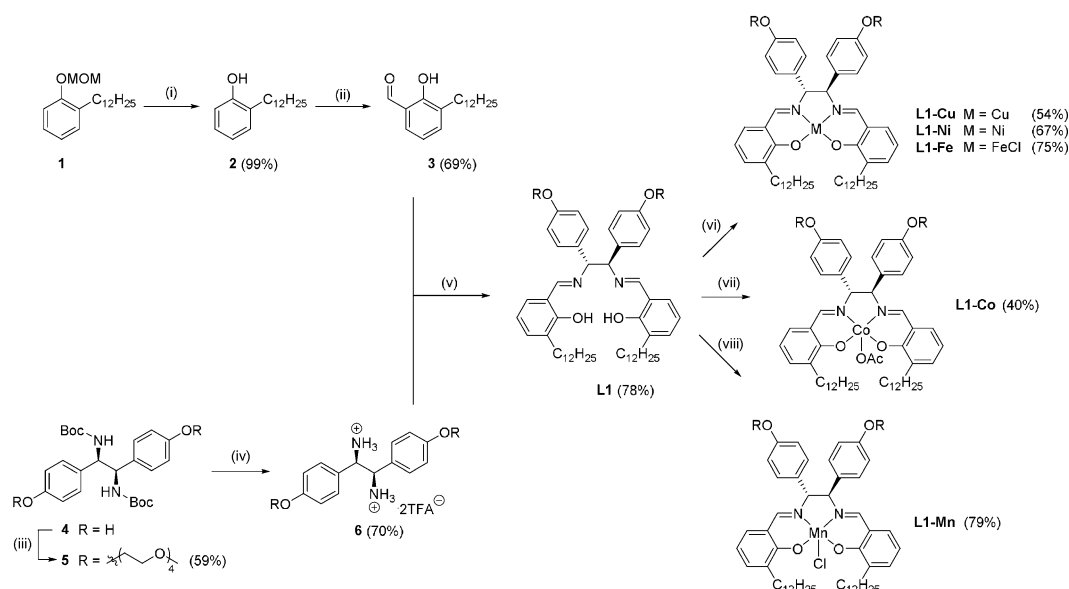
The structure of the amphiphile was confirmed by ^{1}H-NMR, showing both alkyl and tetraethylene glycol chains (Supporting Information, Figure S7), in addition to HRMS. The complexes **L1-Cu** and **L1-Ni** were obtained in good yields by metalation of **L1** with the corresponding acetate salts (Scheme 1). The iron complex **L1-Fe** was obtained in a similar way using $FeCl_3 \cdot 3 H_2O$ as the metal source. As for Cu and Ni, the synthesis of the cobalt complex **L1-Co** was performed using $Co(OAc)_2 \cdot 4 H_2O$, which in this case was followed by oxidation with molecular oxygen in the presence of AcOH.

Scheme 1. Synthesis of the amphiphilic salen ligand **L1** and its metal complexes. (i) HCl, THF, 16 h; (ii) MgCl$_2$, paraformaldehyde, TEA, THF, reflux, 16 h; (iii) Cs$_2$CO$_3$, *p*-toluenesulfonate tetraethylene glycol monomethyl ether, THF, reflux, 16 h; (iv) TFA, TIPS, CH$_2$Cl$_2$, RT, 16 h; (v) NaOH (1 M), CH$_2$Cl$_2$, then MeOH, reflux, 1 h; (vi) Cu(OAc)$_2$·H$_2$O/Ni(OAc)$_2$·4 H$_2$O/FeCl$_3$·3 H$_2$O, MeOH, reflux, 2 h; (vii) Co(OAc)$_2$·4 H$_2$O, CH$_2$Cl$_2$/MeOH 1:1, rt, 1 h then AcOH, RT, air, 3 h; (viii) Mn(OAc)$_2$·4 H$_2$O, MeOH, reflux, 1 h then LiCl (30 equiv), RT, air, 1 h.

The manganese complex **L1-Mn** was synthesized using a similar protocol, starting from **L1** and Mn(OAc)$_2$·4 H$_2$O, followed by oxidation in the presence of molecular oxygen and an excess of LiCl. The successful synthesis of all metal complexes was confirmed by HRMS, showing the expected isotopic patterns (Supporting Information, Figure S8–S13), as well as IR and UV/Vis spectroscopy. The diamagnetic complex **L1-Ni** was additionally characterized by NMR.

The self-assembly behavior of the parent amphiphile and its metal complexes was studied by Cryo-TEM using a sample concentration of 2 mM (for detailed sample preparation procedures, see Supporting Information). The observed morphologies are presented in Figure 2.[56] The ligand **L1** was found to self-assemble in water in the form of a cubic structure (Figure 2a). This structure is typically characterized by a bi-continuous bilayer of inverted micelles, which shows a porous system clearly visible in the convolutions of the soft material.[24] Interestingly, under the same experimental conditions, the metal complexes showed substantially different morphologies. The Cu and Ni complexes both gave aggregates that were characterized as sponges (Figure 2b,c).[57] Apparently, the geometrical constraint of the salen core of the amphiphile in a square planar geometry, as a result of Cu or Ni complexation, results in a very distinct self-assembly behavior with respect to the free ligand. The observed structures, which are smaller than the cubic structure generated by the free ligand **L1**, still belong to the same aggregation domain (namely inverted micelles) and therefore show a similar type of porous and ordered bilayer (Figure 2b,c).

The presence of the metal in the soft material was confirmed by EDX analysis (Figure 3). Elemental mapping clearly showed the presence of Cu and Ni in the sponge aggregates and not in the water solution, although apparently

for Cu some leaching occurred (Supporting Information, Figure S2).
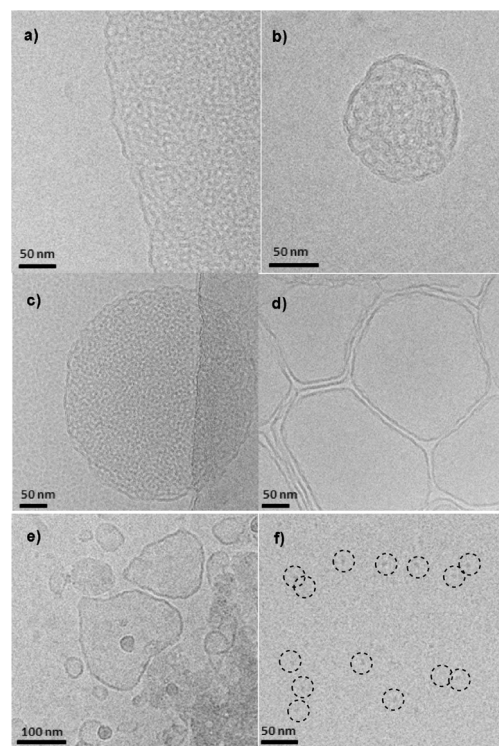
Figure 2. a) Self-assembly of **L1** into cubic aggregates, Q$_{II}$. b) Self-assembly of **L1-Cu** into sponges, Q$_{II}$. c) Self-assembly of **L1-Ni** into sponges, Q$_{II}$. d) Self-assembly of **L1-Co** into vesicles, L$_\alpha$. e) Self-assembly of **L1-Fe** into vesicles, L$_\alpha$. f) Self-assembly of **L1-Mn** into spherical micelles (L$_1$ phase) in dotted circles.
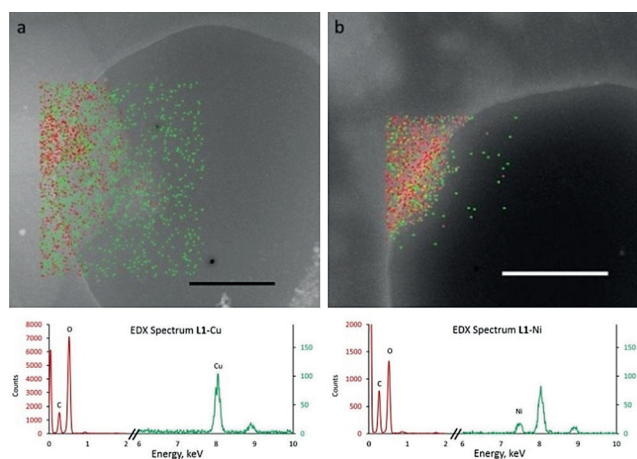
Figure 3. EDX mapping of **L1-Cu** (a) and **L1-Ni** (b) sponges on holey carbon grid: (top) elemental mapping of C, red and Cu (a) Ni (b) green; (bottom) EDX spectrum of the mapping.

A striking difference in assembly behavior was observed with the Co, Fe, and Mn complexes, all of which have a pentacoordinated metal ion. The complexes **L1-Co** and **L1-Fe** were found to form lamellar vesicles[23,58] (Figure 2 d,e). These vesicles feature a bilayer very distinct from the nanostructures formed by the starting ligand **L1**. Furthermore, the **L1-Mn** complex self-assembles into spherical micelles[22] (Figure 2 f), which is an aggregate very distinct from the one formed by the starting ligand **L1**. Dynamic light scattering (DLS) showed sharp peaks for **L1-Cu**, **L1-Ni**, **L1-Co**, and **L1-Fe** with an average D_h value above 70 nm, confirming the presence of large aggregates as observed by Cryo-TEM (Supporting Information, Figure S24). In contrast to the above mentioned amphiphiles, **L1-Mn** showed an average D_h value around 16 nm, confirming the presence of much smaller aggregates as observed by Cryo-TEM in the formation of spherical micelles (Figure 2 f). It is important to note that not only different aggregates are obtained for the metal complexes, but by using the same ligand scaffold a wide range of self-assembled amphiphilic structures can be obtained.

In order to explain the major differences in the assembly behavior, we qualitatively considered the Critical Packing Parameter (CPP) of the amphiphile [Eq. (1)],[59] that is, the ratio between the volume of the lipophilic chain (V), its length (l_c), and the interfacial area occupied by the hydrophilic component (a_0)

$$CPP = V/(l_c a_0)$$

(1)

**Equation 1**. Critical Packing Parameter (CPP) definition.

A change in substitution pattern, length or chain terminus of an amphiphile is known to influence these three terms.[60] In our case, the molecular scaffold of the amphiphile was left intact and by merely changing the metal center the morphology obtained upon self-assembly was altered. Considering the CPP equation, which is an expression of the ratio between hydrophobic and hydrophilic balance in the amphiphile, we imagined that the differences observed could be explained in

terms of the geometrical and electronic characteristics of our metal complexes. The largest deviations in aggregation from the parent ligand **L1** were observed with the complexes of Co, Fe, and Mn, which have a 3 + oxidation state, rather than the 2 + oxidation state of Cu and Ni. Furthermore, they possess an axial ligand and have the possibility to coordinate an additional electron donating ligand. Unlike Cu and Ni, the metal centers of the Co, Fe, and Mn salen amphiphiles may coordinate water as an external ligand.[61–63] Water coordination should lead to a higher hydrophilic character (a_0) resulting in a decrease of the CPP as is reflected in the structural change from cubic to lamellar and eventually micellar aggregates for Mn complexes. At the same time, the hydrophobic volume is reduced, as the metal participates in hydrating the amphiphile. The generation of an octahedral complex, also sterically different from the square planar complexes of Cu and Ni, would cause a significant change in CPP. Overall, the hydration of the amphiphile is therefore expected to drive the self-assembly process from inverted micelles (CPP > 1 for **L1-Cu** and **L1-Ni**) to bilayers ($^1/_2 <$ CPP < 1 for **L1-Co** and **L1-Fe**) and even micelles (CPP $< ^1/_2$ for **L1-Mn**).

To demonstrate water coordination, we prepared the aqua-complexes of Co, Fe, and Mn starting from the model ligand **L2**, which is similar to **L1**, but lacks the hydrophobic and hydrophilic chains (Supporting Information, Figure S3). Thermogravimetric analysis (TGA) showed water desorption upon heating of the samples of Co and Fe ($\pm 160\,^\circ$C and $\pm 196\,^\circ$C respectively, see Figure S3 and S4 in the Supporting Information).[64] However, in the case of Mn we observed decomposition of the complex and formation of HCl (Supporting Information, Figure S5).[65] Since the self-assembly behavior of the Mn amphiphile was surprisingly different, we hypothesized that upon initial water coordination the Cl ion partially dissociates leading to an ion pair, of which the formation has been reported for the core salen structure.[66] The charge formation upon chloride dissociation was successfully proven by electric conductivity (EC) experiments using **L2-Mn**, showing a 1:1 electrolyte dissociation (13.36 µS cm^{-1}),[67] which could not be observed for the model complexes **L2-Co** and **L2-Fe**. Owing to the much better solubility of the charged species in water, the CPP is decreased. Hence, the formation of spherical micelles in our case can be explained by charge formation. Our proposed water-binding model is illustrated in Figure 4.

In conclusion, we have developed a powerful, modular approach, based on an amphiphilic salen scaffold, to access a diverse set of self-assembled structures in water. Cryo-TEM measurements demonstrated that metalation of the salen ligand gave access to a wide range of aggregates. These include: cubic assemblies for the free ligand, sponges in the case of Cu^{II} and Ni^{II} complexes, vesicles for Co^{III} and Fe^{III}, and micelles for Mn^{III}. TGA and EC studies support the hypothesis that water coordination gives rise to the observed differences in aggregation behavior, which can be related to the CPP. As far as we know, our approach is unprecedented in terms of effectively controlling self-assembly of a single amphiphilic structure in water and the diverse structural morphologies obtained by only changing its metal center and
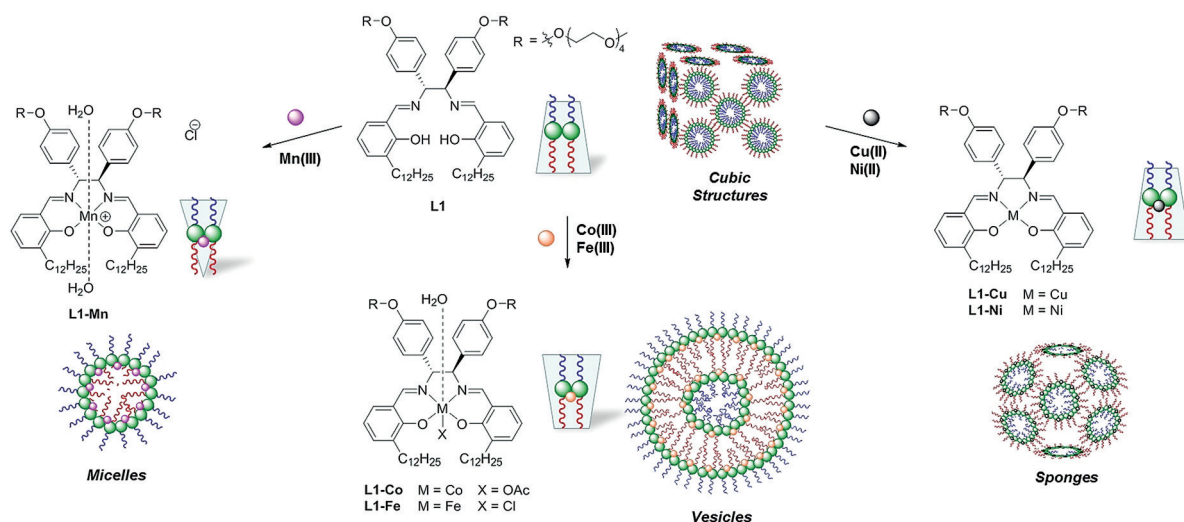
Figure 4. Proposed water-binding model and resulting aggregates with different metal ions.

controlling water binding. These findings open the path for future developments in the field of responsive self-assembly and catalysis in a confined space.

Conflict of interest

The authors declare no conflict of interest.

Keywords: aggregation · amphiphile · self-assembly ·
transition metals · water binding

[1] T. Aida, E. W. Meijer, S. I. Stupp, *Science* **2012**, *335*, 813–817.
[2] I. F. Uchegbu, S. P. Vyas, *Int. J. Pharm.* **1998**, *172*, 33–70.
[3] R. C. MacDonald, G. W. Ashley, M. M. Shida, V. A. Rakhmanova, Y. S. Tarahovsky, D. P. Pantazatos, M. T. Kennedy, E. V. Pozharski, K. A. Baker, R. D. Jones, et al., *Biophys. J.* **1999**, *77*, 2612–2629.
[4] Y. Rui, S. Wang, P. S. Low, D. H. Thompson, *J. Am. Chem. Soc.* **1998**, *120*, 11213–11218.
[5] P. L. Felgner, *Adv. Drug Delivery Rev.* **1990**, *5*, 163–187.
[6] J. P. Behr, *Acc. Chem. Res.* **1993**, *26*, 274–278.
[7] A. D. Miller, *Angew. Chem. Int. Ed.* **1998**, *37*, 1768–1785; *Angew. Chem.* **1998**, *110*, 1862–1880.
[8] A. C. Coleman, J. M. Beierle, M. C. A. Stuart, B. Maciá, G. Caroli, J. T. Mika, D. J. Van Dijken, J. Chen, W. R. Browne, B. L. Feringa, *Nat. Nanotechnol.* **2011**, *6*, 547–552.
[9] J. Chen, F. K. C. Leung, M. C. A. Stuart, T. Kajitani, T. Fukushima, E. Van Der Giessen, B. L. Feringa, *Nat. Chem.* **2018**, *10*, 132–138.
[10] D. J. Van Dijken, J. Chen, M. C. A. Stuart, L. Hou, B. L. Feringa, *J. Am. Chem. Soc.* **2016**, *138*, 660–669.
[11] J. B. F. N. Engberts, *Pure Appl. Chem.* **2007**, *64*, 1653–1660.
[12] T. Dwars, E. Paetzold, G. Oehme, *Angew. Chem. Int. Ed.* **2005**, *44*, 7174–7199; *Angew. Chem.* **2005**, *117*, 7338–7364.
[13] G. Oehme, E. Paetzold, R. Selke, *J. Mol. Catal.* **1992**, *71*, L1–L5.
[14] S. Kobayashi, T. Wakabayashi, S. Nagayama, H. Oyamada, *Tetrahedron Lett.* **1997**, *38*, 4559–4562.
[15] K. Manabe, Y. Mori, T. Wakabayashi, S. Nagayama, S. Kobayashi, *J. Am. Chem. Soc.* **2000**, *122*, 7202–7207.
[16] J. H. Fendler, E. J. Fendler, *Catalysis in Micelles and Macromolecular Systems*, Academic Press, London, **1975**.
[17] F. M. Menger, J. U. Rhee, H. K. Rhee, *J. Org. Chem.* **1975**, *40*, 3803–3805.
[18] S. Serrano-Luginbühl, K. Ruiz-Mirazo, R. Ostaszewski, F. Gallou, P. Walde, *Nat. Rev. Chem.* **2018**, *2*, 306–327.
[19] J. van Esch, M. F. Roks, R. J. M. Nolte, *J. Am. Chem. Soc.* **1986**, *108*, 6093–6094.
[20] J. T. Groves, R. Neumann, *J. Am. Chem. Soc.* **1987**, *109*, 5045–5047.
[21] K. Fuji, T. Morimoto, K. Tsutsumi, K. Kakiuchi, *Angew. Chem. Int. Ed.* **2003**, *42*, 2409–2411; *Angew. Chem.* **2003**, *115*, 2511–2513.
[22] Y. Chevalier, T. Zemb, *Rep. Prog. Phys.* **1990**, *53*, 279–371.
[23] D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967–973.
[24] J. M. Seddon, R. H. Templer, P. Trans, R. S. Lond, *Philos. Trans. R. Soc. London Ser. A* **1993**, *344*, 377–401.
[25] T. G. Barclay, K. Constantopoulos, J. Matisons, *Chem. Rev.* **2014**, *114*, 10217–10291.
[26] L. C. Palmer, S. I. Stupp, *Acc. Chem. Res.* **2008**, *41*, 1674–1684.
[27] Y. V. Zastavker, N. Asherie, A. Lomakin, J. Pande, J. M. Donovan, J. M. Schnur, G. B. Benedek, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 7883–7887.
[28] V. Percec, P. Leowanawat, H. J. Sun, O. Kulikov, C. D. Nusbaum, T. M. Tran, A. Bertin, D. A. Wilson, M. Peterca, S. Zhang, N. P. Kamat, K. Vargo, D. Moock, E. D. Johnston, D. A. Hammer, D. J. Pochan, Y. Chen, Y. M. Chabre, T. C. Shiao, M. Bergeron-Brlek, S. André, R. Roy, H.-J. Gabius, P. A. Heiney, *J. Am. Chem. Soc.* **2013**, *135*, 9055–9077.

[29] A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. Van Leeuwen, J. N. H. Reek, *Inorg. Chim. Acta* **2006**, *359*, 1807–1814.

[30] a) G. Consiglio, S. Failla, P. Finocchiaro, I. Pietro Oliveri, S. Di Bella, *Dalton Trans.* **2012**, *41*, 387–395; b) G. Consiglio, S. Failla, P. Finocchiaro, I. Pietro Oliveri, S. Di Bella, *Inorg. Chem.* **2012**, *51*, 8409–8418.

[31] G. Consiglio, S. Failla, P. Finocchiaro, I. Pietro Oliveri, R. Purrello, S. Di Bella, *Inorg. Chem.* **2010**, *49*, 5134–5142.

[32] J. Reglinski, S. Morris, D. E. Stevenson, *Polyhedron* **2002**, *21*, 2175–2182.

[33] S. J. Wezenberg, A. W. Kleij, *Angew. Chem. Int. Ed.* **2008**, *47*, 2354–2364; *Angew. Chem.* **2008**, *120*, 2388–2399.

[34] L. Leoni, A. Dalla Cort, *Inorganics* **2018**, *6*, 42.

[35] S. Di Bella, G. Consiglio, S. Sortino, G. Giancane, L. Valli, *Eur. J. Inorg. Chem.* **2008**, 5228–5234.

[36] M. J. MacLachlan, J. Jiang, *Chem. Commun.* **2009**, 5695–5697.

[37] A. W. Kleij, M. Kuil, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Inorg. Chem.* **2007**, *46*, 5829–5831.

[38] A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem. Eur. J.* **2005**, *11*, 4743–4750.

[39] S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 2925–2927.

[40] G. Li, W. Yu, J. Ni, T. Liu, Y. Liu, E. Sheng, Y. Cui, *Angew. Chem. Int. Ed.* **2008**, *47*, 1245–1249; *Angew. Chem.* **2008**, *120*, 1265–1269.

[41] G. Li, X. Xi, W. Xuan, T. Dong, Y. Cui, *CrystEngComm* **2010**, *12*, 2424–2428.

[42] J. K.-H. Hui, Z. Yu, M. J. MacLachlan, *Angew. Chem. Int. Ed.* **2007**, *46*, 7980–7983; *Angew. Chem.* **2007**, *119*, 8126–8129.

[43] Q. Jin, L. Zhang, X. Zhu, P. Duan, M. Liu, *Chem. Eur. J.* **2012**, *18*, 4916–4922.

[44] K. Fan, J. Song, J. Li, X. Guan, N. Tao, C. Tong, H. Shen, L. Niu, *J. Mater. Chem. C* **2013**, *1*, 7479–7482.

[45] J. K.-H. Hui, M. J. MacLachlan, *Dalton Trans.* **2010**, *39*, 7310–7319.

[46] I. Pietro Oliveri, S. Failla, G. Malandrino, S. Di Bella, *J. Phys. Chem. C* **2013**, *117*, 15335–15341.

[47] A. M. Shultz, O. K. Farha, D. Adhikari, A. A. Sarjeant, J. T. Hupp, S. B. T. Nguyen, *Inorg. Chem.* **2011**, *50*, 3174–3176.

[48] S. H. Cho, B. Ma, S. B. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Commun.* **2006**, 2563–2565.

[49] 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.

[50] X. Han, Q. Xia, J. Huang, Y. Liu, C. Tan, Y. Cui, *J. Am. Chem. Soc.* **2017**, *139*, 8693–8697.

[51] H. Li, X. Feng, P. Shao, J. Chen, C. Li, S. Jayakumar, Q. Yang, *J. Mater. Chem. A* **2019**, *7*, 5482–5492.

[52] S. V. Pyrlin, N. D. M. Hine, A. W. Kleij, M. M. D. Ramos, *Soft Matter* **2018**, *14*, 1181–1194.

[53] J. A. A. W. Elemans, S. J. Wezenberg, M. J. J. Coenen, E. C. Escudero-Adán, J. Benet-Buchholz, D. Den Boer, S. Speller, A. W. Kleij, S. De Feyter, *Chem. Commun.* **2010**, *46*, 2548–2550.

[54] B. B. Snider, Z. Shi, *J. Am. Chem. Soc.* **1992**, *114*, 1790–1800.

[55] S. Jónsson, F. G. J. Odille, P. O. Norrby, K. Wärnmark, *Org. Biomol. Chem.* **2006**, *4*, 1927–1948.

[56] All samples were studied at different concentrations, namely 0.5 mM, 1 mM and 2 mM. A dependence of self-assembly on the sample concentration was not observed.

[57] W. Helfrich, *J. Phys. Condens. Matter* **1994**, *6*, 79–92.

[58] G. Porte, *J. Phys. Condens. Matter* **1992**, *4*, 8649–8670.

[59] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, **2011**.

[60] R. Nagarajan, *Langmuir* **2002**, *18*, 31–38.

[61] D. P. Barbosa Souza, A. T. Fricks, H. M. Alvarez, G. C. Salomão, M. H. Neves Olsen, L. C. Filho, C. Fernandes, O. A. C. Antunes, *Catal. Commun.* **2007**, *8*, 1041–1046.

[62] A. Das, A. C. Dash, *J. Chem. Soc., Dalton Trans.* **2000**, 1949–1958.

[63] D. Martínez, M. Motevalli, M. Watkinson, *Acta Crystallogr. Sect. C* **2002**, *58*, 258–260.

[64] Decomplexation of water above 100°C in the TGA diagram illustrates that a water molecule was coordinated to the Co and Fe metal centers.

[65] As reported in ref. [63], the crystal structure of the salen-(MnCl)H_2O complex shows a shorter Mn−O bond than the Mn−Cl bond, suggesting that the Mn−Cl bond is weaker. This could explain the observed dissociation of HCl.

[66] A. Panja, N. Shaikh, M. Ali, P. Vojtíšek, P. Banerjee, *Polyhedron* **2003**, *22*, 1191–1198.

[67] EC was measured at 22°C in a sample concentration of 2.5×10^{-4} M. A comparison with a NaCl solution and the concentration dependence are reported in the Supporting Information (Page S12).