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New supramolecular polymers containing both terpyridine metal complexes and quadruple hydrogen bonding units†

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Molecules containing quadruple hydrogen-bonding units as well as metal-complexing terpyridine moieties have been designed and assembled to result in a supramolecular polymer where both interactions are present in the main chain.

During the past few years, supramolecular chemistry has evolved from an exotic side subject to one of the most promising branches of modern research. Moreover, the introduction of non-covalent interactions into synthetic polymers represents a highly interesting research topic. The resulting supramolecular polymers[1] are of special interest due to the tunability of their properties. One of the main approaches to the synthesis of these kinds of materials consists of utilization of hydrogen bonding interactions. Recently, reversible supramolecular polymers, based on the strong dimerization of self-complementary 2-ureido-4[1*H*]-ureidopyrimidinone (UP) units, which exhibit real macroscopic polymeric properties, have been reported.[2] Improvement of materials properties of low molecular weight telechelic polymers, bearing UP-units at the chain ends, was therefore achieved.[3]

A second type of non-covalent interaction frequently used in non-covalent polymers is represented by metal-to-ligand interactions.[4] This kind of interaction is usually stronger than the corresponding hydrogen bonding interactions and can be tuned by the choice of the metals or ligands used. Different specific features such as electrochemical, photophysical or magnetic properties, can be introduced into polymers. However, up to now usually only one directed supramolecular interaction was present within a certain polymer. The reported examples where both interactions have been introduced (called "coordination polymers") are actually solid-state structures.[5] Another example describes a terpolymer bearing side groups for hydrogen-bonding, metal coordination as well as ionic interactions.[6]

Here we report for the first time the design of novel molecules that contain a 2,2′:6′,2″-terpyridine[7] as well as a ureido-4[1*H*]-ureidopyrimidinone[1a] group. The new compounds are capable of forming linear non-covalent polymers with alternating hydrogen-bonding and metal complex systems. In the first approach, compound **1** was prepared utilizing an isocyanate coupling of a 4′-hydroxy-functionalized terpyridine with a ureidopyrimidinone bearing an isocyanate group at room temperature in chloroform using dibutyltindilaureate (DBTDL) as catalyst. Compound **1** was characterized by UV-vis, IR, MALDI-TOF-MS and ^{1}H-NMR spectroscopy. The formation of quadruple hydrogen bonds was indicated by ^{1}H-NMR spectroscopy. A large downfield shift for the N–H protons was observed (between 10 and 13 ppm), giving direct evidence for the involvement of these protons in strong hydrogen bonding,[8] leading to DDAA-dimers in solution (Fig. 1, top).

Subsequently, the terpyridine moieties were complexed by addition of iron(II) and zinc(II) ions (see Schemes 1 and 2). In a UV-vis titration experiment, Fe(II) chloride in methanol was added to a chloroform solution of ligand **1**. An increase of the MLCT charge transfer band of the iron complex at 558 nm was observed; a plateau was reached after a linear increase (Fig. 2). The equivalence point was observed at a ligand:metal ratio of 2:1, indicating quantitative complexation. In a separate experiment, a methanolic solution of zinc(II) chloride was added to **1** in chloroform. After exchange of the counterions by addition of NH_4PF_6, the product was precipitated in diethyl ether in order to obtain compound **3**. ^{1}H-NMR spectroscopy showed a successful formation of the Zn-terpyridine complex as well as the hydrogen bonding interactions (Fig. 1,

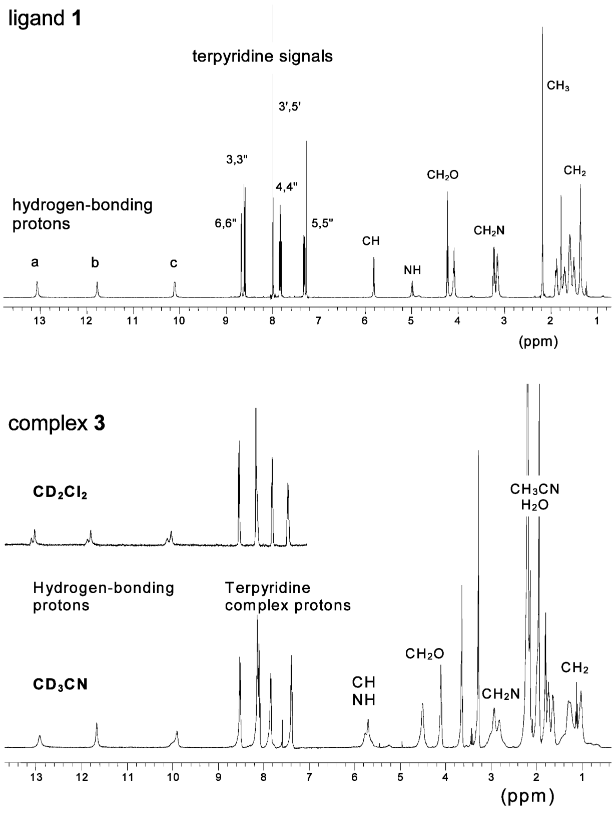
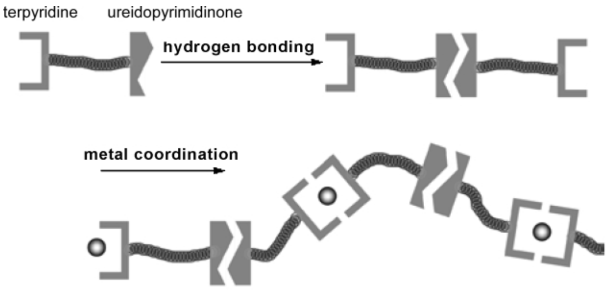


Fig. 1 ^{1}H-NMR spectra of ligand **1** ($CHCl_3$) and complex **3** (CH_3CN).



Scheme 1 Representation of the supramolecular polymers containing both metal complex and hydrogen bonding units in the main chain.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b314459n/

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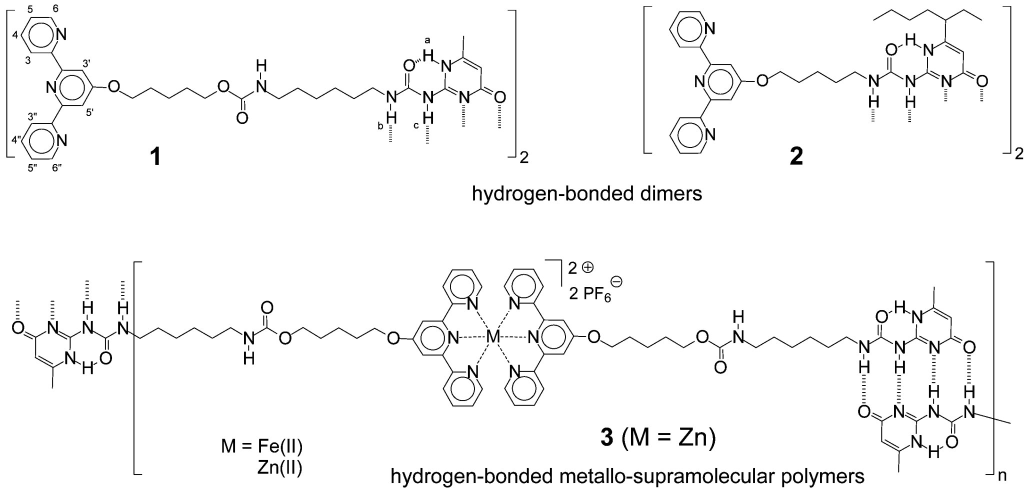

Scheme 2 Representation of the ligands **1**, **2** and a supramolecular polymer from **1** (**3**: M = Zn^{2+}).

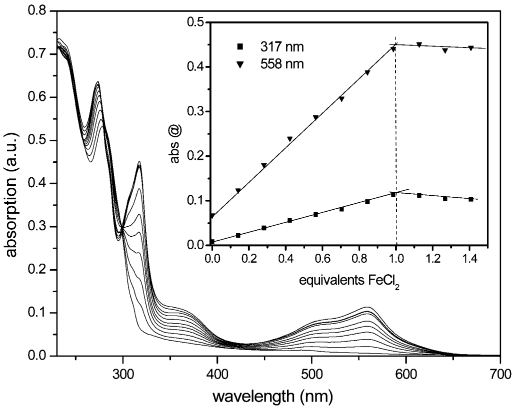

Fig. 2 UV-vis titration of compound **1** with $FeCl_2$ ($CHCl_3$).

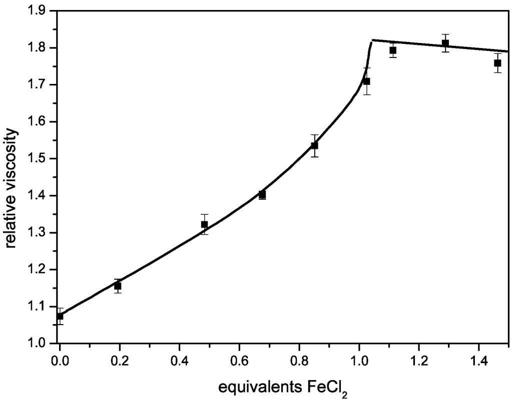

Fig. 3 Viscosity titration of compound **2** ($CHCl_3$) with $FeCl_2$.

bottom). The signals in the aromatic region could be assigned to the terpyridine complex units and the resonances between 10 and 13.2 ppm to the N–H hydrogen bonding protons. In acetonitrile, the signals are clearly visible, but with a slightly lower intensity. The hydrogen bonds are not completely broken in this case. A ^1H-NMR spectrum measured in dichloromethane revealed a quantitative formation of hydrogen bonds (insert in Fig. 1). A splitting of the peaks was observed which could be explained by a partial formation of small cycles.[9] Polymer characterization was critical due to the limited solubility of the complexes. Therefore a different compound (**2**) was prepared by the coupling of an aminoterpyridine with an activated isocytosine, which, due to the 3-heptyl chain, was expected to possess an increased solubility. ^1H-NMR showed hydrogen bonding in the ligand as well as in the corresponding Fe(II) complex. Solution viscosimetry experiments were performed during a stepwise addition of a $FeCl_2$ solution to a solution of **2** in chloroform. An increase of the viscosity was observed, indicating the formation of polymeric species (Fig. 3).

Nevertheless, at the equivalence point, the partial formation of a film-like material on the bottom of the viscosimeter was observed. Therefore, the degree of polymerisation or the ring-chain equilibrium could not yet be quantified. Future work will include the introduction of well-soluble polymeric spacers, concentration-dependant investigation of the polymers as well as the determination of the degree of polymerization.

In conclusion, we synthesized two new compounds containing, for the first time, terpyridine and ureidopyrimidinone moieties, which form linear supramolecular polymers involving both kinds of non-covalent interaction in the main chain, as demonstrated by UV-vis and NMR spectroscopy as well as viscosimetry.

Notes and references

1 (*a*) L. Brunsveld, B. J. B. Folmer, E. W. Meijer and R. P. Sijbesma, *Chem. Rev.*, 2001, **101**, 4071–4097; (*b*) U. S. Schubert and C. Eschbaumer, *Angew. Chem. Int. Ed.*, 2002, **41**, 2892–2926; (*c*) C. F. J. Faul and M. Antonietti, *Adv. Mater.*, 2003, **15**, 673–683.

2 (*a*) R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601–1604; (*b*) J. H. K. K. Hirschberg, F. H. Beijer, H. A. van Aert, P. C. M. M. Magusin, R. P. Sijbesma and E. W. Meijer, *Macromolecules*, 1999, **32**, 2696–2705.

3 B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 874–878.

4 S. Kelch and M. Rehahn, *Macromolecules*, 1997, **30**, 6185–6193; S. Kelch and M. Rehahn, *Macromolecules*, 1999, **32**, 5818–5828; S. Schmatloch, M. Fernandez-González and U. S. Schubert, *Macromol. Rapid Commun.*, 2002, **23**, 957–961.

5 C. Naether, J. Greve and I. Jess, *Z. Naturforsch., B: Chemical Sciences*, 2003, **8**, 52–58.

6 J. M. Pollino, L. P. Stubbs and M. Weck, *Polym. Prepr.*, 2003, **44**, 730–731.

7 U. S. Schubert, C. Eschbaumer, P. R. Andres, H. Hofmeier, C. H. Weidl, E. Herdtweck, E. Dulkeith, A. Morteani, N. E. Hecker and J. Feldmann, *Synth. Met.*, 2001, **121**, 1249–1252.

8 F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 6761–6769.

9 (*a*) A. T. ten Cate and R. P. Sijbesma, *Macromol. Rapid Commun.*, 2002, **23**, 1094–1112; (*b*) S. H. M. Söntjens, R. P. Sijbesma, M. H. P. van Genderen and E. W. Meijer, *Macromolecules*, 2001, **34**, 3815–3818.